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A. BETEKHTIN

A COURSE OF MINERALOGY

Translated from the Russian
by
V. AGOL

Translation editor
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MOSCOW
PEACE PUBLISHERS

U. D. C. 548/549 (075.8) = 20

NOTATION

Å	=	Ångstrom = 10^{-8} cm
mμ	=	millimicron = 0.000001 mm
a, b, c	=	crystallographic axes
(100), (010)...	=	symbols of crystal faces
{100}, {111}, {210}...	=	symbols of simple forms
n	=	index of refraction of optically isotropic minerals
n_x, n_y, n_z	=	axes of ellipsoid of optical indicatrix—the direction of the main refractive indices (maximum, medium, and minimum) in optically anisotropic minerals
a_0, b_0, c_0	=	lengths of edges of elementary cell, Å
a_{rh}	=	length of edge of rhombohedral cell, Å
α, β, γ	=	angles between crystallographic axes in monoclinic and triclinic systems

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Part One

INTRODUCTION

MINERALOGY AND MINERALS. DEFINITIONS

Mineralogy is one of the geological sciences concerned with the study of the earth's crust. The term literally means *the science of minerals* and embraces all aspects of minerals including their genesis. The word *mineral* comes from "minera", which once meant an ore specimen, which shows that it dates back to the beginnings of mining.

By minerals we mean the constituents of rocks and ores which differ from one another in chemical composition and physical properties (colour, hardness, lustre, etc.). Biotite granite, for instance, is composed of three principal minerals of different composition: light-coloured feldspar, grey quartz, and black mica (biotite). Magnetite (magnetic iron ore), on the other hand, is virtually a monomineral, i.e., composed of crystalline magnetite grains.

Genetically, minerals are *natural chemical compounds* (more seldom native elements) and are natural products of various physico-chemical processes going on in the earth's crust (including the products of the life activity of various organisms)*. The vast majority of these natural products occur as solid minerals with definite chemical and physical properties which are related to the chemical composition and crystal structure of their constituents. With some degree of approximation, it may be stated that within the space occupied by any mineral regardless of its dimensions it may be regarded as a homogeneous crystalline mass**.

The study of minerals, as they occur in nature, as well as experimental work indicate that every mineral is formed under definite physico-chemical conditions (temperature, pressure, and concentration of chemical components in the system). Individual minerals remain unaltered until their limits of stability are overcome by the operation of environmental factors (e.g., oxidation or reduction, temperature or pressure rise or fall, etc.). Therefore, in the course of development of

* A wide variety of synthetic products, i.e., laboratory- or factory-made compounds, are not considered to be minerals. Very many of them do not and even cannot occur in nature. The only synthetic compounds conditionally called minerals are those the chemical composition and crystal structure of which correspond to those of the natural compounds.

** No mineral is perfectly homogeneous either chemically or physically.

geochemical processes, many minerals are altered, destroyed or replaced by other minerals which are stable under the new conditions.

Quite a few minerals, however, such as diamond, graphite, corundum, rutile, etc., remain in a state of equilibrium within a wide range of environmental conditions.

A great many minerals known at the present time constitute important raw materials, provided, of course, their accumulation in a particular locality, called a mineral deposit, is large enough. The percentage of the useful component is high enough to make mining worthwhile. Some minerals contain important metals, such as iron, manganese, copper, lead, zinc, tin, tungsten, molybdenum, etc., which are extracted by concentration and smelting. Other minerals (diamond, asbestos, quartz, feldspars, micas, gypsum, soda, mirabilite, etc.) owing to their important physical and chemical properties may be used either as found, without any pretreatment, or as stock materials for industrial synthetic compounds, building materials, etc.

Thus *as a science of natural chemical compounds* (minerals), *mineralogy concerns itself with the study of their interrelated properties, such as composition, crystal structure, properties, occurrence and economic importance.* Therefore, mineralogy is closely associated, on the one hand, with the progress of allied sciences (physics, chemistry, crystal chemistry, etc.), and, on the other hand, with the practical requirements of geological prospecting and exploration.

At the present time mineralogy has the following principal tasks:

1. Comprehensive study and a deeper penetration into the *physical and chemical properties of minerals in relation to their chemical composition and crystal structure*, for the purpose of practically using them and to reveal new mineral raw materials.

2. Study of the *dependences governing the association of minerals and the order in which mineral associations are formed in ores and rocks* for the purpose of establishing the conditions of the formation of minerals, as well as the specific features of the processes of mineral formation (genesis), and using this knowledge in prospecting and exploration of economic mineral deposits.

In solving these problems mineralogy relies upon the laws of exact sciences: physics, chemistry, crystallography, crystal chemistry, colloidal chemistry, and physical chemistry. The data made available by mineralogical research in turn is used in geochemistry, petrography, the science of economic mineral deposits, geological prospecting and exploration, as well as in some applied sciences (metallurgy, ore beneficiation, etc.).

Conceptions of the nature of minerals and correspondingly the substance of mineralogy have developed historically and altered with the progress of our knowledge in the field of geology and natural science on the whole. We shall discuss below the main stages in natural history that have influenced the development of mineralogy as a distinct science.

THE MAIN STAGES IN THE DEVELOPMENT OF MINERALOGY

The origins of mineralogy. In prehistoric times, long before the art of writing was known, minerals began to attract man. The growth of the store of mineralogical knowledge is closely associated with the history of the development of material culture, in which mining played

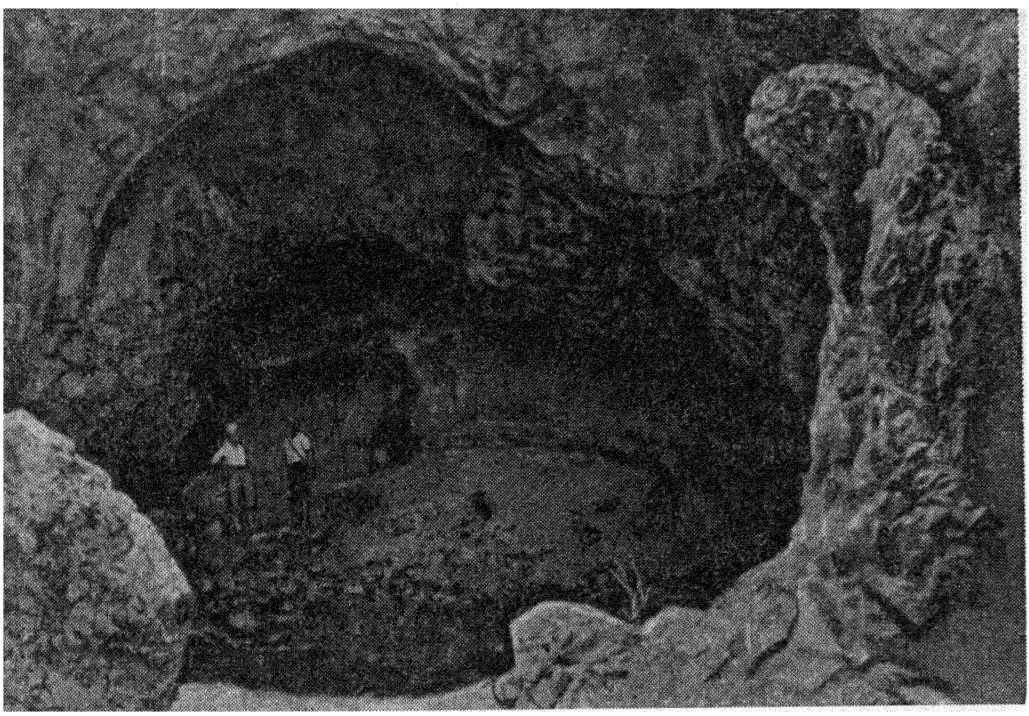


Fig. 1. An ancient working at an antimony mine.

an important part, particularly in the Bronze and Iron ages. Archeological findings show that the ancient Chinese, Babylonians, Egyptians, Greeks, etc., were among the pioneers of mining.

From time immemorial man has known not only native copper, gold and silver, but also ores rich in copper, tin, and iron compounds. Gradually he learned to extract them and smelt them into metals, at first to make ornaments, then weapons, so essential in the constant struggle for survival, and finally, instruments of labour. Besides metals, the ancients recognised and collected various coloured stones which struck them by their beauty and gave rise to various superstitions.

They must have known from experience certain properties of minerals and ores, as well as some empirical dependences of their occurrence, which enabled them to prospect for mineral deposits. In places, ancient mine workings have survived to our time (Fig. 1). Of course, no scientific concepts of the occurrence of ores and minerals could have existed at that time.

Aristotle (384-322 B. C.) was the first author in whose writings we find mentions and an attempt to classify inorganic natural bodies. Metal-like mineral formations were classed by him as "metalloids". His disciple Theophrastus (371-286 B. C.), in a special mineralogical treatise *On Stones*, described 16 mineral species, mostly gemstones, this time in practical terms. Pliny the Elder of Rome, who lost his life in the eruption of Vesuvius in 79 A. D., wrote four treatises in which he collected all the contemporary knowledge about minerals, including legends and myths.

The early Middle Ages were marked by obvious progress of science in the Arab countries, which have assimilated ancient Greek and Indian culture. A tremendous role in that progress was played by the scholars of Central Asia (Uzbekistan), then under the rule of the caliphs of Baghdad. Outstanding contributions to mineralogy were made early in the 11th century by a scholar, mathematician, and astronomer Biruni (972-1048), a native of Khorezm (Uzbekistan). Writing about gemstones he gave a very remarkable, for his day, description of minerals, using for the first time in the history of mineralogy such physical constants as relative hardness and specific gravity to differentiate between mineral species. Another great scholar of that time, Avicenna of Bokhara (980-1037), in his *Treatise on Stones* divided all the then known minerals into four classes: (1) stones and earths; (2) combustible or sulphur minerals; (3) salts, and (4) metals.

In the meantime complete stagnation reigned in the scientific thought of Europe. The so-called lapidaries (from the Latin *lapis*— stone), the only mineralogical literature of the day, were mainly tales about the magic properties of stones.

Thus, the first stage in the development of mineralogy, which included the Middle Ages, ended with the science still in the embryonic state. For the most part only ores were recognised as minerals, and their classification was rather primitive. There existed no conception of chemical elements, or of chemistry as such; hence the concept of the chemical nature of elements could not emerge. Chemistry appeared in the late Middle Ages in the form of alchemy which persisted through the 17th century. The alchemists' goal was to obtain the "philosophers" stone" which would make it possible to turn base or "imperfect" metals into noble metals, mainly, gold. It was held that metals consisted either of arsenic, sulphur, and water or of mercury and sulphur mixed in different proportions. Moreover, what was meant by sulphur and mercury was very different from what it is today. For a long time the search for the "philosophers' stone" stifled natural science in general and chemistry in particular, and often led the experimenter to the most fantastic conclusions.

Mineralogy becomes a science. In the 16th century a number of important mineralogical treatises appeared in Europe. Independently of each other, Biringuccio (d. 1538) in Italy and especially, Georgius Agricola (1490-1555) in Bohemia summed up the mineralogical knowl-



M. V. Lomonosov

edge of their day derived from practical mining experience in Saxony, Bohemia, Italy, and elsewhere in Europe.

Having discarded alchemy, Agricola made many accurate observations on the conditions of occurrence of different minerals in ore deposits. As a result he suggested a system of classification of minerals which, though roughly identical with that of Avicenna, was much more thorough. Agricola classified mineral formations as combustible minerals, earths, salts, gemstones, metals, and mineral mixtures. Although he had nothing to say as yet about chemical composition of minerals, Agricola described in detail such diagnostic features as colour, transparency, lustre, taste, odour, weight, hardness. He also touched upon the origin of ore deposits. His works influenced generations of mineralogists.

In Russia the beginning of mineralogy as a science is linked with the name of Mikhail Lomonosov (1711-1765). A son of an Archangel peasant, he was exceptionally gifted and erudite, and in his scientific thinking he was far ahead not only of his German-born colleagues at the Russian Academy of Sciences, but also of many of the best minds of Western Europe. Proceeding from his "corpuscular philosophy" he formulated a theory of the structure of crystalline matter, and developed the kinetic theory of gases and the mechanical theory of heat,

in which he was at least a hundred years ahead of his time. Being a talented chemist, he applied quantitative analysis of chemical processes, clarified the role played by air in the burning of organic matter, and formulated the law of conservation of matter long before Lavoisier.

Mineralogy proper began to interest Lomonosov during the second half of his scientific career. In 1742 he began to study minerals and compile a catalogue of the Mineralogical Museum of the Academy of Sciences. The remainder of his life was spent in writing the *General System of Russian Mineralogy*, a stupendous undertaking for his day. In 1761 he submitted to the Senate a project for the collection all over Russia of "various sands, various stones, various clays as indicated by their colour", to be delivered to St. Petersburg for further study. In 1763 he appealed to the mine owners asking them "to supply specimens of various metalliferous ores and thus share in the compilation of a Russian Mineralogy".

An ardent patriot, Lomonosov wrote his geological treatises in Russian (*How Metals are Born Through the Quaking of the Earth*, *The Strata of the Earth*, etc.). In them he gave much practical advice on prospecting for ores.

In Western Europe, by the middle of 18th century there rose to prominence a number of Swedish mineralogists, such as K. Linnaeus and Kronstedt who were Lomonosov's contemporaries. K. Linnaeus (1707-1778), the author of *Systema Naturae*, extended the application of his binomial nomenclature (genera and species) from botany and zoology to mineralogy. To A. Kronstedt (1702-1765) goes the credit for eliminating fossils from the domain of mineralogy. He also improved the blowpipe method and studied the chemical composition of minerals.

The late 18th century saw the appearance of the Freiberg school of mineralogy. At first headed by A. G. Werner (1750-1817) and then by I. A. Breithaupt, the school influenced the development of mineralogy in many countries.

Meanwhile, mineralogical knowledge in Russia developed independently and rose to such a high level that it acquired renown and recognition throughout the Western Europe. A great role in this was played by great scientific expeditions to various provinces over the vast territory of Russia, principally in the Urals and Siberia, organised by the Academy of Sciences in the second half of the 18th century. Fundamental treatises appeared dealing with the geography of the country, its etnography, fauna, flora, and mineral resources. The authors of these works were I. I. Lepekhin (1771-1772), P. S. Pallas (1771-1788), I. F. Hermann (1789-1811), V. F. Zuyev, V. M. Severgin, and others.

Quite a few mineral deposits were discovered by peasants and miners. In the late 18th and early 19th centuries they discovered numerous deposits of gemstones and gem materials (tourmaline, topaz, rock crystal, emerald, malachite, etc.), gold and platinum first discovered in the Urals (Fig. 2) as well as deposits of iron, copper, lead, silver,

etc. All these discoveries, especially of new minerals which were often displayed at international fairs, were generally recognised outside Russia as highly important contributions to the development of world science.

Eminent Russian mineralogists of that time were V. M. Severgin and D. I. Sokolov.

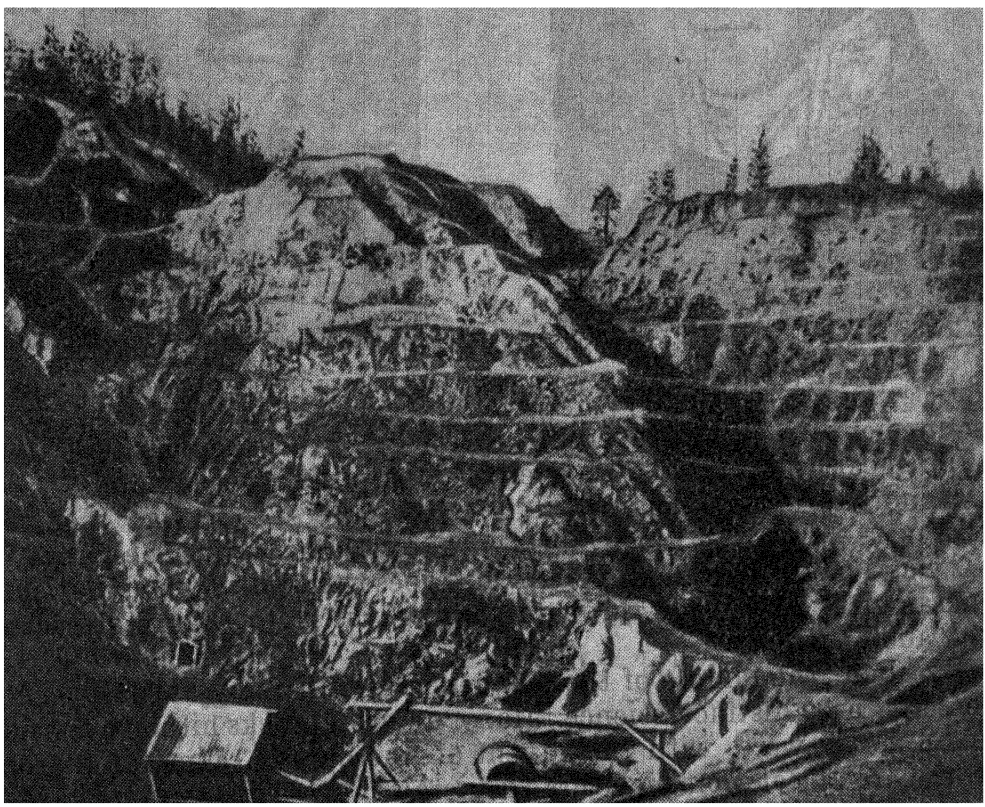
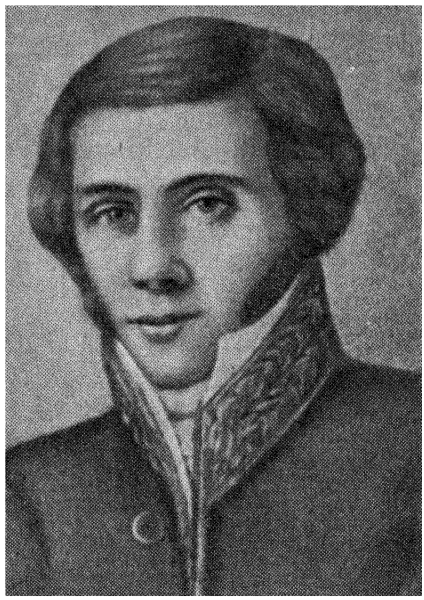


Fig. 2. Open-cut mining on Mt. Vysokaya in the Urals.

V. M. Severgin (1765-1826), Lomonosov's successor, was intolerant of all sorts of scholasticism, especially that of the Werner school. It was Severgin who brought to completion Lomonosov's project for compiling a *General System of Russian Mineralogy* in which he summed up the vast data collected by the Academy expeditions. In 1809 he published a two-volume *Essay of Mineralogical Description of the Russian State.* Among his numerous writings the following are the most important: *Elements of Mineralogy or the Natural History of Mineral Bodies* (1798), *The Art of Assaying or a Manual for the Chemical Testing of Metallic Ores* (1801), *Comprehensive Mineralogical Glossary* (1807), *A New System of Minerals Based upon External Features* (1816). His writings did much to disseminate mineralogical knowledge. Many terms he coined won a permanent place not only in mineralogy but



V. M. Severgin



D. I. Sokolov

also in chemistry, since Severgin extended his study beyond the external physical properties to the chemical composition of minerals.

Honorary Academician D. I. Sokolov (1788-1852) was a gifted lecturer. *A Manual of Mineralogy* in two volumes which he wrote in 1832 was a model textbook. To him also goes the credit for popularising mineralogical knowledge through lectures which invariably attracted large audiences.

By about the middle of the last century, mineralogy at last began to emerge as a distinct science. Many names of rocks hitherto considered minerals were, with the advent of microscopy, eliminated from the mineralogical nomenclature. Minerals were increasingly looked upon as *crystalline entities* possessing definite properties. Verbose dissertations on minerals in the tradition of the Werner school now gave way to the description of the crystallographic forms, physical and chemical properties of minerals with full chemical analyses.

Academician N. I. Koksharov (1818-1892), whose name is associated with the flourishing of Russian mineralogy, was an outstanding crystallographer and research worker. He carried out an enormous work in precise study and systematisation of the minerals found in Russia, and his numerous descriptions and measurements of crystals (still unsurpassed in accuracy), mainly of those from the Urals, have become standard in all textbooks and manuals on mineralogy.

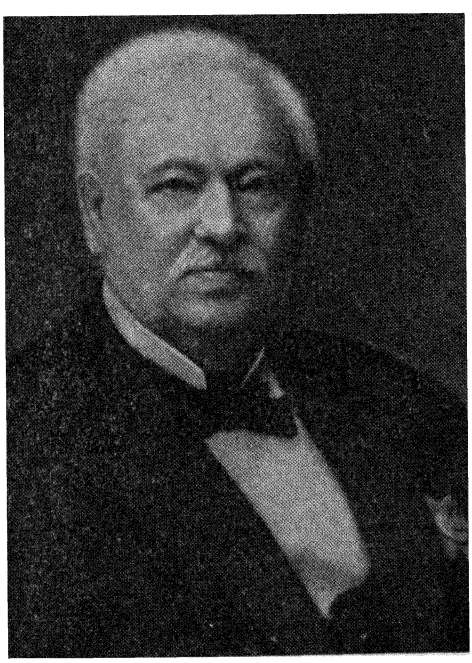
His eminent contemporary, Academician P. V. Yeremeyev (1830-1899) took an active part in studying all the new specimens arriving at the Mineralogical Society. His extensive research in the physiography of minerals, especially of twins and pseudomorphs, was a great contribution to the development of Russian mineralogy.

As the number of full chemical analyses performed by research workers (such as Academician T. Y. Lovits, Vauqueline, Wollaston, Lubarsky, Moscow apothecary R. Hermann, P. Yevreinov, Tennant, and others) was increasing, scientists began to consider developing a system of mineralogy based upon the chemical composition of minerals. However this became possible only when the great Russian scientist D. I. Mendeleyev (1834-1907) had suggested the *periodical system of chemical elements.* The tremendous importance of the periodic law is emphasised by the fact that it has become the foundation for many of the great modern breakthroughs in the field of natural sciences.

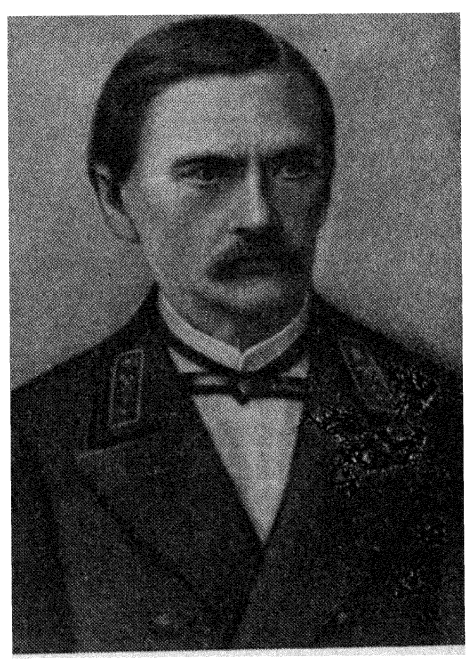
At the same time A. M. Butlerov (1826-1886) laid the foundations of the theory of chemical structure of matter which played an important role in the advancement of chemistry and crystallography.

The modern period in the development of mineralogy. Russian crystallography owes its greatest achievements to Y. S. Fyodorov (1853-1919) who, proceeding from purely mathematical analysis, formulated the *theory of the structure of crystals* and in 1890 published his classical work *Symmetry of Regular Systems of Figures* in which he deduced the only possible 230 space groups of symmetry. A year later (1891) German mathematician A. Schoenflies published his own work on the same space groups into which he later introduced corrections suggested by Fyodorov.

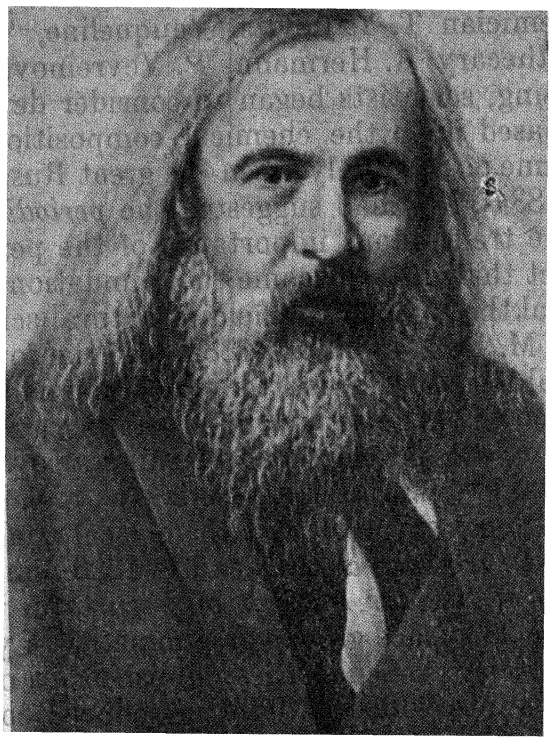
Another field to which Fyodorov made a great contribution was the microscopic study of minerals. He developed a universal optical method of studying crystal grains in thin sections with the help of



N. I. Koksharov



P. V. Yeremeyev

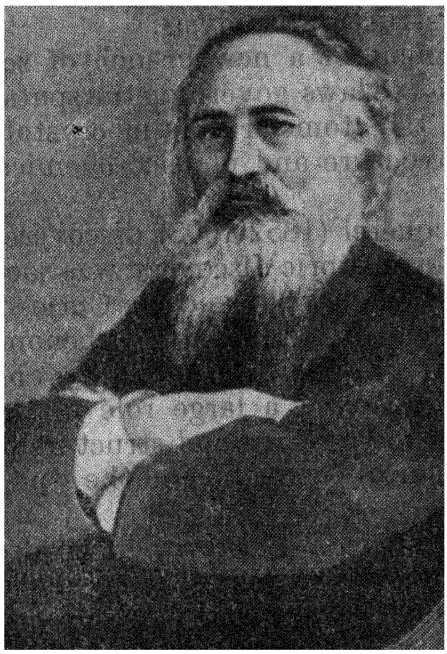


D. I. Mendeleyev

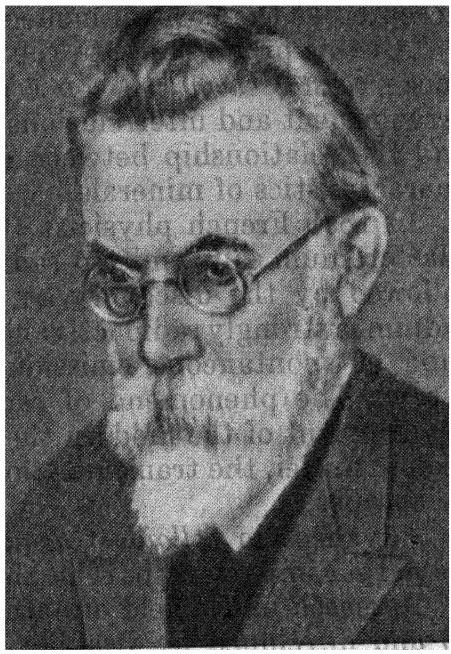
what we now call Fyodorov universal stage. The last years of his fruitful career Fyodorov spent in developing crystallo-chemical analysis, i. e., in determining the chemical composition of minerals based on goniometric measurements of crystals and his theory of crystal structure. Having critically revised the enormous amount of empirical data on crystal measurements that had accumulated by that time in literature, he arranged them in a systematic order. The fruit of this research was his capital *The Kingdom of Crystals* which was published posthumously in 1920.

Mendeleyev's periodic law and periodic system played a singular role in the development of mineralogy.

The idea that minerals are *products of chemical reactions* in the earth's crust is most remarkably expressed in the numerous works of the great Russian naturalist Academician V. I. Vernadsky (1863-1945). Regarding mineralogy as "the chemistry of the earth's crust", Vernadsky initiated a new trend in mineralogical research. He conducted extensive studies of the chemical composition of minerals in the light of modern science, the paragenesis of minerals, and the conditions of their existence in nature viewed historically. In 1891 Vernadsky proved experimentally that in alumosilicates tetravalent silicon may be replaced by trivalent aluminium whose role was that of an acid function. Thirty years later this experiment was not only fully confirmed by X-ray study of feldspars but also helped to further the study of the structures of alumosilicates other than feldspars.



Y. S. Fyodorov



V. I. Vernadsky

Vernadsky's mineralogy struck a new note in the development of mineralogical knowledge. The result of his enormous, painstaking work done between 1908 and 1914 was the first volume of his classical monograph on the mineralogy of Russia *Essay on Descriptive Mineralogy* which dealt with native elements. Unfortunately, he has not completed in his lifetime this work, nor his other book *The History of Minerals in the Earth's Crust.*

Geochemistry was a new science which Vernadsky created and for which his own generalisations served as the foundation, though the first attempts at generalising the chemical processes in the earth's crust had been made in the middle of the last century by K. Bischoff (1792-1870) and Elie de Beaumont (1798-1874). Modern geochemistry also owes much to V. M. Goldschmidt (1888-1947) and, last but not least, to Soviet Academician A. Y. Fersman.

In 1895 while studying cathode rays, W. Roentgen (1845-1923) discovered X-rays (also known as Roentgen rays) and, as a result, new methods were developed for the analysis of mineral substances. The discovery in 1912 by physicist M. Laue of the diffraction of X-rays by crystals, and the subsequent research in this field by G. V. Wulf in Russia, W. G. Bragg and W. L. Bragg (father and son) in England, L. Pauling in the U.S.A., and by other workers, revealed a close relationship between the internal crystal structure and the chemical composition and physical properties of minerals. This research confirmed Lomonosov's conjectures on crystal structure and Fyodorov's deduction (1890) of the only possible 230 patterns of arrangement of

atoms in crystals. Fyodorov's concept of symmetry has been fully accepted as the basis of modern X-ray structural analysis.

All this progress led to the development of a new branch of science — *crystal chemistry* concerned with the laws governing the spatial arrangement and interrelations between the atoms or ions in crystals, and the relationship between crystal structure and physico-chemical characteristics of minerals.

In 1896 French physicist Henri Becquerel (1852-1908) discovered that uranium salts emitted radiation. This historic discovery was soon followed by the discovery by M. Curie-Sklodowska and P. Curie of radium, a strongly radioactive chemical element, exhibiting the phenomenon of spontaneous emission of energy in the form of α-, β-, and γ-rays. The phenomena of radioactivity played a large role in the development of the modern theory of the composition and structure of atomic nuclei, the transmutations of chemical elements, and the study of isotopes.

Advances in *colloidal chemistry and physical chemistry* have also played an important part in the development of modern mineralogy.

Research in the field of natural colloidal systems was first summed up and developed by Russian scientist P. P. Weimarn and Austrian scientist F. Kornu. Other studies deserving mention are those by Van Bemellen concerning the properties of the principal colloids in the earth's crust, and those by R. Liesegang of diffusion phenomena and rhythmic reactions in natural colloids.

Highly important were also the advances of physical chemistry, especially in the fields of the theory of phases (in the physico-chemical sense of the word), and the equilibrium of physico-chemical systems. World science is indebted not only to Gibbs who formulated the phase rule, but also to Soviet Academician N. S. Kurnakov (1860-1941) who developed the method and technique of physico-chemical analysis of alloys and other complex bodies using graphic means of expressing the relationship between the composition and properties of substances. He was also, at least in part, the founder of the thermal analysis of minerals.

The study of natural compounds was accompanied by experimental work in the *synthesis of compounds* identical with those occurring in nature. Minerals were produced artificially as early as the 18th century, but it was not until the middle of the last century that the experiments such as those carried out by G. Daubrée, F. Fouqué, and others, became systematical. In Russia considerable success in this field was achieved by K. D. Khrushchov.

Thus, the turn of the century was marked by many major achievements in crystallography, physics, and physical chemistry. These discoveries made on the basis of Mendeleyev's periodic law led to the greatest discoveries of modern science.

Mineralogy in the Soviet Union. The Great October Socialist Revolution was the turning point in the development of Russian science

in general, and mineralogy in particular. Geological prospecting, exploration, and research launched on a vast scale throughout the Soviet Union have added immeasurably to our knowledge, especially in regional mineralogy. Within a relatively short time both the regions already explored and those either entirely or partially unexplored became the object of systematic study. Some of these regions proved exceptionally interesting mineralogically and otherwise. However, without detailed mineralogical studies, it would have been impossible to discover most numerous deposits of economic minerals to supply the needs of the burgeoning industry.

Mineralogical research ceased to be an end in itself, since mineralogy had to satisfy the increasing demands of industry. It was therefore essential for it to become more purposeful than it was before the Revolution. Soviet mineralogists attacked problems important to the national economy. This called for applying their theoretical knowledge to the solution of practical tasks which, in turn, involved thorough study of natural phenomena and the further expansion of theoretical knowledge in the best traditions of Koksharov, Fyodorov, Vernadsky, and others.

Earlier abstract descriptions of minerals gave way to purposeful investigation of mineral substances. No longer fascinated only with the esthetic aspect of mineral substances and well-shaped crystals, mineralogists concerned themselves with the peculiarities of composition and those finer properties of minerals that might prove of value to science and industry. As far as the problems of the formation of minerals were concerned, research workers discarded speculations often utterly unfounded and delved into the realities of nature instead. They began working out scientific methods for the analysis of the paragenesis of minerals by applying the laws of physical chemistry.

The discovery and development of mineral resources depended greatly on the expeditions of the U.S.S.R. Academy of Sciences led by A. Y. Fersman (1883-1945), Vernadsky's gifted disciple and continuer whose versatility and energy showed themselves most fully in Soviet times. Among his numerous works is a monograph *Pegmatites* which sums up his research of many years and is of special importance to mineralogy.

The study of mineral resources was considerably advanced by A. K. Boldyrev (1883-1946), Fyodorov's closest pupil. His detailed *A Course of Descriptive Mineralogy* (in three issues), and the two editions of an undergraduate course in mineralogy prepared under his supervision by a team of lecturers of the Leningrad Mining College, had a great influence on the spreading of mineralogical knowledge.

The name of Academician S. S. Smirnov (1895-1947), a noted mineralogist and explorer of ore deposits, is known to every Soviet geologist, chiefly through his classical monograph *The Zone of Oxidation of Sulphide Deposits.*



A. Y. Fersman

Major contributions to the mineralogy of economic mineral deposits were made by other Soviet scientists as well.

Extensive work was also done in the development of different methods for the investigation of mineral substances, and it was this work that made possible rapid advances in mineralogical research, particularly in the field of finely dispersed mineral matter and opaque ore minerals. Coarse methods of research were superseded by accurate and rapid methods, such as spectral analysis, X-ray examination, electronography, the examination of opaque substances in polished sections and reflected light, luminescent analysis, and thermography. Great progress was made in the synthesis of minerals and in the field of experimentation.

Improved research techniques due to advances in auxiliary exact sciences permitted a deeper approach to the study of minerals and revealed new, hitherto unknown, properties which could be used for practical purposes. This elevated descriptive mineralogy, an important aspect of mineralogy as a whole, to a new, higher plane. An accurate description of new natural phenomena and their analysis in terms of the exact sciences is always a contribution to the progress of science in general.

In recent years, Soviet scientists have made enormous progress also in deciphering the crystal structures of minerals which put them far ahead of their foreign colleagues. Thus, to N. V. Belov goes the credit for evolving the theory of crystal structure based on the principle of closest packing of atoms or ions, a theory which helped to decipher within a short time many complex crystal structures, and to reveal some



A. K. Boldyrev



S. S. Smirnov

new structural types. These highly laborious investigations are of importance not only for determining the chemical composition of minerals, but also for establishing the relationship between the properties of minerals, on the one hand, and their composition and crystal structure, on the other, thus giving a key to rational mineral classification.

Modern mineralogy is of fundamental importance to a number of other geological sciences, above all to those dealing with rocks (petrography) and ores (mineragraphy), i. e., mineral aggregates which form independent components of the earth's crust.

Summing up, it may be said that Russian mineralogy, ever since Lomonosov, developed along its own original lines.

The work of Russian scientists holds a place of honour in the history of mineralogy as a whole. Russian and Soviet scientists made an indisputable and very substantial contribution to the progress of mineralogy as a world science. The foundations of modern mineralogy were laid by many great Russian mineralogists, from Lomonosov and Severgin to Fyodorov, Vernadsky and other outstanding scientists of our time.

THE ECONOMIC IMPORTANCE OF MINERALS AND MINERALOGICAL RESEARCH

There is virtually a single industry where minerals have not been used either in their crude state or after appropriate treatment. Everybody knows the tremendous role played in mankind's life by iron extract-

ed from iron-rich ores by smelting the latter into various grades of cast iron and steels. Iron is vital to metallurgy, mechanical engineering, ship-building, railway transport, bridges, reinforced-concrete structures, manufacture of mining machinery and the production of consumer goods. In turn, iron smelting consumes about 40 per cent of the total output of coking coal. Liquid mineral fuels such as oil and its fractions play an enormous economic role. Natural gas is also increasingly used by modern industry.

Non-ferrous metallurgy, electrical engineering, ship building, and the aircraft industry, etc., depend greatly on the so-called non-ferrous metals extracted from the ores of copper, zinc, lead, aluminium, nickel, and cobalt. The so-called rare metals such as tungsten, molybdenum, titanium, vanadium and cobalt are indispensable strategic materials.

Modern farming is inconceivable without mineral fertilisers, minerals containing potassium (potassium salts), phosphorus (apatites, phosphorites), nitrogen (nitre), etc. Minerals are often used by the chemical industry as stock materials for the production of chemicals, e. g., sulphuric acid from pyrites. Native sulphur, nitre, fluorspar, and minerals of boron, potassium, sodium, magnesium, and mercury are used to make chemical preparations; sulphur, talc and barite find uses in the rubber industry; asbestos, quartz, graphite, etc., go to make acid-resistant materials and refractories; galena, sphalerite, barite, minerals of titanium, copper, iron, arsenic, mercury, cobalt, and boron, cryolite, orthoclase, and zirconium are used in making pigments, enamels, and glazes; talc, kaolin, sulphur, alum, magnesite, etc., are used for paper-making.

Rock and common salts form a vital part of the human diet. Some minerals and the products thereof are used as medicines. They include Glauber salt or mirabilite, mineral waters like narzan and borzhomi of Georgia and also salts of bismuth, barium, boron, and iodine. Mineral springs (hydrosulphuric, carbonated, chalybeate, hydrochloric, etc.) and natural muds also find medical uses. Radioactive substances obtained from radioactive minerals, or the man-made radioactive isotopes of certain chemical elements are important not only to medicine but also to industry.

Besides gemstones which are used as ornaments or jewelry, there exist beautifully coloured ornamental stones used as wall facings. The Soviet Union's finest buildings are decorated with pink rhodonite, varicoloured jasper, marble, and quartzite. Quartz, Iceland spar, mica, tourmaline, and fluorite are used in optical instruments. Agate, corundum, zirconium, and other hard minerals make good bearings for watches and precision instruments. Diamond (carbonado), corundum, garnet, and quartz are used as polishing abrasives. Soft and unctuous minerals such as talc and graphite find employment as fillers and lubricants.

Now that the problem of releasing the tremendous power of the atom in so-called atomic piles or reactors has been solved, vast pros-

pects have opened for harnessing this power to peaceful uses. In 1954 the world's first power station burning atomic fuel was commissioned in the U.S.S.R. Thermonuclear reactions releasing an enormous amount of energy through the fusion of heavy hydrogen (deuterium and tritium) into helium, with the participation of lithium, are fraught with still even greater promise.

The economic importance of minerals and of their immediate products is far from being completely covered in this account.

The industry of tsarist Russia was at a very low level of development, and largely depended on foreign capital which owned all the larger mines. After the Revolution the country faced the task of most rapid industrialisation. This involved the establishment of entirely new technologically up-to-date industries. This, in turn, called for forced development of mining to meet the ever-increasing demand for mineral raw materials.

In the course of this work numerous new deposits of highly important commercial minerals were discovered and developed, including some that had never been mined in old Russia: the Solikamsk deposits of potassium and magnesium salts, the boron deposits of the northern coast of the Caspian Sea, aluminium in the Northern Urals, the copper ores of Kazakhstan, the oil fields in the West of the Urals and those of the European plain. The known reserves of ferrous, non-ferrous, and rare metals: iron, manganese, chromium, copper, zinc, lead, tin, tungsten, molybdenum, nickel, etc., increased immensely. The U.S.S.R. became self-sufficient with regard to metals and mineral raw materials, and has been able to discontinue entirely imports thereof.

Knowledge of mineralogy is highly important for geological prospecting and exploration which depend primarily *on accurate identification of minerals, on knowledge of the conditions and associations in which they occur in nature, etc.* Many a valuable deposit has been missed because of the failure on the part of the geologist to identify the minerals correctly. In the search for outcrops of mineral deposits it is important to know the mineralogical characteristics of the oxidised zones of ore deposits and to be able to determine the composition of the primary ores below the ground-water table.

Apart from this, a number of physical properties of minerals (magnetism, electrical conductivity, specific gravity, etc.) have great importance for geophysical prospecting and exploration methods in the search for minerals and ores (magnetic, electrical, gravimetric, and other methods).

The study of the qualitative characteristics of ore deposits that are being exploited is a major task of the mining geologist. Observing daily the behaviour of ores in mine workings, the mine geologist grasps better than anybody else the dependences governing the spatial alteration of the mineral composition of ores which is highly important for directing further mining operations.

In many instances, prior to smelting or processing, the extracted ore is mechanically enriched at ore-dressing plants where the mineral is either separated from gangue or divided into concentrates of different composition. Ore concentration with preliminary crushing and milling is carried out in special installations that take advantage of certain properties of the minerals such as specific gravity, magnetism, electrical conductivity and flotation characteristics. These processes, to a considerable degree, depend on the size of grains composing the ore and the nature of their intergrowth. The evaluation of these characteristics comes within the scope of the special mineragraphic laboratories of ore-beneficiation research centres. However, any geologist proficient in the techniques used in mineralogy, provided he pays close attention to the study of mineral constituents and the structure of ores, may be able to predict the behaviour of an ore during concentration and to say which components will be lost, and why.

Therefore, mineralogical study of deposits of economic minerals is important not only in geological exploration and prospecting but also in mining and subsequent treatment of these minerals.

Chapter I

THE EARTH'S CRUST. STRUCTURE AND COMPOSITION

The structure of the earth. Geology, and hence mineralogy, is mainly concerned with the study of the *earth's crust** by which is meant the uppermost shell accessible to direct examination. This includes the lower atmosphere, the hydrosphere, and the upper lithosphere.

Our knowledge of the structure and composition of the earth's crust depends almost entirely upon observations of the uppermost parts of our planet. The only exception to this are those deeper parts penetrated by mine openings and oil wells. At the Witwatersrand gold fields in South Africa the maximum depth of mines is about 2.5 km. The world's deepest oil wells reach the depth of 4 to 5 km.

The orogenic processes throughout geologic time, which resulted in the formation of mountain ranges, often lifted from the interior of the earth to the surface rocks which are never formed under surface conditions. The geological data and estimates thus gained give a more or less reliable picture of the structure and composition of the globe only to a depth of 16-20 km, as compared with the earth's total radius of more than 6300 km.

An idea of the structure and composition of the deeper parts of the earth's interior may be formed only on the basis of indirect data. A comparison of the density of the entire globe (5.527) and its crust (2.7-2.8) shows that the inner parts of our planet must possess much greater density than the outer ones. Various data (geophysical observations, comparison between the earth and other celestial bodies, the composition of meteorites, etc.) indicate that this should be attributed not only to the increase in pressure with depth but also to the different composition of the deeper parts.

According to V. M. Goldschmidt, the earth consists of three principal concentric zones (geospheres): (1) the upper lithosphere; (2) the intermediate chalcosphere rich in oxides and sulphur compounds of metals, mostly iron; and (3) the central siderosphere or an iron-nickel core**. The lithosphere is subdivided into two parts: an upper one

* The term "earth's crust" is purely metaphorical and bears no relation to the crust formed by the original cooling of the earth.

** Recent astronomic evidence indicates that the core at a depth of about 3000 km possesses the properties of a liquid.

extending to a depth of 120 km chiefly composed of common silicate rocks, and a lower eclogite shell (120-1,200 km) composed of silicate rocks enriched with magnesium.

Characteristics of Individual Geospheres According to Goldschmidt

Geospheres	Thickness, km	Density	Composition
Atmosphere	Several hundred	0-0.0015	N_2, O_2, H_2O, CO_2, noble gases
Biosphere	0-11	About 1	Organic matter and minerals of skeletons
Hydrosphere	0-11	1	H_2O, etc. (oceans, partly inland waters, ice and snow)
Upper silicate shell	60-120	2.73	Lithophylic[1] elements: O, Si, Al, Ca, Mg, Na, K, Li, Rb, Ba, etc.
Eclogite shell	1100	3.6-4	Silicates, chiefly of Mg, Fe
Sulphide-oxide shell	1700	5-6	Chalcophile[2] elements: S, Se, Te, Fe, Cu, Zn, Pb, Cd, Hg, Sb, Bi, As, Au, Ag, etc.
Iron-nickel core	3500	8-10	Siderophyle[3] elements: Fe, Ni, Co, the platinum group; Mo, P, C, etc.

[1] "Lithos" is the Greek for stone; most lithophyles characteristically have an affinity to oxygen.
[2] "Chalcos" is the Greek for copper; most chalcophiles characteristically have an affinity to sulphur.
[3] "Sideros" is the Greek for iron ("meteorite").

The relation between the geospheres is diagrammatically represented in Fig. 3 in accordance with geophysical data obtained at depths of 1,200 and 2,900 km from the surface of the earth.

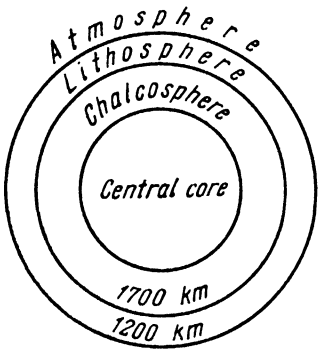


Fig. 3. Diagram of the earth's structure.

The composition of the earth's crust. The average chemical composition of the outer 16 km of the crust which is accessible for study and which includes the hydrosphere, biosphere, and the lower atmosphere, has been estimated by many scientists. In 1889 American investigator F. Clarke was the first to compute the composition of the solid crust of the earth in weight percentages. These percentages were calculated more precisely by V. I. Vernadsky, A. Y. Fersman, I. and V. Noddak, G. Hevesi, V. M. Goldschmidt, and A. P. Vinogradov. The latter calculated the average composition of the lithosphere alone leaving out the hydrosphere and the atmosphere.

Academician A. Y. Fersman introduced the term "Clark numbers" or simply "clarks" for the average figures of the contents of individual elements in the earth's crust, and also suggested that these values be expressed not only in weight percentages but in atomic percentages as well.

Of the 102 chemical elements listed in the Mendeleyev periodic table (Table 1) very few are widespread in the earth's crust. These are found mainly at the top of the table, i. e., are elements with low atomic numbers.

The most widespread elements are O, Si, Al, Fe, Ca, Na, K, Mg, Ti, H, and C. All the others make up as little as a few tenths of a per cent of the earth's crust (by weight). The vast majority of these elements occur solely in the form of compounds, and only very few are found in the native state. Both types are formed as a result of chemical reactions occurring in the course of the various geologic processes in the earth's crust giving rise to most diverse rock masses and economic mineral deposits.

According to weight percentages, the major elements comprising the earth's crust may be arranged in tabular form (see Table 2).

The table shows that the compounds of the elements of the first two groups must constitute the overwhelming mass (by weight) of the minerals in the earth's crust. Indeed very widespread in the earth's crust are oxygen compounds of silicon, aluminium, and iron as well as those of the alkali-earth and alkali metals (calcium, magnesium, sodium, potassium). They occur for the most part as oxides and oxygen salts (chiefly silicates, alumosilicates, carbonates, sulphates, etc.) and enter into the composition of various rocks composing the earth's crust.

The economically important heavy metals generally have the lowest clarks and fall into the last columns of the elements, arranged in the order of occurrence (Table 3).

Some special characteristics of the distribution of the heavy metals in the earth's crust. Many of these elements, though rare in the earth's crust as a whole, through the agency of natural geochemical processes, often form very large accumulations called ore deposits. Were it not for these processes, the extraction of the metals so vital to our industrial civilisation would not be worthwhile. Many of them extracted from rocks in the laboratory would be extremely expensive. Although the clarks of metals like vanadium, caesium, and gallium, are much higher than those of mercury, bismuth, silver and gold, the former, despite their valuable properties are not employed by man on any large scale because they seldom occur in the form of deposits with concentrations that would make their extraction economic.

Most of the natural compounds of heavy metals are relatively simple. Some of the heavy metals (Fe, Mn, Sn, Cr, W, Nb, Ta, Th, U) occur in the form of oxygen compounds, whereas many others (Fe, Ni,

Group periods	0	I	II	III	IV
I		1. H Hydrogen 1.0080			
II	2. He Helium 4.003	3. Li Lithium 6.940	4. Be Beryllium 9.013	5. B Boron 10.82	6. C Carbon 12.01
III	10. Ne Neon 20.183	11. Na Sodium 22.991	12. Mg Magnesium 24.32	13. Al Aluminium 26.97	14. Si Silicon 28.09
IV	18. Ar Argon 39.944	19. K Potassium 39.000	20. Ca Calcium 40.08	21. Sc Scandium 44.96	22. Ti Titanium 47.90
		29. Cu Copper 63.54	30. Zn Zinc 65.38	31. Ga Gallium 69.72	32. Ge Germanium 72.60
V	36. Kr Krypton 83.80	37. Rb Rubidium 85.48	38. Sr Strontium 87.63	39. Y Yttrium 88.92	40. Zr Zirconium 91.22
		47. Ag Silver 107.880	48. Cd Cadmium 112.41	49. In Indium 114.82	50. Sn Tin 118.70
VI	54. Xe Xenon 131.30	55. Cs Caesium 132.91	56. Ba Barium 137.36	57. La* Lanthanum 138. 92	72. Hf Hafnium 178.50
		79. Au Gold 197.0	80. Hg Mercury 200.61	81. Tl Thallium 204.39	82. Pb Lead 207.21
VII	86. Rn Radon 222	87. Fr Francium (223)	88. Ra Radium 226.05	89. Ac Actinium 227	90. Th Thorium 232.05

* 58-771. TR –rare earths (lanthanoids)
** Actinoids:

Group Periods		0	I	II	III	IV
58. Ce Cerium 140.13	59. Pr Praseodymium 140.92	60. Nd Neodymium 144.27	61. Pm Promethium 147.0	62. Sm Samarium 150.1	63. Eu Europium 152.0	64. Gd Gadolinium 156.9
65. Tb Terbium 158.9	66. Dy Dysprosium 162.46	67. Ho Holmium 164.94	68. Er Erbium 167.2	69. Tu Thulium 168.9	70. Yb Ytterbium 173.04	71. Lu Lutecium 174.99

Note. In parentheses: mass numbers of the stablest isotopes.

V	VI	VII	VIII		
7. N Nitrogen 14.008	8. O Oxygen 16.0000	9. F Fluorine 19.00			
15. P Phosphorus 30. 975	16. S Sulphur 32.066	17. Cl Chlorine 35.457			
23. V Vanadium 50.95	24. Cr Chromium 52.01	25. Mn Manganese 54.94	26. Fe Iron 55.85	27. Co Cobalt 58.94	28. Ni Nickel 58.71
33. As Arsenic 74.91	34. Se Selenium 78.96	35. Br Bromine 79.916			
41. Nb Columbium 92.91	42. Mo Molybdenum 95.95	43. Tc Technetium (99)	44. Ru Ruthenium 101.1	45. Rh Rhodium 102.91	46. Pd Palladium 106.4
51. Sb Antimony 121.76	52. Te Tellurium 127.61	53. I Iodine 126.91			
73. Ta Tantalum 180.95	74. W Tungsten 183.86	75. Re Rhenium 186.22	76. Os Osmium 190.2	77. Ir Iridium 192.2	78. Pt Platinum 195.08
83. Bi Bismuth 209.00	84. Po Polonium 210	85. At Astatine (210)			
91. Pa Protactinium 231	92. U** Uranium 238.07				

V	VI	VII	VIII			
92. U Uranium 238.07	93. Np Neptu-nium (237)	94. Pu Pluto-nium (242)	95. Am Ameri-cium (243)	96. Cm Curium (245)	97. Bk Berke-lium (249)	98. Cf Califor-nium (249)
99. En Einstei-nium (253)	100. Fm Fermium (255)	101. Mv Mendele-vium	102. No Nobe-lium			

Table 2

The Average Chemical Composition of the Lithosphere in Weight Percentage

(A. P. Vinogradov, 1949)*

I	O 47.0 Si 27.5		Ni 0.008 Li 0.0065 Zn 0.005		Se $6 \cdot 10^{-5}$ Cd $(5 \cdot 10^{-5})$
				VII	Sb $(4 \cdot 10^{-5})$
	Al 8.6 Fe 5.0 Ca 3.5		Ce 0.0045 Sn 0.004 Co 0.003		I $3 \cdot 10^{-5}$ Bi $(2 \cdot 10^{-5})$ Ag $(1 \cdot 10^{-5})$
II	Na 2.5 K 2.5	V	Y 0.0028 La 0.0018		In $(1 \cdot 10^{-5})$
	Mg 2.0		Pb 0.0016		
			Ga 0.0015		Hg $7 \cdot 10^{-6}$
	Ti 0.60		Nb 0.001		Os $5 \cdot 10^{-6}$
III	H (0.15)			VIII	Pd $1 \cdot 10^{-6}$
	C (0.10)				Te $(1 \cdot 10^{-6})$
	Mn 0.09		Th $8 \cdot 10^{-4}$		Au $5 \cdot 10^{-7}$
	S 0.09		Cs $7 \cdot 10^{-4}$		Pt $5 \cdot 10^{-7}$
	P 0.08		Ge $7 \cdot 10^{-4}$	IX	Ru $(5 \cdot 10^{-7})$
	Ba 0.05		Be $6 \cdot 10^{-4}$		Ir $1 \cdot 10^{-7}$
	Cl 0.045	VI	Sc $6 \cdot 10^{-4}$		Rh $1 \cdot 10^{-7}$
	Sr 0.04		As $5 \cdot 10^{-4}$		Re $1 \cdot 10^{-7}$
IV	Rb 0.031		Hf $3.2 \cdot 10^{-4}$		
	F 0.027		Mo $3 \cdot 10^{-4}$		
	Cr 0.02		B $3 \cdot 10^{-4}$		Ra $1 \cdot 10^{-10}$
	Zr 0.02		U $3 \cdot 10^{-4}$	XI	Pa $(1 \cdot 10^{-10})$
	V 0.015		Tl $3 \cdot 10^{-4}$		
	Cu 0.01		Ta $2 \cdot 10^{-4}$		
	N (0.01)		Br $1.6 \cdot 10^{-4}$		
			W $1 \cdot 10^{-4}$		

* Some of the rare earths and noble gases the quantitative determinations of which are unreliable have been omitted. For the first eight elements and also for sulphur, the data are corrected in accordance with the latest calculations of Soviet scientist A.P. Vinogradov.

Co, Zn, Cu, Pb, Hg, Mo, Bi, As, Sb, Ag) chiefly in accumulations of sulphur, arsenic, and antimony compounds.

A graph (Fig. 4) in which the atomic numbers of the elements are plotted on the x-axis and the logarithms of their atomic clarks along the y-axis shows that as the atomic numbers increase, the curves for the clarks of both odd and even elements tend to go downward. This

Table 3

Distribution of the Principal Metals in the Earth's Crust

Groups (decades)	II	III	IV	V	VI	VII	VIII	IX-XI
Metals	Al, Fe Mg	Ti	Mn, Cr, V, Cu	Ni, Zn, Sn, Co, Y, La, Pb, Ca, Nb	Th, Cs Ge, Be, As, Mo, U, Tl, Ta, W	Cd, Sb, Bi, Ag In	Hg, Os, Pd, Te	Au, Pt, Ru, Ir, Rh, Re, Ra

means that the average content of most chemical elements in the earth's crust is inversely proportional to their atomic numbers, although there are some exceptions (Li, Be, B and a few others).

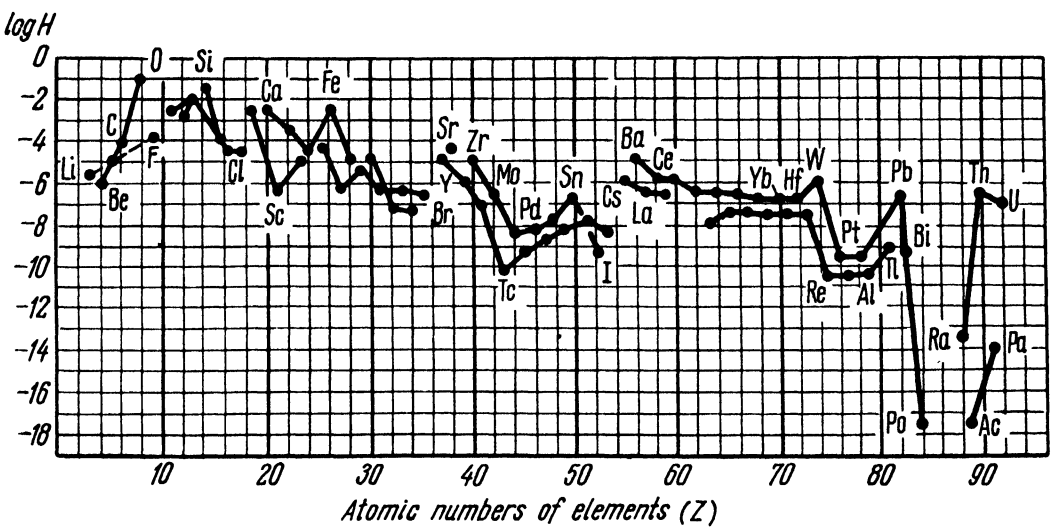


Fig. 4. Distribution of the elements in the upper lithosphere.

Graph gives the logarithms of atomic clarks (*H*) as functions of atomic numbers (*Z*), with oxygen taken as unity.

Soviet scientist P. P. Pilipenko noted that, generally, with a few exceptions, there is a direct relationship between the occurrence of elements in the earth's crust, in terms of atomic clarks, and the number of the minerals in which they are found. This is especially true in the case of elements with low atomic weights*:

* The number of minerals does not include only the varieties which contain the element as an isomorphous admixture.

Element	Atomic clark	Number of minerals	Element	Atomic clark	Number of minerals
O	53.39	1,221	Fe	1.31	170
H	17.25	798	K	1.05	43
Si	16.11	377	C	0.51	194
Al	4.80	268	Ti	0.22	30
Na	1.82	100	Cl	0.10	67
Mg	1.72	105	F	0.07	50
Ca	1.41	194			

This relationship does not hold in the case of certain heavy metals. Tellurium, whose atomic clark in the earth's crust is roughly one-hundredth that of selenium, forms about 40 separate minerals under natural conditions, whereas only 28 selenium minerals are known and these mainly in association with sulphur. Zinc, whose atomic clark is 50 times that of lead, forms 26 minerals in nature, whereas lead forms as many as 130, etc.

These differences obviously stem from the chemical properties of the elements themselves which, in turn, depend upon the structure of their ions and the position they occupy in Mendeleyev's periodic table. In the case of elements possessing similar properties, structures and ionic sizes but of different concentrations in a given solution or melt, it would be but natural to expect that during crystallisation, elements of lower concentration would dissolve, as it were, in the crystal structures formed by the predominant elements. Conversely, if in a given environment an element fails to find ions of other elements similar in size and structure, it will form a compound of its own, whatever its concentration in the solution. Characteristically, divalent manganese in most cases is present in minerals as an isomorphous admixture to divalent iron and calcium, whereas tetravalent manganese always forms compounds of its own. This also helps to explain why in nature elements like rubidium, scandium, hafnium, indium, and rhenium with low atomic clarks never form minerals on their own, but occur, instead, as disseminated isomorphous admixtures to other elements. This is also true to a large extent of more widespread elements such as selenium, vanadium, caesium, and cadmium. On the other hand, elements with very low atomic clarks such as tellurium, gold, platinum metals, and bismuth quite often form their own minerals.

1. GENERAL

When arranged in a systematic collection, mineral specimens present a great diversity of external features.

They may be transparent (rock crystal, rock salt), translucent, or absolutely opaque (magnetite, graphite).

The colour of a natural compound is often its most striking property. In the case of some minerals it is constant and very characteristic. Thus, cinnabar (mercury sulphide) is always carmine-red, malachite is bright-green; the cubic crystals of pyrite are readily identifiable by their pale brass-yellow colour, etc. On the other hand, some minerals exhibit a great variety of colour: different varieties of quartz are colourless (transparent), milk-white, yellowish brown, almost black, violet, or pink.

Lustre is also a very characteristic property of minerals. In some instances, minerals have the bright appearance of metals, and they are said to have a metallic lustre (galena, pyrite, arsenopyrite); in others, minerals have the appearance of glass and are said to have a vitreous lustre (quartz); or they may have the iridescent appearance of pearls, in which cases the lustre is termed pearly. There are many minerals which have no lustre and show a dull surface even when freshly broken.

Minerals often occur in crystals which are sometimes very large, and sometimes so small as to be visible only under a hand lens or a microscope. Minerals may possess peculiar crystal forms. Examples are the cubes of pyrite, the rhombododecahedra of garnet, the hexagonal prisms of beryl. However for the most part mineral masses occur as massive granular aggregates in which the individual grains have no external crystal form. Many minerals are also found in sinter forms which often assume strange shapes that have nothing in common with crystals, such as reniform (kidney-shaped) masses of malachite, or stalactitic formations of limonite (iron hydroxides).

Minerals also differ in other physical properties. Some are so hard that they readily scratch glass (e. g., quartz, garnet, pyrite), while others themselves are readily scratched with a fragment of glass, the point of a knife (e. g., calcite, malachite), or even with the finger nail (gypsum, graphite). Some minerals split easily along definite planes, the pieces having a regular form similar to that of a crystal (rock salt,

galena, calcite), others exhibit upon fracture curved, conchoidal surfaces (quartz). Properties, such as specific gravity, fusibility, etc., also exhibit a great variety.

Chemical properties of minerals vary no less widely. Some, rock salt for instance, are readily soluble in water, while others such as calcite are only soluble in acids, and still others like quartz are insoluble even in acids. Most minerals are stable in the air, but there are many natural compounds which readily oxidise or decompose under the action of atmospheric oxygen, carbon dioxide, and moisture. It has also been known long since that on exposure to light certain minerals gradually change their colour.

There is an increasing mass of evidence that shows that all these properties of minerals *depend on chemical composition and crystal structure of matter*. These are in turn determined by the size of the atoms and ions entering into the composition of the mineral, the structure of the electron shells (especially the outer ones), and by the properties of the elements as determined by their position in the periodic table. Therefore much that once seemed mysterious, now in the light of modern knowledge, becomes more and more clear. This not only gives us a better understanding of natural phenomena, but is also of use in putting the properties of minerals to practical uses.

It is therefore relevant at this stage to recall some of the fundamentals of physics, chemistry, crystal chemistry, and colloidal chemistry.

The aggregate states of minerals. In accordance with the three existing states of matter, three states of minerals are recognised: solid, liquid, and gaseous.

Any inorganic substance may be in any of these states depending on temperature and pressure or may change from one state to another when these factors change.

Depending upon the nature of the substance, the temperature limits of stability for each aggregate state may differ widely. Under atmospheric pressure and at room temperatures, most minerals remain solid, melting only at high temperatures. But under the same conditions mercury is a liquid, while hydrogen sulphide and carbon dioxide are gases.

The majority of solid minerals are *crystalloids*, i.e., substances with a crystal structure. Each crystalloid has a definite melting point at which the changes of the aggregate state involves absorption of heat which is clearly reflected in the behaviour of the heating curves (Fig. 5*a*). Over a certain interval of time, the heat which has been imparted to the system is spent for fusion (the curve flattens out).

Although the crystallisation of a homogeneous liquid upon cooling should occur at the same temperature as the melting of a solid body of the same composition, usually it occurs *at certain supercooling*, and this must be borne in mind.

Chemically pure solids characterised by the absence of an ordered structure, i.e., those lacking a regular arrangement of atoms are known

as *amorphous* bodies. They are classed with isotropic substances, i. e., those which have uniform physical properties in all directions. In contrast to crystalline substances, in amorphous substances the *change* of the aggregate state is *gradual.* This is shown by the gentle slope of the curve in (Fig. 5*b*), which is similar to the one given by sealing wax, a substance which on heating gradually becomes plastic, then viscous and finally fluid.

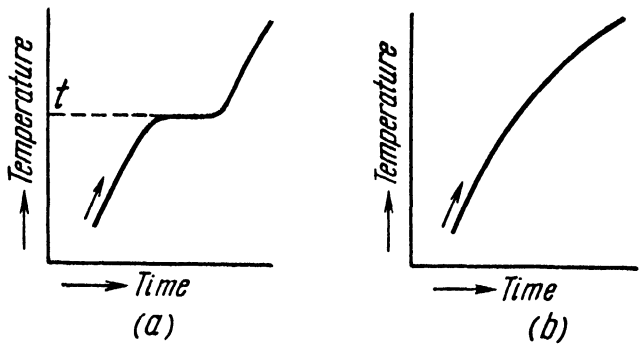


Fig. 5. Heating curves of crystalline (*a*) and amorphous (*b*) substances.

Amorphous substances often result from extremely rapid solidification of melted viscous masses. An example is the formation of lechatelierite, amorphous quartz glass, when lightning strikes crystalline quartz rocks. Amorphous substances are liable to change to crystalline masses only when kept for a prolonged period in a softened state at a temperature close to the melting point.

Crystal structure. The structure of a crystalloid, it will be recalled, is determined by: (1) the number of structural units (atoms, ions, molecules) held in space in a regular pattern by electrostatic forces; (2) the ratio of the sizes of the structural units which in turn determine the density of packing and the coordination number (i. e., the number of the nearest anions surrounding a given cation); (3) the type of chemical bonding which also has a major bearing on the spatial arrangement of atoms or ions giving rise to different types of structure.

The bonds maintaining the structural units of crystals in equilibrium are different for various types of chemical compounds. *Ionic* bonding which predominate in inorganic crystal substances depends on the electrostatic attraction between oppositely charged ions (e. g., Na^{1+} and Cl^{1-} in NaCl crystal structure). Directional, *covalent* (homopolar) bonding is characteristic of many crystal substances in which adjacent atoms form stable electron shells by sharing one or more electron pairs (e. g., in diamond each atom forms four stable covalent bonds with four surrounding atoms). The crystal structure of metals is characterised by *metallic* bond due to the fact that excess electrons in the outer electronic shells of the atoms are not lost, but form a com-

mon electron cloud, among the positively charged nuclei of the structural units. In molecular structures, the structural units which are electrically neutral molecules (e. g., many organic substances, native sulphur, antimony oxide, etc.) are held together by weak *van der Waals* (residual) forces. There also exist crystal substances with more than one type of bonding, one of the types being predominant. Many properties of minerals (optical, mechanical, electrical and heat conductivity, etc.) depend on the type of bonding between the structural units.

In ionic compounds the anions, being relatively large units, occupy most of the space in crystal structures and tend toward regular arrangement in space in accordance with the law of cubic (treble layer) or hexagonal (double layer) closest packing. The cations, being smaller, fill the spaces between anions which are either tetrahedral or octahedral depending on their relative dimensions. As a rule, the number of octahedral spaces in a closely packed arrangement is equal to the number of the anions, while the tetrahedral spaces, which are smaller in size, are double that number. However not all these spaces are filled with cations, nor are they filled in the same way. They may be filled in rows, layers, rings, zigzags, etc. The tetrahedral and octahedral shapes of the spaces largely explain why 4 and 6 are the most common coordination numbers for cations.

The theory of closest packings for inorganic compounds elaborated by N. V. Belov and fruitfully applied to the deciphering of the complex crystal structures of many minerals has helped to reveal most essential structural features which determine certain properties of crystalline substances. It should be noted, however, that depending on the size of the cations there may be less closely packed structures (with wider spacing between the anions), or some which are not at all closely packed (e. g., feldspars).

As known, crystallisation is an exothermal process, i. e., one which takes place with the evolution of heat. The energies of ionic-bound crystalline substances which do not contain strongly polarising or polarisable ions are the greater, the greater is the number of structural units, the higher are their valencies and the smaller their sizes (ionic radii). The energy of crystalline matter determines such properties as solubility, volatility, melting point, to some extent hardness, and others on which the stability of the compound depends.

Polymorphism. Polymorphism (*poly* is the Greek for many) is the ability of a crystalline substance to undergo one or more changes in crystal structure, and hence in physical properties, due to changes in environmental factors (mainly temperature). The most striking example is the dimorphism of natural carbon which, depending on the conditions, crystallises either as diamond (cubic system) or as graphite (hexagonal system) which, though identical in composition, widely differ in physical properties. On heating in the absence of oxygen at over 3,000 °C under atmospheric pressure, the crystal structure of

diamond changes to that of graphite which is more stable under these conditions. The reverse change does not occur.

Sometimes polymorphic conversion involves changes in crystalline structure so slight, as in the case of conversion of the so-called α-quartz into β-quartz, and vice versa; that they may be detected only upon very close examination of the physical properties of the mineral. However, optical examination (Fig. 6) positively shows that at the

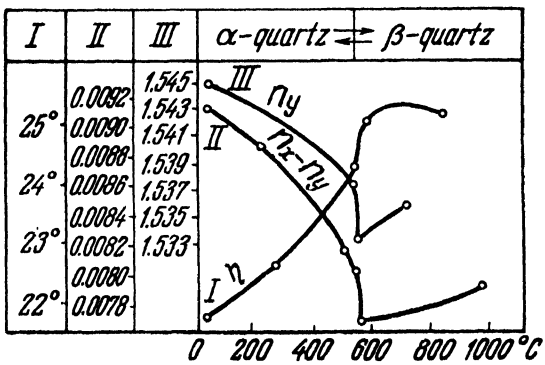


Fig. 6. Variation of the properties of quartz on heating.
I – rotation of polarisation plane; *II* – birefringence value; *III* – refractive index n_y (for the *D* line of the spectrum).

transition point (about 573 °C) there is an abrupt change in such properties as refractive index, double refraction, and rotation of the plane of polarisation.

The varieties of a crystalline substance which remain stable under given physico-chemical conditions are called *modifications*, each modification possessing a definite crystal structure of its own. A crystalline substance may have two, three, or more polymorphous modifications (sulphur has six, only three of which occur in nature; SiO_2 has nine, etc.).

Polymorphous modifications are usually indicated by the Greek letters α, β, γ, etc. (i. e., α-quartz which is stable below 573°; β-quartz which is stable above 573°). There is no agreement in literature on this matter. Some designate modifications by the letters α, β . . . etc., according to the order of lower or higher transition temperatures, others use these letters to indicate the extent of their occurrence or the order in which they were discovered. The first method seems to be the most reasonable.

Although common in natural compounds, polymorphism still awaits thorough study. Polymorphous modifications may be stable under a most wide range of environmental factors (temperature, pressure, etc.). Some remain stable within a wide range of temperatures and pressures (e.g., diamond, graphite), while others undergo polymorphic transformations within a narrow range of variation of external factors (sulphur).

A drop in temperature during the rearrangement of the crystal structure usually results in a modification with a higher cation coordination number (i.e., 8 instead of 6 for ammonium chloride, NH_4Cl, at 184° C), which is accompanied by the shrinking of the volume, with a consequent increase in density (specific gravity), and hence with an increase in the related refractive index. Lower pressure, on the other hand, favours a decrease in the coordination number, and consequently, lower transition temperature. Another important factor with certain compounds is the chemical nature of the environment. Thus, when alumosilicates are formed, a strongly alkaline environment tends to decrease the Al coordination number (from 6 to 4).

V. M. Goldschmidt has demonstrated that for a given type of chemical compounds (e.g., carbonates) the transition from one crystal structure to another is associated with the phenomenon of morphotropy, i.e., with a change in form. Thus, in the carbonate series (cationic radii are given in parentheses):

$$MgCO_3\ (0.74) - ZnCO_3\ (0.83) - CaCO_3\ (1.04) - \\ - SrCO_3\ (1.20) - BaCO_3\ (1.33)$$

we find that up to $CaCO_3$ the carbonates (with smaller cations) crystallise in the cubic system, and from $CaCO_3$ onwards, (with larger cations) they crystallise in the orthorhombic system. The $r_K{:}r_A$ ratio of $CaCO_3$ is such that either calcite (cubic system) or aragonite (orthorhombic system) are formed, depending on the environmental factors. In other words, near the boundary of morphotropic conversion calcium carbonate is dimorphous. As compared with aragonite, calcite has lower specific gravity and refractive index.

If, for example, the α-modification of a crystalline substance changes into the β-modification due to variations in external factors (e.g., temperature) and the process is reversed when the factors return to their initial state, such polymorphous conversions are said to be *enantiotropic**. Such is, for instance, the case of orthorhombic α-sulphur which changes into monoclinic β-sulphur and vice versa. If, on the other hand, the process is irreversible, such transformation is called *monotropic*. An example is the transformation of orthorhombic aragonite ($CaCO_3$) into cubic calcite (on heating).

Both modifications often occur in nature under the same physicochemical conditions and even side by side (i. e., pyrite and marcasite, calcite and aragonite, etc.). Apparently, in such cases the transition from the less stable to the more stable modification has been delayed for some reason or other, and the substance is said to be in a *metastable* (sometimes also called labile or unstable) state.

It should be noted that the stable modifications have lower vapour pressure, lower solubility, and higher melting points than the unstable one.

* "Enantios" is the Greek for opposite; "tropos" means change.

Breakdown of crystal structure. The principal features of the crystal structure of a mineral are the ordered arrangement and the strict equilibrium of the structural units. However, once the inner bonds of the structural units have been disturbed due to changes in the environment, a crystalloid with an ordered spatial structure turns into an amorphous mass.

Ferrobrucite, (Mg, Fe) $[OH]_2$, a mineral containing an isomorphous admixture of almost 36 per cent (by weight) of ferrous oxide, is a vivid illustration of this phenomenon. The mineral, when freshly extracted from deep horizons of a mine, is perfectly colourless, transparent, and has a vitreous lustre. In a few days upon exposure to air, its small crystals, while retaining their external crystal form, gradually change in colour, successively becoming brass-yellow, brown, and opaque dark-brown.* Chemical analysis shows that almost all the divalent iron becomes trivalent during this process (i.e., is oxidised), and X-ray analysis does not reveal any signs of crystalline structure. Apparently, the oxidation of the iron disturbs the inner bonds of the crystal lattice, and this results in the breakdown of the ordered structure.

What happens to ferrobrucite in conditions of oxidation at room temperature and atmospheric pressure, may happen to other minerals at higher temperatures and pressures.

Very interesting phenomena are observed in minerals containing rare-earth and radioactive elements (orthite, fergusonite, aeschynite, etc.). In these very often, though not always, the crystalline substance alters to an amorphous one, presumably under the action of α-radiation given off in the course of radioactive decay**. The resultant vitreous minerals do not belong to the cubic system as they are optically isotropic, do not diffract X-rays, i. e., behave as amorphous bodies. In addition, these substances are partly hydrated. Brögger suggested the term *metamict* to describe these minerals.

Many other examples similarly confirm the phenomena of disintegration of crystalline structures with the formation of amorphous or colloidal masses. These, however, should not be regarded as the stable form of the substance. Quite a few examples are known of a secondary

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* Brucite that contains no iron remains stable under the same conditions.

** In such cases, radioactivity alone is not enough to achieve the amorphous state and the following two conditions are also essential:

(1) the initially appearing crystalloids should have a sufficiently loose ionic structure to allow rearrangement or hydrolysis; such lattices are formed chiefly by the combination of weak bases with weak anhydrides;

(2) the lattice should possess one or more types of ions (e.g., rare-earth ions) capable of readily reversing their charges or even turning into neutral atoms (e.g., formation of atomic fluorine in fluorite on external radioactive irradiation).

The Soviet scientist V.M. Goldschmidt interprets the decay itself as the rearrangement of matter. Thus, the compound $YNbO_4$ turns into a finely dispersed mixture (solid pseudosolution) of the oxides Y_2O_3 and Nb_2O_5. This explains why such simple compounds as ThO_2 (thorianite) or the salts of strong acids with weak bases such as (Ce, La...) PO_4 (monazite) never become amorphous.

rearrangement of the matter leading to the formation of new crystalline bodies which are stable under the new conditions. Thus, "ilmenite crystals" ($Fe{\cdot\cdot}TiO_3$) on microscopic examination are found to be a mixture of two minerals: hematite (Fe_2O_3) and rutile (TiO_2). Apparently, at some moment in the life of ilmenite, as a result of development of strongly oxidising conditions, Fe^{2+} changed into Fe^{3+} with the simultaneous collapse of the crystal structure followed by gradual rearrangement of the matter and the formation of a mixture of stable minerals. Similarly, cases are known of tillite ($PbSnS_2$) being replaced by galena (PbS) and cassiterite (SnO_2), in close intergrowth with each other but retaining the former lamellar-granular structure of the aggregate, characteristic of tillite. Evidently, owing to an increase in the oxygen content of the environment, tin with its greater affinity for oxygen, segregated from the originally homogeneous mineral mass as an oxide, while the lead changed into a separate sulphide compound.

Colloids*. Apart from obviously crystalline formations whose crystalline nature is clearly visible either to the naked eye or under the microscope, widely distributed in the earth's crust are colloids.

Colloids may be defined as heterogeneous dispersed** systems consisting of a "dispersed phase" and a "dispersion medium".

The dispersed phase is represented in these systems by minute particles of a substance disseminated in some mass (dispersion medium). The particles vary roughly in size from 100 to 1 mμ (10^{-4} to 10^{-6} mm), i.e., are far larger than ions and molecules, but small enough to be beyond the resolving power of an ordinary microscope. Each such particle may contain hundreds and even thousands of ions or molecules of a given compound; in solid particles, the ions and molecules form crystal structures, i.e., the particles are actually tiny crystal phases.

Both the dispersed phase and the dispersing medium may occur in any of the aggregate states (solid, liquid, gaseous) and in any of the combinations of these states. Here are some examples, in which the capital letters stand for the aggregate state of the dispersing medium and the small letters stand for that of the dispersed phases:

G+S: tobacco smoke; soot
G+L: fog
L+S: yelow peat-bog water; medicinal muds
L+G: hydrogen-sulphide springs; foam
L+L: typical emulsoids (e. g., milk)
S+L: native sulphur crystals in which liquid bitumens are dispersed
S+S: red calcite in which iron oxide is finely dispersed
S+G: milk-white minerals containing occluded gases

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* "Colla" means glue in Greek, "colloid", glue-like.

** The term dispersion, or scattering, is restricted here to the particle form of matter; the degree of dispersion is determined by the size of the particles.

Colloidal formations are divided into *sols* and *gels.*

In typical *sols*, which are also known as colloidal solutions or pseudosolutions, the dispersing medium strongly predominates over the dispersed phase (e.g., tobacco smoke, yellow-brown chalybeate water, milk). To the eye, they look perfectly homogeneous and often transparent, indistinguishable from true (ionic or molecular) solutions. In sols where water is the dispersing medium ("solvent"), the dispersed phase, though it easily penetrates through conventional filters, cannot pass through animal membranes. If the particles are larger than 5 mμ, they are readily discernible under the ultra-microscope with the aid of a Tyndall cone which is produced when a special glass vessel filled with the colloidal solution is illuminated laterally. The effect thus obtained is similar to one usually observed in a light beam thrown by a projector in a dark room: in the cone of light we see the Brownian movement of the dispersed-phase particles. This phenomenon is never observed in true solutions, with the exception of those of certain organic substances composed of very large molecules.

In *gels*, the number of the dispersed particles is so great that they form gelatinous, gluey, and glassy blobs. The dispersing medium, as it were, occupies only the remaining available space between the particles. Examples of gels are soot, mud, opal (silica gel), limonite (a gel of iron hydroxides), etc.

Depending on the nature of the dispersing medium, there are distinguished hydrosols and hydrogels (in which water is the dispersing medium), aerosols and aerogels (dispersing medium—air), pyrosols and pyrogels (dispersing medium—a melt), crystallosols and crystallogels (dispersion medium—a crystalline matter), etc.

We will limit this discussion to hydrosols, crystallosols, and hydrogels as being the most widespread in the earth's crust.

The simplest way to obtain *hydrosols* is by *mechanical action*, i.e., by finely grinding or otherwise reducing the substance to the size of the dispersed phase in water. In nature, coarsely and finely dispersed systems are often formed by attrition and erosion of rocks under the action of natural forces (running water, glaciers, tectonic movements, etc.).

However, it is *chemical* reactions in aqueous media—oxidation, reduction, and primarily exchange decomposition reactions—that lead to the condensation of the molecules that play the principal role in the formation of natural colloidal solutions. At the very surface of the earth life activities of organisms (biochemical processes) play as important a part in the formation of colloids.

It is important to note that the dispersed particles of colloidal solutions are electrically charged, which may be easily proved by passing an electric current through the solution. All the particles of the colloid have the same charge and are, therefore, kept suspended in the dispersion medium by mutual repulsion. The charge is believed to be due to the adsorption by the dispersed particles of some of the ions present in the solution. This phenomenon will be treated in more detail.

Consider, for example, a solid dispersed particle of AgBr, which, despite its ultramicroscopic dimensions, has a crystal structure, a diagrammatic section of which is presented in Fig. 7. Each of the Ag^{1+} cations and the Br^{1-} anions inside the lattice is surrounded by six oppositely charged ions: four in the plane of the drawing, one above the given ion, and one beneath. The inner ions of the particle are thus fully saturated with valencies. The ions on the boundaries of the crystal lattice present a different picture. By the same line of reasoning one may easily establish that most of the boundary ions on the face perpendicular to the drawing are saturated only by five oppositely charged ions (three in the plane of the drawing, one above, and one beneath the plane). Hence, each of Ag and Br ions situated on the plane surface of the particle have $^1/_6$ of their valency unsaturated, those at the edges $-^2/_6$, and the ions at the corners have as much as $^3/_6$ of their valencies unsaturated. It is this residual uncompensated charge that makes possible the adsorption from the solution of additional Ag or Br ions which are held at the surface of the dispersed particles in the form of the so-called diffuse layer.

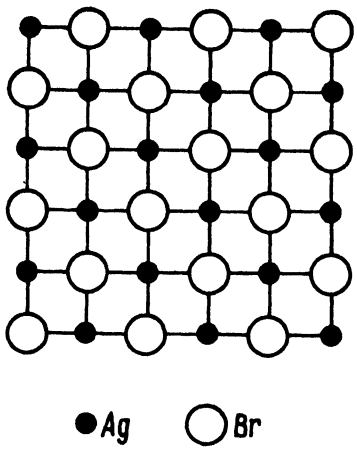


Fig. 7. Section of AgBr crystal structure.

In practice, an AgBr colloid is obtained by mixing $AgNO_3$ and KBr solutions, which react as follows: $AgNO_3 + KBr = AgBr + KNO_3$. If equivalent quantities of the solutions are mixed, an AgBr crystalline precipitate (not a colloid) will be formed. If silver nitrate solution is poured into potassium bromide, a sol is formed whose dispersed AgBr particles will assume a negative charge owing to the adsorption of Br^{1-} ions. If the order of pouring is reversed, the dispersed AgBr particles will adsorb Ag^{1+} cations and will, therefore, assume a positive charge.

An electrochemical approach will give a better understanding of hydrosols and the structure of the dispersed phases.

Figure 8 presents diagrammatically a colloidal particle in a dispersing medium (water in the given case) containing Na^{1+}, K^{1+}, Ca^{2+}, Mg^{2+}, Cl^{1-}, $[SO_4]^{2-}$, and other ions, which usually occur in soil waters containing dissolved salts. As in the previous example, the particle is shown as a crystalline phase whose corners are unsaturated with regard to valency. Consequently, these will serve as points of attraction for adsorbed ions. In our case, this will be cations: Na^{1+}, K^{1+}, NH_4^{1+}, Mg^{2+}, and Ca^{2+} which impart a positive charge to the particle and form a diffuse layer.

The anions at the lattice corners influence not only the ions in the solution but also the electrically neutral water molecules. It will be shown later in this chapter, that the H_2O molecule is a dipole of a pecul-

In this way, a whole swarm of ions and oriented H_2O molecules forms around the particle (Fig. 8). The thickness of the water film depends on the kind of hydrated cations (which hold the H_2O molecules) present. Most strongly hydrated are cations of alkali metals. Thus, in an aqueous medium, a Na^{1+} ion is capable of keeping 60 to 70 oriented H_2O molecules in suspension, while Ca^{2+} can hold no more than 14.

Sometimes, under the action of acids, the cations in the diffuse layer such as Cl^{1-}, $[SO_4]^{2-}$, etc., may be replaced by anions. The latter, like cations, may be hydrated. In this case, however, the orientation of the water molecules will be *opposite* to that which is observed in the case of cations (Fig. 8, right).

From the foregoing, the following conclusions may be drawn:

1. From the electrochemical standpoint, the charged dispersed phase may be considered as a large ion (macro-ion) which, in sols, is capable of moving towards one or the other electrode under the action of electric current (electrophoresis).

2. In relation to the dispersed phase, the dispersing medium is not a true solvent, though it may, and usually does, contain certain compounds dissociated into ions.

3. The cations of the diffuse layer may be replaced by others, if there is a change in the composition and concentration of the electrolytes in the dispersing medium. The mutual replacement or displacement of different kinds of ions in adsorbents (adsorbing colloids) are governed by Guldberg and Waage's Law of Mass Action.

The phenomena of unsaturated valencies at the surface of dispersed particles, and the resultant adsorption of cations and anions from solution, must be also observed in the case of macro- and microcrystals. However, should we consider this question from the viewpoint of the energy relationships governing the phenomena, a tremendous difference will be observed between true crystals and dispersed phases.

In so far as colloidal adsorption phenomena are confined to the boundary between the dispersed phase and the dispersing medium, the total surface of the dispersed particles per unit volume is of great importance for determining the overall surface energy of a substance. The finer the dispersion particles of a substance, the more abrupt is the increase in the total surface of its dispersed phase which is known as the *specific surface*. This may be easily proved.

Let us assume that we have a cubic crystal of some mineral with an edge 1 cm long. Its total surface will be 6 cm^2 (specific surface 6). If the cube is divided into eight equal parts (Fig. 9), the total surface of the eight smaller cubes will be 12 cm^2 and, if it is further divided into cubes with an edge of 1 mm, the total surface will be 60 cm^2. If this division is carried to cubes with a 1 mμ edge, i.e., the size of a colloidal dispersed phase, the surface will reach the enormous total of 6000 m^2, against the volume of 1 cm^3 (i.e., the specific surface will be $6 \cdot 10^7$). The number of the cubes will then be 10^{21}.

Thus, specific surface x and grain size y are inversely proportional. This dependence is expressed by the simple formula $x = \frac{6}{y}$, and is presented graphically in Fig. 10.

Hence it will be seen that in coarse crystalline systems the specific surface, and hence the surface energy are so small that they may be ignored for all practical purposes. In colloidal systems, on the other hand, it assumes a tremendous importance. It is owing to this that many physico-chemical properties of colloids that find wide practical applications differ sharply from those of coarse crystalline substances.

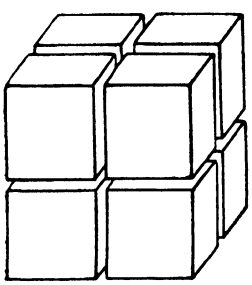


Fig. 9. Cube divided into eight cubes.

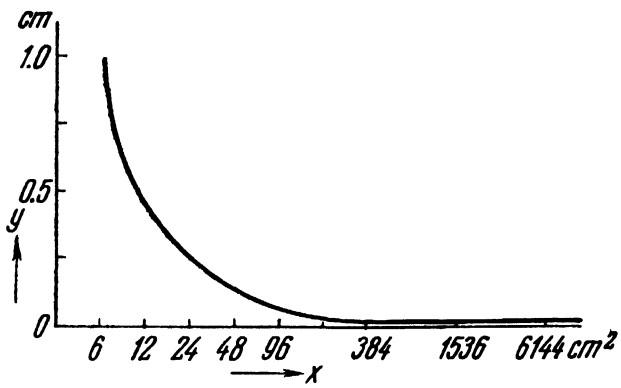


Fig. 10. Relationship between grain size (y) and specific surface (x).

Diffusion phenomena in colloidal solutions are far less pronounced than in true solutions, which is due to the fact that their dispersed-phase particles are much larger than ions. This, at least partly, accounts for the fact that mineral masses formed out of colloidal solutions often are widely nonuniform both in structure and composition.

Crystallosols, i.e., typically crystalline dispersing media, containing some substance as a dispersed phase, are often formed as a result of the crystallisation of hydrosols. The process may be compared to the crystallisation (freezing) of turbid water, i.e., water containing suspended dispersed particles. The ice thus formed will be similarly turbid or, in other words, will retain the suspensions present in the water and hence will be a crystallosol.

We may class as crystallosols, in the first place, many coloured minerals, which generally occur as colourless, transparent crystals. Examples are reddish carnallite, red barite (coloured by dispersed iron oxide), and black calcite whose colour depends in some cases on finely dispersed sulphides, and, in others, on organic matter. We may also include here milk-white quartz, calcite, etc., in which finely dispersed gases and liquids which are often visible in thin sections under the microscope appear as the dispersed phase. Crystals of quartz, calcite, and other minerals sometimes exhibit banded or zonal crystalline structure, i.e., consist of alternating transparent, coloured or milk-white bands.

There is no doubt but that crystallosols exist among opaque minerals as well. This is attested by admixtures of such elements detected by chemical and spectral analyses which from the crystal chemistry standpoint cannot be explained as resulting from isomorphous impurities. Such are, for instance, the admixtures of copper in pyrite crystals, of gold in pyrite, galena, arsenopyrite, etc. Microscopic examination of their crystals in polished sections at high magnifications often reveals minutest inclusions of chalcopyrite, native gold, etc., which implies that they may contain even more finely dispersed particles, which escape detection by conventional microscopes.*

Hydrogels are often formed in nature from hydrosols through *coagulation*, i.e., the formation of clots in an aqueous medium. Coagulation begins only when the dispersed particles, for some reason or other, lose their charges and become electrically neutral. The particles, which no longer repel each other, coalesce into larger bodies called polyions which thereupon precipitate under the action of gravity.

Neutralisation of dispersed particles, and hence coagulation, may be achieved by different methods:

(a) by adding electrolytes (ionic solutions) to a colloidal solution, in which case, depending on the sign of the dispersed-phase charge, neutralisation will be caused either by the anions or the cations of the electrolyte. Such is the mechanism of the deposition of silty sediments at the mouths of large turbid rivers which carry colloidal solutions. The latter, upon contacting sea water containing dissolved salts playing the role of electrolytes, undergo coagulation and precipitates in the near-shore zones of marine basins;

(b) through mutual neutralisation of equivalent quantities of colloidal solutions containing oppositely charged colloidal particles. In this case a mixture of gels results (e.g., brown hematite rich in colloidal silica);

(c) through spontaneous coagulation of colloidal solutions with time, especially if the system loses water (the dispersing medium) through evaporation; this process naturally increases the concentration of the electrolytes in the colloidal solutions; an example are silty sediments and muds in drying-up lakes;

(d) through circulation of the colloidal solutions in capillaries of rocks; owing to the high dielectric constant of water the moistened capillary walls are negatively charged by $[OH]^{1-}$ ions, which cause the precipitation of the positively charged particles in the form of flakes or coatings from circulating colloidal solutions; e.g., the frequent "ferrugination" of limestones and other rocks appearing as brown staining of the rock on the surface or along crevices by flocculent iron hydroxides;

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* Ordinary modern microscopes generally have a maximum resolving power ranging from 0.5 to 1.0 μ. Finer particles are absolutely undetectable at any magnification.

(e) through metasomatosis (replacement) of rocks which readily react with chemically active salt solutions to form colloidal solutions which immediately coagulate (e.g., the formation of malachite from the vitriolic waters in limestones), etc.

Gels of organic origin are abundant in the region of the biosphere. Their formation is often associated with the life activity of bacteria. Thus, it has been found that the so-called ferrobacteria reworking silty lacustrine sediments gradually deposit colloidal iron hydroxides (limonite).

Colloids, in which the dispersed particles are prone to become covered by a film of water molecules, are known as *hydrophilic*, while their opposites are called *hydrophobic*. Coagulation of hydrophilic colloids commonly results in the precipitation of mucous, gluey, gelatinous gels, while hydrophobic colloidal solutions yield powdery and flocculent masses.

Gels, especially those deriving from hydrophilic colloids, with time readily lose their water (the dispersing medium), i.e., are dehydrated. Water-rich hydrogels, which are of almost liquid consistency at the time of their formation, on exposure to air and evaporation of the dispersing medium successively become more elastic, and then hard and brittle. Complete removal of water, however, is possible only by ignition.

On addition of the dispersing medium, some of the gels not only swell (like gelatin), but are reconverted to sols, the process being known as *peptisation*. Such gels, which occur mostly in the biosphere, are called reversible. On the other hand, almost all inorganic colloidal formations are irreversible, i.e., they cannot revert to sols from gels.

Gels are also good adsorbents, the *adsorption* often being *selective*. Clayey substances, for example, will adsorb pre-eminently cations of potassium and radioactive elements, while manganese-dioxide gels will adsorb those of Ba, Li, K (but not their anions), etc.

As we have already shown, colloids sharply differ in properties from both true solutions and coarsely dispersed systems (with dispersed-phase particles exceeding 100 mμ). Indeed, the salient features of colloids are neither the vectorial properties of the crystal lattices nor the chemical affinities, but the tremendous surface energy and the electric forces associated with it. Nevertheless, there exist gradual transitions from colloidal solutions to true solutions, and similar transitions to coarse dispersions.

W. Ostwald proposed the following classification of dispersed systems:

DISPERSED SYSTEMS

↓	↓	↓
Coarse dispersions	Colloids	True solutions

Increasing degree of dispersion →

Particles > 100 mμ from 100 to 1 mμ < 1 mμ

This classification applies both to liquid and solid systems.

Now it has already been firmly established that the colloidal state is a common state of matter, i.e., any substance may be obtained in the form of a colloid. The important point is that *colloids may form under most diverse temperatures, pressures, and under most diverse conditions.*

On strict theoretical grounds, solid colloids cannot be classed as minerals, since they in fact constitute mechanical mixtures of different substances (the dispersed phase and the dispersing medium). Externally, however, they are absolutely indistinguishable from typical minerals. Neither has it been possible to establish any distinction between them and minerals in the strict meaning of the term by any microscopic investigation techniques known so far. Therefore, in standard textbooks on descriptive mineralogy they are conditionally treated as minerals.

Solid colloids (gels) were formerly regarded as amorphous bodies since they never occur in phanerocrystalline forms (with the exception of crystallosols). X-ray analysis, however, shows that they are *cryptocrystalline*, and, therefore, cannot be classed as homogeneous, amorphous bodies, to which they bear a very strong resemblance.

Recrystallisation of gels. Hydrogels formed through coagulation are subject to *ageing*, i.e., a gradual change in structure and composition. This is expressed first of all in the loss of water, or dehydration, in the course of time.

One example are silica hydrogels – opals which widely occur in nature. Water-rich silica hydrogels have the consistency of semi-liquid or gelatinous masses. As they gradually lose water, they harden exhibiting a vitreous or semi-dull fracture. Opals have this appearance owing to their generally low water content. Such formations are characterised by most fine porosity which is invisible to the naked eye and even under the microscope. It can be detected only when they are stained with some organic substance. The residual water can be removed only by heating.

On thorough dehydration, water-rich gels develop visible porosity. Occasionally, wrinkling or cracks similar to the reticules appearing often on caked mud may be observed.

X-ray investigation of typical solid and semi-solid gels by the Debye-Scherrer method shows that many of them fail to produce interference bands, whereas aged colloidal formations exhibit an unmistakably crystalline structure. Sometimes this can be seen under the microscope as in the case of many stalactitic formations of calcium carbonate. Opals (solid silica hydrogels) recrystallise into cryptocrystalline aggregates of anhydrous chalcedony or quartz, such as flints and agates. Gels which have changed into crystalline granular aggregates are termed *metacolloids.*

The crystallisation of gels may be presented as the coalescence of randomly oriented dispersed phases into larger units with a common crystal structure. This phenomenon which is called *collective crystallisa-*

tion reflects the general tendency of substances to assume the state with minimum specific surface and hence with minimum surface energy.

Often, and this is especially true of reniform gel masses, fine-fibrous aggregates are developed with radial arrangement of the individual fibres, clearly visible on the fracture surface. The periphery of the crusts of spheroidal and reniform aggregates of certain minerals often exhibits crystal faces which terminate the individual radial elements.

Gels depend for their recrystallisation on many factors, the most important being temperature and pressure, which speed up the process of recrystallisation as they are increased. Another factor is climate, since the dehydration and recrystallisation of gels formed on the surface proceed much faster in arid and hot zones than in humid and temperate ones. Time during which gels gradually change into phanerocrystalline aggregates under most diverse geologic conditions is also an important factor in the process of gradual conversion of gels into phanerocrystalline aggregates.

2. CHEMICAL CHARACTERISTICS AND FORMULAS OF MINERALS

As stated earlier in this book, the overwhelming majority of naturally occurring minerals are chemical compounds. These fall into two categories: (a) *definite* compounds, both simple and binary, and (b) compounds of *variable composition.*

Widely distributed are also *solid solutions* or the so-called *isomorphous mixtures.* These true solid solutions should be distinguished from solid pseudosolutions as in the case of liquid solutions.

Finally, special reference should be made to *hydrous compounds*, the understanding of which has become of late much more precise.

Definite compounds. All definite chemical compounds conform to the law of constant proportion expressed in chemical formulas. They also conform to the law of multiple proportions which correlates the constituents of one compound to those of another. These laws fully agree with Mendeleyev's periodic system, the laws of crystal chemistry and the concept of symmetry in crystalline media.

Definite compounds possess a number of specific physical properties, clearly manifested in physico-chemical graphs of fusibility, solubility, electrical conductivity, hardness, specific gravity, refractive index, etc.

Simple compounds include oxides (Cu_2O, MgO, Fe_2O_3, SiO_2, etc.), various oxysalts ($CaCO_3$, $CaSO_4$, YPO_4, Mg_2SiO_4, etc.), sulphides (NiS, FeS_2, Sb_2S_3, etc.), halides (NaCl, AgBr, CaF_2, etc.), and so forth.

The composition of chemical compounds may be expressed either by empirical formulas or by constitutional or structural formulas.

Empirical formulas express the composition of minerals either as the elements present in a given compound ($BaSO_4$, Na_3AlF_6, $NaAlSi_3O_8$,

etc.) or as its simple component compounds ($BaO \cdot SO_3$, $3NaF \cdot AlF_3$, $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$, etc.). Although far from reflecting the nature of chemical compounds as understood in modern chemistry, the latter type of formulas have the advantage that they facilitate memorising the composition of minerals.

The formulas of more complex compounds have been materially corrected by using crystallochemical data obtained by X-ray structural analysis of minerals. Since most inorganic crystalloids have the ionic type of bonding between structural units, complex formulas of chemical compounds should somehow reflect these units (cations and anionic groups) found in different types of crystal structures. Anionic groups are usually separated from cations by square brackets, e.g., $Ca[CO_3]$, $Ba[SO_4]$, $Na[AlSi_3O_8]$, $Mg_3[Si_2O_5]_2[OH]_2$, etc.

Such crystallochemical formulas often help to predict certain physical properties of a compound. For instance, optical properties (e.g., double refraction) often depend on the form and orientation of the anionic group. If a crystal structure includes parallel-oriented flat anions, for example $[CO_3]^{2-}$ or $[Si_2O_5]^{2-}$, double refraction will be greater (clearly pronounced optical anisotropy). If an anionic group has an isometric form, $[SO_4]^{2-}$, or a framework more or less uniformly developed in space, $[AlSiO_3O_8]^{1-}$, the double refraction of a mineral will be lower. The form of complex anions also has a bearing upon the habit of crystals. Thus, micas with anionic sheets which extend continuously in two directions, often form platy crystals, while pyroxenes in which the anions occur as chains extending continuously in one direction have crystals of prismatic habit, etc.

Binary compounds. Besides simple chemical compounds, widespread in nature are binary compounds, especially binary salts, i.e., definite compounds composed, as it were, of two simple salts which are present in multiple proportions. In most instances these are binary with regard to cations, more seldom with regard to anions or to cations and anions simultaneously. Examples are: $CaMg[CO_3]_2$, $K_3Na[SO_4]_2$, etc.

Comparing the formulas of binary salts shows that their cations, owing to the great difference in ionic radii, cannot replace each other isomorphously, viz., Ca^{2+} (1.04 Å) and Mg^{2+} (0.74 Å), K^{1+} (1.33 Å) and Na^{1+} (0.98 Å), etc. This explains why they differ somewhat from their simple constituent salts in crystal structure and physical properties.

Compounds of variable composition. In addition to definite chemical compounds, there are quite a few the composition of which is not constant and varies within narrow or wide limits, the variations being inexplicable by assuming any mechanical impurities. On the other hand, they can readily be explained crystallochemically, by the restricted solubility of the constituents in a given compound. Such chemical formations are known as compounds of variable composition.

Compounds of variable composition are abundant among minerals. They are mostly binary salts in which the constituent simple salts,

although similar in crystal structure, are not completely isomorphous, since they differ considerably in ionic radii or polarisation capacity. Therefore, these compounds are characterised by certain variations in composition which is expressed in the fact that their chemical formulas do not correspond precisely to the strictly stoichiometric ratio of the components.

In small quantities, isomorphous admixtures of foreign constituents are found in very many compounds, both simple and complex, e.g., sphalerite (ZnS), which may contain as much as a few per cent of iron in the form of an isomorphous admixture. Many other examples are given in the descriptions of minerals.

Chemical compounds of variable composition cannot be distinguished from solid solutions by their properties and should be regarded as such, but with limited miscibility of their constituents.

Solid solutions (isomorphous mixtures). The ability of crystalline substances of different composition to form mixtures of similar crystal structure, but continually varying in composition largely depends on isomorphism, i.e., the ability of elements to substitute for each other in chemical compounds of related composition.

It has long been established in physical chemistry that the miscibility of constituents depends upon environmental factors, primarily on temperature: at high temperatures the isomorphous replacement of constituents is much more pronounced than at low temperatures.

In mineralogy, the dependence of isomorphism on thermodynamic conditions was first noted in 1910 by V.I. Vernadsky. He pointed out the existence of wider isomorphous series of chemical elements in plutonic magmatic formations (high p and t) as compared with methamorphic rocks in the lithosphere (high p and medium t), and rocks in the zone of weathering (low p and t).

At the present time isomorphism is much better understood owing to modern advances in crystal chemistry. Two principal forms of isomorphism—isovalent and heterovalent—are recognised in crystalline substances of analogous structure.

Isovalent isomorphism. The substitution of ions having the same valency in a crystal structure is highly pronounced if the ions replacing each other are very similar in properties and size (the difference between their ionic radii should not exceed 15 per cent of the smaller radius). This is the case, for example, of divalent cations (their ionic radii are given in parentheses): Mg^{2+} (0.74), Fe^{2+} (0.80), Ni^{2+} (0.74), Zn^{2+} (0.83), Mn^{2+} (0.91), etc.; of trivalent cations: Fe^{3+} (0.64), Cr^{3+} (0.64), Al^{3+} (0.57), etc. This also applies to the anions taking part in the crystal structure: S^{2-} (1.82), Se^{2-} (1.93), etc. The following series of the simplest compounds could be quoted as being perfectly isomorphous: $MgCO_3$—$FeCO_3$, CuS—CuSe, etc. It should be emphasised that when isovalent substitution takes place, the number of structural units in a crystal structure remains constant.

Heterovalent isomorphism is distinguished by the fact that it involves the replacement of one ion in a crystal structure by a roughly equidimensional ion of a different valency, which requires, however, the compensation of charges in some other pair of ions which are part of the crystal structure of the substance but differ considerably in size from the former pair. A well-known example of such isomorphism is that observed in the plagioclase series: $NaSi_3AlO_8$—$CaSi_2Al_2O_8$. Here Na^{1+} (0.98) is replaced by Ca^{2+} (1.04) which has a higher valency, and simultaneously one ion of Si^{4+} (0.39) is replaced by Al^{3+} (0.57) which has a lower valency. In this case the total electrostatic balance of the compound remains undisturbed.

Apart from the compensation of charges, the decisive factor in heterovalent isomorphism is the size of the structural units, cations and anions, mutually replacing each other, which must be roughly equidimensional. However, upon substitution the number of structural units does not always remain constant. In micas, for instance, three divalent Mg cations (in sixfold coordination) may be replaced by two trivalent Al cations (Mg_3—Al_2), the third space remaining vacant.

As known, the ionic radii become larger in the vertical groups of the periodic system as the atomic number increases, and smaller in the horizontal direction as the group number (valency) becomes higher. From this A.Y. Fersman deduced the law of diagonal rows of isomorphous ions which holds for the left-hand side of the periodic system. The following heterovalent rows of ionic isomorphism may be distinguished (ionic radii in angstrom units are given in parentheses):

$Li^{1+}(0.68)$ —$Mg^{2+}(0.74)$—$Sc^{3+}(0.83)$—$Zr^{4+}(0.82)$
$Na^{1+}(0.98)$—$Ca^{2+}(1.04)$—$Y^{3+}(0.97)$
$K^{1+}(1.33)$ —$Sr^{2+}(1.20)$
$Rb^{1+}(1.49)$—$Ba^{2+}(1.38)$
$Al^{3+}(0.57)$ —$Ti^{4+}(0.64)$—$Nb^{5+}(0.66)$

Indeed in natural compounds lithium minerals, for instance, often contain isomorphous admixtures of magnesium; magnesium minerals contain admixtures of scandium; sodium minerals contain calcium; calcium minerals contain yttrium, and so on.

In addition to that, in complex anions the $[SiO_4]^{4-}$ ion may be replaced by ions of $[AlO_4]^{5-}$, $[PO_4]^{3-}$, and $[SO_4]^{2-}$ equal or almost equal in size to the substituted ion. Numerous examples of this will be found in the descriptions of minerals.

Two principal types of solid solutions should be distinguished from the standpoint of their origin: (1) true solid solutions, and (2) solid pseudosolutions.

True solid solutions, also called isomorphous mixtures, are mixtures in any proportions of two or more substances of completely similar crystal structure which do not form chemical compounds. Examples are solid solutions of silver and gold, manganese and iron tungstates, plagioclases, etc.

The physical and chemical properties of solid solutions are additive, i.e., subject to gradual and regular change when the concentration of the second component is increased. For instance, changes in melting point, specific gravity, refractive index, reflecting power and electrical conductivity are graphically expressed either by straight lines (specific gravity) or by gentle curves (melting points, optical properties, etc.). These curves for isomorphous series are so characteristic of the basic properties of a given mineral species that no chemical analysis is required to determine its composition. This method, for instance, can be successfully applied to determine the composition of a plagioclase by means of special graphs, once its optical properties are determined by microscopic study of thin sections.

True solid solutions are subdivided into two types: (1) replacement solid solutions (solutions of the first order), and (2) interstitial solid solutions (solutions of the second order).

Solid replacement solutions are characteristic of metals and ionic compounds. In essence they may be described as compounds of analogous crystal structure in which the atoms and ions of one are substituted by those of another (i.e., take the place of other atoms or ions). Such are, for instance, the isomorphous series: $ZnCO_3$—$FeCO_3$, $MnWO_4$—$FeWO_4$, etc.

Interstitial solid solutions are those in which the second constituent fits only into interstices of the lattice, i.e., the spaces between the atoms or ions forming the lattice of the first constituent. Such solid solution may only occur when the atoms (ions) of both constituents vary greatly in size. The most typical example of interstitial solid solutions is that of carbon in iron, which is readily formed at high temperatures and which decomposes into iron and iron carbide (Fe_3C) upon slow cooling.

In chemical formulas of solid solutions, isomorphous atoms or ions are enclosed in parentheses, separated by comas, and arranged in the order of decreasing content: (Au, Ag), (Zn, Fe)S, (Zn, Fe)CO_3, (Fe, Mn)WO_4, etc. Minor isomorphous admixtures are either not shown at all or are indicated by smaller type. If in a binary salt, either of the constituents contains isomorphous admixtures, the formula is written as follows: Ca(Mg, Fe) $[CO_3]_2$.

It must be added that the solid solutions formed at high temperatures will not always remain stable at lower temperatures, undergoing partial or complete disintegration into simpler compounds. Thus in a NaCl—KCl system which was studied experimentally, these compounds form a continuous series of solid solutions at high temperatures. Upon gradual cooling to room temperature, however, minute intergrown NaCl and KCl bodies develop in the crystallised mass, their stoichiometric ratios depending on the initial composition of the solid solution. The disintegration of solid solutions is chiefly limited to cases where there is a considerable disparity in the size or properties of the substituted and substituting ions. It may also occur as a result of one of the

compounds undergoing polymorphous transformation upon the lowering of temperature.

Solid pseudosolutions differ from true solid solutions in that they contain finely dispersed foreign admixtures whose presence cannot be explained by the laws of crystal chemistry. Examples of solid pseudosolutions are crystallosols (p. 50) such as coloured translucent pink quartz, red calcite, and black sphalerite, which appear to be quite homogeneous (so finely dispersed is the colouring pigment).

In many instances, however, the mechanical impurities in minerals are so coarse that they can be seen in polished sections under the microscope or even with the naked eye. These inclusions may have diverse origins (1) entrapment of foreign substances (solids, liquids, and gases) by the growing crystal; (2) disintegration of a solid solution; (3) decomposition of a chemical compound due to changes in the environment, for instance, in an oxidising environment tiny inclusions of tin oxide SnO_2 develop in tin-bearing sphalerite ZnS. Foreign inclusions are especially common as the residue of replacement in crystals formed metasomatically in metamorphic rocks. Naturally, the chemical analysis data for such crystals will not conform precisely to chemical formulas with a stoichiometric ratio of the constituents.

Hydrous compounds. First, it should be noted that by hydrous compounds are meant only those containing electrically neutral *water molecules*. Formerly minerals with hydroxyl $[OH]^{1-}$ anions were also classed as hydrous compounds. However, there is difference of principle between an H_2O molecule and a negatively charged $[OH]^{1-}$ ion, which difference substantially affects the physical and chemical properties of minerals. Like an ion, the hydroxyl is capable of replacing such anions as F^{1-}, Cl^{1-} in compounds and is firmly held in crystal structures. The H_2O molecule which lacks this property and, being loosely held in the lattice, is readily removed by heating. The fact that upon ignition of hydroxyl-containing minerals the hydroxyl leaving the lattice may turn into water vapour is no reason to identify it with the H_2O molecule. In writing the chemical formulas of minerals it is therefore extremely important to denote the presence of hydroxyl ions, and water. From this standpoint a mineral such as malachite, $Cu_2[CO_3][OH]_2$, is not a hydrous, but a basic anhydrous copper carbonate, although in chemical analysis hydroxyl ion appears as H_2O. The same is true of minerals which are acid salts and include hydrogen among their cations.

According to the manner in which water is held in minerals, it is designated as: (1) crystallisation or bound water which is incorporated in the crystal structure of minerals, and (2) free water that does not take part in the crystal structure proper.

Bound water is present in the crystal structure in the form of H_2O molecules which occupy strictly definite positions. The number of water molecules present in a compound is in a simple relationship to the other constituents. Examples: $Na_2CO_3 \cdot 10H_2O$ (soda), $CaSO_4 \cdot 2H_2O$ (gypsum), $Ni_3[AsO_4]_2 \cdot 8H_2O$ (annabergite), $Al_2[PO_4][OH]_3 \cdot 5H_2O$ (wavellite), etc.

These are so-called crystallohydrates, or according to Werner, "complex compounds" in which the water molecules as structural units are situated in a definite coordination about certain ions forming, as it were, complex ions.

It has been shown by X-ray study that in the crystal structure of the $NiSO_4 \cdot 6H_2O$ compound six dipole H_2O molecules immediately surround the Ni^{2+} cation, apparently, being oriented in a definite way in relation to the cation (with two H^{1+} protons towards the periphery of the complex ion). Since the H_2O molecule, as such, is electrically neutral, the hydrated cation $[Ni(H_2O)_6]^{2+}$ retains the Ni^{2+} charge. Therefore, the chemical formula of the compound should be written more correctly as $[Ni\ (H_2O)_6]\ [SO_4]$.

The cause of hydration of ions in crystal lattices will be discussed later (in the introduction to oxysalts). Here we shall limit ourselves to saying that their hydration is strictly explained by the laws of crystal chemistry; Ni^{2+} cations present in the solution are too small to form stable crystal structures with such large anions as $[SO_4]^{2-}$, and hence the tendency to an increase in volume without any change in the charge. It goes without saying that crystallohydrates can form only in a water-rich environment and at low temperatures.

Crystallohydrates readily give up water upon heating either abruptly or step-by-step, periodically losing groups of water molecules. The resulting rearrangement of structure does not change the ratio between the number of the H_2O molecules and those of the basic compound. On artificial dehydration, chalcanthite ($CuSO_4 \cdot 5H_2O$) will successively form $CuSO_4 \cdot 3H_2O$, $CuSO_4 \cdot H_2O$, and $CuSO_4$. Such physical characteristics as refractive index and specific gravity also change abruptly. Water is removed from different compounds at different temperatures: some lose it at room temperature (water-rich copper and iron sulphates), others at higher temperatures, sometimes even above 100°.

Free water present in mineral masses takes no direct part in the crystal structure of minerals, and is removed gradually on heating. Three types of free water are recognised: zeolitic, colloidal, and hygroscopic.

Zeolitic water derives its name from the zeolite group of minerals, in which the specific characteristics of its occurrence are most conspicuous. The water molecules in this group do not occupy definite positions in the crystal structure, but fit only into the free spaces (channels, interlayer spaces, etc.). Therefore, the "solubility" of water in these minerals is very limited. An interesting point is that the amount of water present may vary without disturbing the crystalline homogeneity of matter which is accompanied by a *gradual* change in the physical properties of the minerals such as transparency, refractive index, specific gravity, etc. This indicates that the water, as it were, is in the solid solution state. It is removed on heating at temperatures between 80 and 400°. Another interesting point is that zeolites dehydrated by gradual heating may re-absorb water, whereupon their former physical properties are restored.

Colloidal water, as the name implies, most commonly occurs in hydrogels in which it is held at the surface of the dispersed phase by very weak bonds. It is in fact adsorbed water and its presence in hydrogels does not depend on the structure of the adsorbent (of course, the adsorbent itself may contain crystallochemically bound water). An example is opal (silica hydrogel)—$SiO_2 \cdot aq$ (abbreviation of the Latin "aqua" meaning water).

Hygroscopic (capillary) water is retained by surface tension in thin cracks, pores, and powdery masses. For the most part it is readily removed on heating to 100-110°. No sharp distinction exists between capillary and colloidal water.

Moreover, water may be present as a mechanical impurity, in the form of gas-liquid inclusions entrapped by crystals during their growth. Such inclusions frequently occur in many minerals.

3. PHYSICAL PROPERTIES OF MINERALS

Minerals as physical bodies, as has already been stated, possess widely different properties such as colour, lustre, hardness, specific gravity, etc. These vary from mineral to mineral depending on chemical composition and crystal structure. Each mineral has its own special features which readily distinguish it from others.

Very many minerals may be determined quite accurately by physical characteristics alone without resorting to such laborious operations as chemical or X-ray analyses. Many minerals possess peculiarities so subtle and specific that they cannot be easily grasped or described. This refers specifically to shades and intensity of colour, fracture, lustre, etc. To the trained eye, however, these characteristics serve as positive diagnostic features. In the remote past when man had no idea of chemistry in general, and of chemical elements in particular, these characteristics of important minerals and ores were well known and skilfully used by "ore diviners".

Of course not all minerals occurring in nature can be identified by such means. Some of them for positive identification require more detailed investigation, in particular qualitative chemical reactions and more accurate determination of specific gravity, optical, mechanical, and other physical properties. Fine-grained mineral masses are studied in polished sections under the microscope. Whenever spectral analysis reveals admixtures of such metals as cobalt, indium, cadmium, lithium and caesium, which are commercially important even if their concentration is very low, chemical analysis becomes indispensable. The study of cryptocrystalline mineral formations requires X-ray analysis, while special methods have to be used for investigating radioactivity, piezoelectricity, magnetism, and similar physical phenomena in minerals.

Below we shall consider the principal physical properties of minerals, which are important as diagnostic features, namely: *morpholog-*

ical features—habit of crystals, twinning, striation; *optical** features—transparency, colour, streak, lustre; *mechanical* characteristics—cleavage, fracture, hardness, brittleness, malleability, elasticity; and also such properties as specific gravity, magnetism, radioactivity, and others.

MORPHOLOGICAL FEATURES

In nature most solid minerals occur as irregularly-shaped grains without any crystal faces but regardless of this and their size possessing an internal crystal structure. Well-formed crystals, i.e., individuals bounded by natural plane surfaces are much more rare. What makes such finds important is the fact that they increase the number of features by which a mineral may be identified. There exist even special determinative tables for identifying minerals by their crystallographic forms.

Since courses in crystallography include a most detailed discussion of the morphology and symmetry of crystals, we shall discuss here only such general morphological characteristics of crystals and crystal faces as are of practical use in identifying minerals.

Habit (Form). Considering that any physical body must have three dimensions, the following basic types can be distinguished among all the numerous forms of crystals and crystal grains.

1. *Isometric forms*, i.e., those equally developed in all three directions of space, such as the rhombododecahedra of garnet, the octahedra of magnetite (Fig. 11), cubes of pyrite (Fig. 12), etc.

2. Forms *elongated in one direction*, i.e., prismatic, columnar (Fig. 13), rod-like, acicular (Fig. 14), fibrous, capillary. Examples: crystals of aquamarine, tourmaline.

3. Forms *elongated in two directions*, the third direction remaining short, represented by tabular, platy, foliated, and scaly crystals, such as the platy crystals of hematite (Fe_2O_3), mica, etc.

There are also transitional forms. Such are, for instance, the coarse-bladed crystals of kyanite (Al_2SiO_5) of a form intermediate between the second and third types (flattened columnar crystals); the barrel-shaped crystals of corundum (Al_2O_3) and scalenohedral crystals of calcite ($CaCO_3$), intermediate between the first and second types; the flattened crystals of sphene ($CaTiSiO_5$), monazite ($CePO_4$), etc., almost lenticular in shape, intermediate between the first and third types.

In addition to these, there exist complex types of crystal forms such as dendrites (Fig. 15) or utterly irregular crystal growths (Fig. 16).

In the Soviet literature besides crystal form, there is also sometimes distinguished crystal habit, though it is restricted to well-developed crystals only. Habit is essentially characterised by the predominance of particular crystallographic forms in the crystals of a given

* Omitting crystallooptical properties (refraction, birefringence, pleochroism, etc.) which are dealt with in treatises on crystallography and crystallooptics.

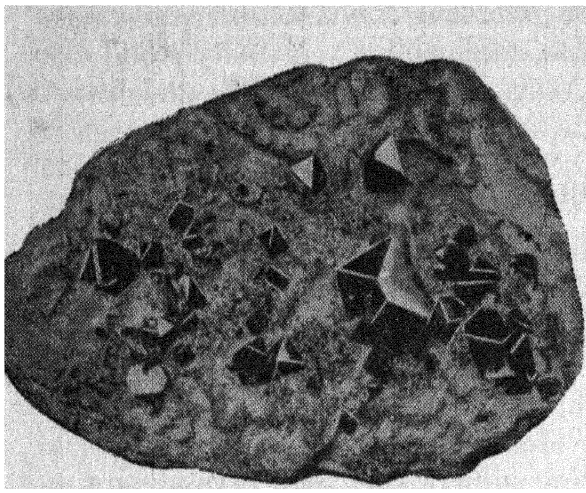


Fig. 11. Octahedral magnetite crystals in chlorite schists.

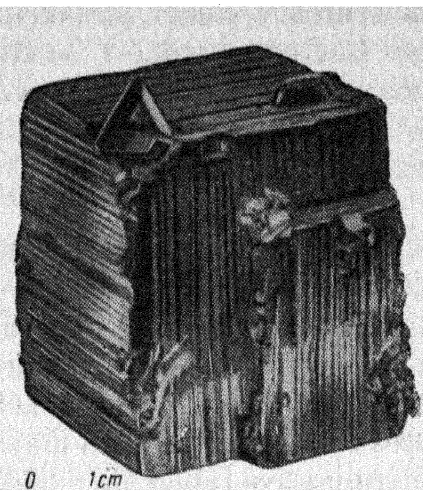


Fig. 12. Pyrite crystal overgrown with small crystals of tetrahedrite (at the corner) and galena (upper face).

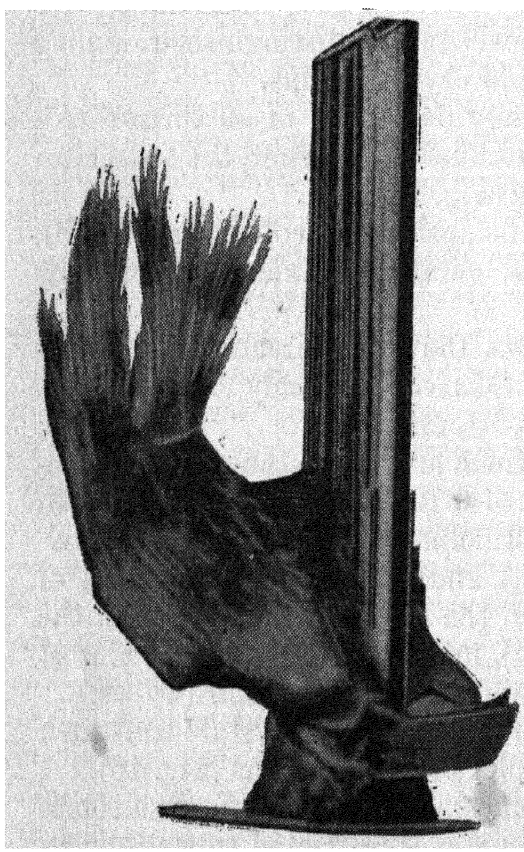


Fig. 13. A columnar crystal of epidote and an aggregate capillary crystal of byssolite (a variety of actinolite).

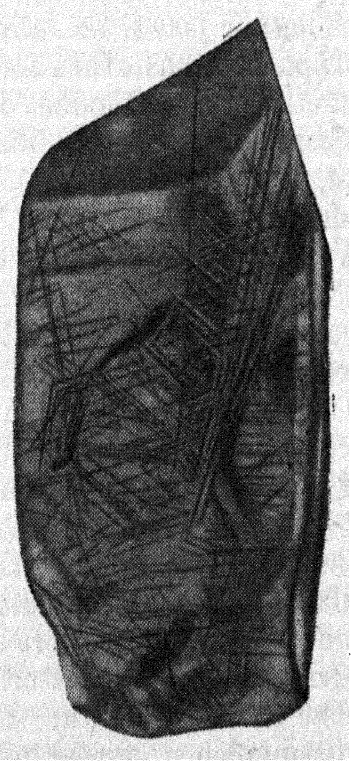


Fig. 14. Ingrowths of acicular tourmaline in transparent quartz.

mineral. Thus crystals of galena (PbS) usually occur as cubes which are sometimes slightly truncated by octahedral faces, less often as cubooctahedra, and occasionally as octahedra slightly truncated by cube faces. Their general form is isometric, but the habit of the crystals is different. In the first case, it is predominantly or solely the cubic faces that are developed; in the third case, the octahedral faces predominate, whereas in the second case the cubic and the octahedral faces are more or less equally developed. It seems that the habit of a crystal

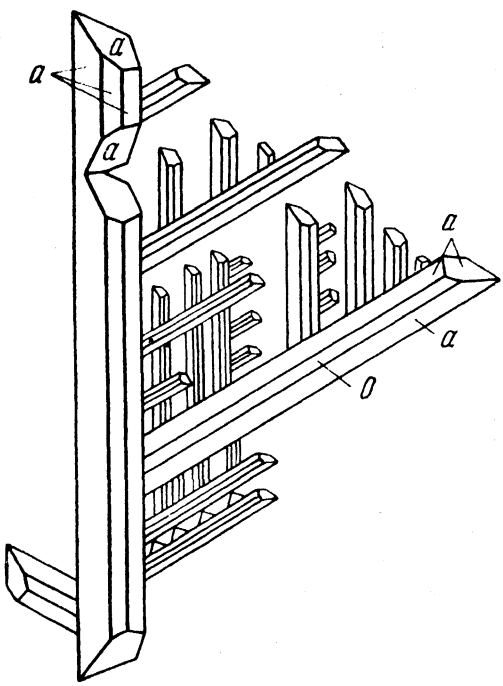


Fig. 15. Crystalline dendrite of native copper composed of a number of elongated twins.

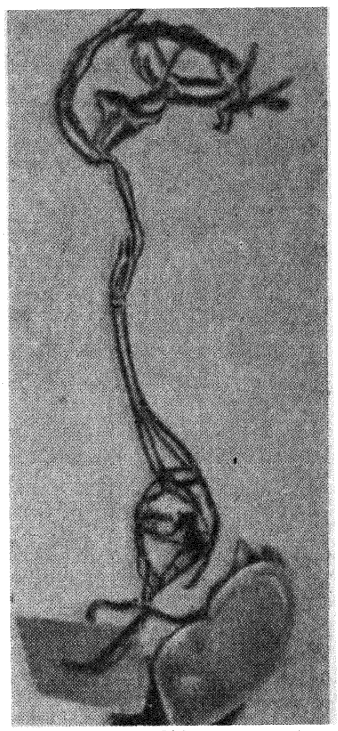


Fig. 16. Filiform native silver on crystals of calcite.

is determined to some degree by the environment in which the formation of the mineral took place.

Although far from all minerals are easily recognisable by crystal form alone, for a number of minerals the crystal forms are so characteristic that they are the most important diagnostic feature. For instance, the prismatic crystals of quartz truncated by rhombohedral and trapezohedral faces are always readily identified irrespective of their colour. No less characteristic are the cubic or pentagon-dodecahedral crystals of pyrite, the octahedra of spinel, magnetite, the rhombododecahedra of garnet, etc.

The characteristics of crystal forms are reflected in the names of some minerals. Examples: actinolite (Greek for radiant stone), lepidolite (from Greek "lepis" meaning fishscale), axinite ("axine"—the Greek

Table 4

Nomenclature of the Fyodorov Institute (U.S.S.R.) for the 32 Classes of Crystal Symmetry (1935)

Category	System	Class of symmetry						
		Primitive	Central	Planar	Axial	Planar-axial	Gyroido-primitive	Gyroido-planar
Lower	Triclinic	1 —	2 C					
	Monoclinic			3 P	4 L_2	5 L_2PC		
	Orthorhombic			6 $L_2 2P$	7 $3L_2$	8 $3L_2 3PC$		
Medium	Trigonal	9 L_3	10 L_3C	11 $L_3 3P$	12 $L_3 3L_2$	13 $L_3 3L_2 3PC$		
	Tetragonal	14 L_4	15 L_4PC	16 $L_4 4P$	17 $L_4 4L_2$	18 $L_4 4L_2 5PC$	19 $Li_4(\rightarrow\!\!=L_2)$	20 $Li_4(\rightarrow\!\!=L_2)$ $2L_2 2P$
	Hexagonal	21 L_6	22 L_6PC	23 $L_6 6P$	24 $L_6 6L_2$	25 $L_6 6L_2$ $7PC$	26 $Li_6 =$ $= L_3P$	27 $Li_6 3L_2 3P =$ $= L_3 3L_2 4P$
Higher	Cubic	28 $4L_3$ $3L_2$	29 $4L_3$ $3L_2$ $3PC$	30 $4L_3$ $3L_2$ $(3Li_4)$ $6P$	31 $3L_4$ $4L_3 6L_2$	32 $3L_4 4L_3$ $6L_2 9PC$		

for axe), corundophyllite ("phyllon"—the Greek for leaf), chrysotile (golden fibre in Greek), etc.

Table 4 gives the names and symbols for 32 classes of crystal symmetry according to the nomenclature of the Fyodorov Institute.*

Twins and intergrowths. A twin is an intergrowth of two crystals of the same mineral in which the individuals are related to one another, either by rotation about a certain axis through 180° (Fig. 17) or by reflection across a plane of symmetry (Fig. 18) or, lastly, by inversion. When three individuals are intergrown, a trilling results; when there are four individuals, the result is a fourling, etc. N.V. Belov showed that the twin plane often coincides with the plane of closest packing, e.g., in accordance with the spinel law of crystal intergrowth on (111) in the cubic system.

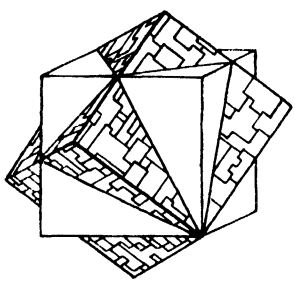


Fig. 17. Fluorite twin. Individuals intergrow parallel to (111).

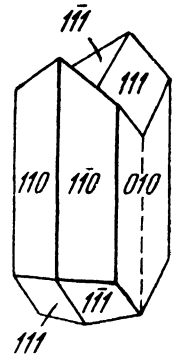


Fig. 18. Gypsum swallow-tail twin parallel to (100).

Twins may develop due to: (1) the intergrowth of newly-forming crystals in solution as they come in contact with one another during growth; (2) mechanical influences (unilateral external pressure); and (3) polymorphous rearrangement of the crystal structure.

Certain minerals have a peculiar mode of twinning, which often facilitates their identification. Examples: the geniculated (knee-shaped) twins of rutile (TiO_2) and cassiterite (SnO_2), "swallow-tail" twins of gypsum (Fig. 18), trillings of chrysoberyl ($BeAl_2O_4$), cruciform twins of staurolite ("stauros" is the Greek for cross), etc.

Ordered intergrowths of various minerals have also been described in literature long since. The ordered orientation of intergrowing minerals is explained by the identity or close similarity of the closely packed composition planes. There are different kinds of ordered intergrowth: (1) crystals of one mineral are overgrown by another mineral (crystals of tetrahedrite, Cu_3SbS_3, are covered by regularly oriented crystals or by a solid "coating" of chalcopyrite—$CuFeS_2$); (2) regularly oriented

* Although the names of the principal crystal symmetry classes which are given in Table 4 are adopted in the teaching of crystallography at the Leningrad Institute of Mining and at Moscow and Leningrad Universities, old names are preferred in this course for the designation of symmetry classes.

ingrowths, for instance, of ilmenite ($FeTiO_3$) in crystalline grains of magnetite ($FeFe_2O_4$) as a product of a disintegrated solid solution (discernible in polished sections under the microscope); (3) oriented replacement of one mineral by another along the periphery (e.g., sphalerite, ZnS, by chalcopyrite, $CuFeS_2$), sometimes even with the twin structure of the substituted mineral remaining intact, etc.

Surface of crystal faces. Crystal faces which are designated by plain symbols are not ideal planes. When examined in reflected light (especially on magnification) they nearly always show defects such as crenulation, vicinal forms, striations, etch figures or solution pits, etc., caused probably by the uneven growth of the crystals or their partial solution due to changes in the concentration of the constituents in the residual solution, temperature fluctuations, and sometimes by mechanical damage.

Striation is quite common in minerals and may be an important diagnostic feature. In some minerals, like tourmaline and epidote, (Fig. 13) it occurs parallel to the crystal elongation; in others, it is perpendicular to it, as on the prismatic faces of quartz. In the cubic crystals of pyrite (Fig. 12), the striae of one face are perpendicular to those of each adjoining face.

Striation on crystal faces may be of different origin: (1) *combinative* striation arises from the frequent repetition of narrow vicinal faces (diamond, tourmaline); (2) *twinning* striation is the result of the polysynthetic contact of crystals (sphalerite, sometimes plagioclase, etc.).

Solution pits or etch figures appear on crystal faces as a result of the initial stage of the solution of the crystals. It was found experimentally that the apexes and edges of crystals are dissolved more quickly than the faces. As was shown by I.I. Shafranovsky, some natural crystals, when subjected to partial solution, often produce tapered pits on their faces (quartz, topaz, etc.). In diamond crystal ideal cones were found having fourfold and threefold axes of symmetry and forming rounded rhombododecahedra ("dodecahedroids").

On smooth faces of crystals of different minerals, etch figures differ in symmetry owing to the specific features of their crystal structure. The orientation of etch figures may, therefore, often show whether the crystals, of quartz for instance, are left-handed or right-handed, twinning, etc.

TRANSPARENCY

Transparency is the ability of a substance to transmit light. Although there are no absolutely opaque bodies, many minerals, particularly metals (even in thin films) will transmit visible light in quantities so small as to appear perfectly opaque. Nor is there any absolutely transparent matter that does not absorb any of the light it transmits. Even pure water, which is a most transparent medium, when in a thick layer becomes blue owing to considerable absorption of the rays at the red end of the visible spectrum.

It will be remembered from physics that some of the incident light is thrown back or reflected, while the rest enters the medium. Leaving, for the time being, the subject of reflection (which is dealt with in the section on lustre), we shall examine the behaviour of the light which enters the medium.

As known, on entering the medium, the velocity of the ray of light diminishes and it is refracted. As it penetrates to a greater depth, its energy is gradually spent in the course of transformation into other kinds of energy (mostly thermal); the quantity of light will decrease accordingly, i.e., the light will be *absorbed.*



Fig. 19. Birefringent transparent Iceland spar, $CaCO_3$.

Thus the intensity of the light leaving the medium (I) will be less than that of the light entering the medium (I_0), i.e., the ratio $I : I_0 = a$ will always be expressed by a proper fraction. The value a is the transmission factor for a unit (1 cm) thickness of a given medium. This factor depends on the chemical nature of the medium and the wavelength of the light (but not on its luminous intensity). The closer the factor is to unity, the more transparent is the mineral, and vice versa.

All minerals occurring in large crystals fall into the following groups, according to their transparency:

(1) *transparent*—rock crystal, Iceland spar (Fig. 19), topaz, etc.;
(2) *translucent*—emerald, sphalerite, cinnabar, etc.
(3) *opaque*—pyrite, magnetite, graphite, etc.

Many minerals which are opaque in large crystals and fragments, become translucent in thin fragments or sections (biotite or black mica, rutile, etc.).

In contrast to large crystals, in *fine-grained* aggregates, the question of transparency appears in a different form. In a body composed of

numerous small particles or grains which differ in optical orientation, the rays of light cannot travel in straight lines. In this case, the light which is refracted in various directions will in the end be dispersed and reflected so that such media will appear opaque. Compare, for example, a thin plate of transparent calcite (Iceland spar) and an equally thin plate of a fine-grained aggregate of white marble (also calcite) polished on both sides. While one can easily read the inscription on a label viewing it through Iceland spar, the marble does not transmit light. Such bodies become transparent only in very thin sections.

If a fine-grained aggregate does not absorb any appreciable amount of light, it will generally appear milk-white. This colour is especially typical of the disaggregated state of matter, i.e., when air is present in interstices between the tiny fragments and particles. This is a familiar phenomenon. For instance, if one strikes transparent bluish ice with a hammer, a milky-white colour appears where the ice has been struck, due to the appearance of numerous tiny air-filled cracks and vacuities.

COLOUR

Since the colour of a mineral is its most conspicuous property it is also one of the most distinguishing features of minerals.

For this reason many minerals have been named according to their colour. Examples: lazurite, azurite (from "azure"), chlorite (from "chloros", the Greek for green), rhodonite ("rodon", the Greek for pink), ruby ("ruber", the Latin for red), orange-coloured crocoite ("crocos", the Greek for saffron), auripigment ("aurum", the Latin for gold), chrysolite, chrysoberyl ("chrysos", the Greek for gold), erythrite ("erythros", the Greek for red), hematite ("hematicos", the Greek for sanguine), albite ("albus", the Latin for white), melanite ("melas", the Greek for black), etc.

Conversely, such terms as *cinnabar*, *malachite green* derived from minerals have become standard names for the colours of pigments which indicates that these colours are permanent features of the given minerals.

The colour of minerals is a very complex problem. Although our knowledge of the causes of colouring of crystal substances has greatly increased due to the advances of modern physics and crystallochemistry, there are still many points which are not clear. In his *Colours of Minerals* (1937) A.Y. Fersman made the first serious attempt to sum up the available data on the subject, and also to relate the colour of natural compounds to their crystallochemical features.

In the colouring of natural chemical compounds three types are recognised in accordance with their origin: (1) idiochromatism, (2) allochromatism, and (3) pseudochromatism.

Idiochromatism.* Often the colour of those natural compounds

* "Idios" means one's own in Greek.

which never occur as colourless crystals is due to the inherent properties of the compounds themselves. Examples: the black magnetite ($FeFe_2O_4$), the brass-yellow pyrite (FeS_2), the carmine-red cinnabar (HgS), the green and blue oxygen salts of copper (malachite, azurite, turquoise, etc.), the deep-blue lazurite, etc.

These typical colours of minerals are termed idiochromatic. In different minerals they may be due to different factors.

1. The colour of many minerals depends on a *chromophore*, i.e., a pigmenting chemical element entering into the composition of the compound itself. Such chromophores are Ti, V, Cr, Mn, Fe, Co, Ni, i.e., the elements of the iron family found in the centre of Mendeleyev's Periodic Table divided into long periods. To a lesser degree, this applies to W, Mo, U, Cu, and TR.

The most outstanding of the chromophores is chromium, as its very name implies.* The most intense colours, such as red (pyrope, ruby), bright-green (uvarovite, emerald, and fuchsite) and violet (rhodochrome, kaemmererite) depend on chromium. The strong pigmenting effect of chromium is illustrated by the fact that an isomorphous admixture of 0.1 per cent of chromium oxide to aluminium oxide imparts a deep red colour to this colourless compound. When chromium is present in this amount, the distance between the two closest chromophore particles in a corundum mass will be some 20 Å, i.e., many times greater than the ionic radii (0.57 Å in Al and 0.64 Å in Cr). Apparently, the ions of chromium, greatly differing in the configuration of their electron shells from aluminium ions, produce considerable disturbances in the symmetry of the electric field around themselves and, despite their highly dispersed state, affect the entire structure of the compound.

The green and violet colours of minerals mentioned above are due to a considerable Cr_2O_3 content (running into a few per cent, or even a few tens of per cent). Pure chromium oxide itself is green. Nevertheless it is not true that green colour is always caused by a high chromium content. It was found, for example, that green beryls, commonly known as emeralds, owe their beautiful bright colour to an infinitesimal isomorphous admixture of Cr_2O_3 in Al_2O_3 (a few hundredths of a per cent). Therefore, the colour of minerals is a much more complex problem than it appears at first glance.

The $[CrO_4]^{2-}$ ion, which contains Cr^{6+}, in artificial compounds generally produces yellow colouring, but when it is combined with strongly-polarising cations, a deep orange-red colour results. One example is the mineral crocoite ($PbCrO_4$).

2. A mineral may be coloured in the absence of any chromophores or changes in chemical composition, because neither chemical nor spectral analyses reveal any traces of a pigmenting agent.

Thus rock salt (NaCl) may assume a beautiful blue tint. It has been found that some ions of that compound (Na) have turned into neutral

* "Chroma" is the Greek for tint or colour.

atoms by picking up the missing electrons. Artificially, this colour may be induced in transparent rock salt by impregnating it with vapours of metallic sodium or by irradiating it with cathode rays carrying free electrons.

Consequently, the colouring of certain transparent minerals may be due to changes in the homogeneity of the crystal structure and the electrostatic state of the ions which may be converted into either neutral or excited (weakly charged) atoms. In fact, the colour of minerals of such origin should be regarded as allochromatic (see below).

3. A special, though very small, group of coloured minerals, are compounds whose colour depends neither on the presence of chromophores nor on the disturbance of the electrostatic homogeneity of the crystal structure, but on the presence of ions or ionic groups in the interstices of the structure. This is particularly characteristic of those silicates in which "intrusion" by extra anions like Cl^{1-}, $[SO_4]^{2-}$, etc., takes place. Example: bright-blue lazurite.

Although the true nature of this phenomenon which is called stereochromatism still remains obscure, the colour of such minerals is certainly associated with groups of attachment or intrusion, which, in themselves, are not chromophores. These colours are extremely fast and heat-resistant. These qualities of theirs were recognised already thousands of years ago when lazurite was used as a pigment.

Allochromatism.* Quite a few instances are known when one and the same mineral exhibits different colours and shades. For example, quartz, which commonly occurs in colourless, sometimes perfectly transparent, crystals (rock crystal), may be tinted in various beautiful colours, such as violet (amethyst), pink, yellow-brown (due to the presence of ferric oxides), golden (citrine), grey or smoky (rauchtopaz), deep black (morion), and milk-white. Similarly, rock salt (halite) may be white, grey, yellow, dark-brown, pink, and sometimes blue.

In the majority of cases the colour of such minerals is due to the presence of foreign finely-dispersed mechanical impurities, which are pigmented by chromophores. These pigmenting impurities may be either organic or inorganic compounds. Even infinitesimal quantities often produce a most intense coloration in colourless minerals, the colour depending both on their quantity and the degree of dispersion.

Such colours which do not depend on the chemical nature of the minerals themselves are referred to as allochromatic (foreign to the minerals themselves). The minerals thus coloured are in effect crystallosols (p. 50).

Coarser dispersions, i.e., inclusions of minerals visible to the naked eye are also observed sometimes. Such are, for example, the greenish crystals of quartz with microinclusions of actinolite, black calcite which is virtually crammed with minute inclusions of sulphides or carbonaceous matter, etc.

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* "Allos" means alien in Greek.

There are also found allochromatically stained semitransparent and transparent colloids (gels) and metacolloids. The pigmenting impurities are mostly brown ferric hydroxides, red ferric oxide, black manganese oxides, organic matter, etc. Very often the pigment in them is disseminated unevenly, sometimes in concentric bands. Such is the case of agates with their remarkable fine and multicoloured patterns.

Pseudochromatism.* In some transparent minerals a "play of colour" may be produced by the interference of incident light which is reflected from the internal surfaces of cleavage cracks or the surfaces of inclusions. This phenomenon is familiar to us from the iridescent films of paraffin (kerosene), petroleum, or oil floating on water and showing "rainbow colours". It is explained by the interference of rays of light reflected from the upper surface of the transparent film (at its interface with air) and the lower surface (at the interface with water).

Such phenomena of false colouring are also observed in transparent mineral solids. A fine example is labradorite, a facing stone, the polished surfaces of which at certain angles of rotation show a beautiful blue and green chatoyancy apparently due to the reflection of light from fine lamellar inclusions of minerals differing in composition from the principal mineral.

Iridescent films are often seen on the reniform surface of limonite or brown hematite (iron hydroxides), on crystals of iron glance, as well as on slightly oxidised surface of bornite—Cu_5FeS_4 (violet and blue chatoyancy), etc. In all these cases the colouring has nothing to do with the nature of the mineral itself. Such films on minerals are called *tarnishes.*

Classification of colours. The extremely diversified hues of the colours of minerals are beyond comparative description both because they are too numerous and because the eye can distinguish only the rough differences between them. If two green minerals, malachite and garnierite (nickel hydrosilicate) are examined separately, they both appear to be of the same colour to the inexperienced eye, but when examined side by side, a substantial difference will be noticed at once. Systematical training of the eye gradually develops visual chromatic memory to the point where one distinguishes more and more different hues. This ability comes in handy in identifying minerals.

The usual practice is to compare the colours of minerals to those of some familiar objects or substances. That is why there are so many composite names for mineral colours, e.g., milk-white, honey-yellow, brass-yellow, carmine-red, emerald-green, apple-green (the colour of unripe apples), chocolate-brown, lead-grey, tin-white, etc. Relative as they are, these names are generally accepted and used throughout the world in literature on mineralogy.

At any rate, first there must be agreement on the names at least for the main colours. As a basis we may take the following most fre-

* "Pseudo-" is a Greek prefix meaning false.

quently used names of colours which are more or less constant for a number of minerals.

1. Violet—amethyst
2. Blue—azurite
3. Green—malachite
4. Yellow—auripigment
5. Orange—crocoite
6. Red—cinnabar (powdered)
7. Brown—porous limonites
8. Yellow-brown—ochreous limonites
9. Tin-white—arsenopyrite
10. Lead-grey—molybdenite
11. Steel-grey—tetrahedrite
12. Iron-black—magnetite
13. Indigo-blue—covellite
14. Copper-red—native copper
16. Brass-yellow—chalcopyrite
16. Metallic-golden—gold

Colourless rock crystal, milk-white quartz, grey rock salt, and black pyrolusite are examples of lack of colour due to uniform absorption of the entire visible spectrum.

STREAK

The streak is the colour of the fine powder of a mineral. Such powder is readily obtained by rubbing the mineral on a flat surface of unglazed porcelain known as the streak plate. The colour of the streak thus obtained is characteristic of the given mineral.

As a diagnostic feature, streak is better than the colour of a mineral, being more stable, and, therefore, more reliable.

In many instances the colour of a mineral and the colour of its streak are the same. Thus, both the colour and streak of cinnabar are red, in magnetite they are both black, in lazurite both are blue, etc. In other cases they differ materially, examples being hematite (colour steel-grey or black, streak red), pyrite (colour brass-yellow, streak black), etc.

The majority of transparent and translucent coloured minerals have a colourless (white) streak or faintly coloured streak. Therefore, streak is most important as a diagnostic feature of opaque and translucent strongly coloured minerals.

In nature the same mineral frequently occurs in either a compact or a powder-like form which sometimes differ sharply in colour. Examples are limonite (iron hydroxide) which occurs either as compact black masses or as powder-like (ochreous) yellow-brown masses; hematite (dehydrated iron oxide) occurs as black crystalline aggregates or as a bright red powder-like substance, etc. In other instances the colour of a mineral is the same both in compact crystalline masses and in the dispersed state, e.g., malachite remains green in either variety, azurite is blue, cinnabar is red, auripigment is bright yellow, etc.

It should be noted that the allochromatic colouration of many translucent minerals caused by the admixture of some particular compounds in the form of a dispersed phase, essentially corresponds to the colour of

these compounds in powder-like form. Such are brown opals coloured by iron hydroxides, and red jaspers which are intimately permeated with finely dispersed anhydrous iron oxide, etc.

LUSTRE AND REFRACTIVE INDEX

When incident light is partly reflected by a mineral, its frequency does not change. It is this reflected light that creates the impression of lustre. The intensity of lustre, i.e., the quantity of light reflected is the higher, the greater is the difference in the velocity of light before and after it enters the crystalline medium, i.e., the higher is the mineral's refractive index. The lustre is almost independent of the colour of minerals.

Knowing the refractive indices, it is easy to calculate the reflecting power R for most minerals using Fresnel's formula

$$R = \left(\frac{n-1}{n+1}\right)^2,$$

where R = reflective index;

n = average refractive index of a mineral in relation to air.

By substituting definite values for n in this formula a curve can be plotted giving the relationship between the reflecting power (lustre) and the refractive index (Fig. 20). The curve has its minimum at $n=1$ which is the refractive index closest to that of air. Since most minerals have refractive indices greater than unity, we shall concern ourselves with the values of the reflective index R to the right of this minimum.

The long established gradations in the intensity of the lustre of minerals are almost exhaustively covered by the following scale:

1. *Vitreous* lustre (the lustre of glass) is characteristic of minerals with refractive indices between 1.3 and 1.9. Examples: ice ($n=1.309$), cryolite ($n=1.34$-1.36), fluorite ($n=1.43$), quartz ($n=1.544$); numerous halides, carbonates, sulphates, silicates, and other oxygen salts; and finally, spinel ($n=1.73$), corundum ($n=1.77$), and garnets (n up to 1.84).

2. *Adamantine* lustre (the lustre of diamond) is characteristic of minerals with refractive indices between 1.9 and 2.6. Examples: zirconium ($n=1.92$-1.96), cassiterite ($n=1.99$-2.09), native sulphur with adamantine lustre on crystal faces ($n=2.04$), sphalerite ($n=2.3$-2.4), diamond ($n=2.40$-2.46), rutile ($n=2.62$); the latter often shows a submetallic lustre in deeply coloured modifications.

3. *Submetallic* lustre is found in transparent and translucent minerals with n (for Li-light) = 2.6-3.0. Examples: alabandite ($n=2.70$), cuprite ($n=2.85$), cinnabar ($n=2.91$), hematite ($n=3.01$).

4. *Metallic* lustre is typical of minerals with n greater than 3. Examples (in the order of increasing reflective index): pyrolusite (crystalline), molybdenite, antimonite, galena, chalcopyrite, pyrite, bismuth, etc.

Left of the minimum (Fig. 20), the curve of reflecting power rises steeply. Only some pure (native) metals such as silver ($n=0.18$), gold ($n=0.36$), copper ($n=0.64$), etc., in which n is less than unity fall within this portion of the curve.

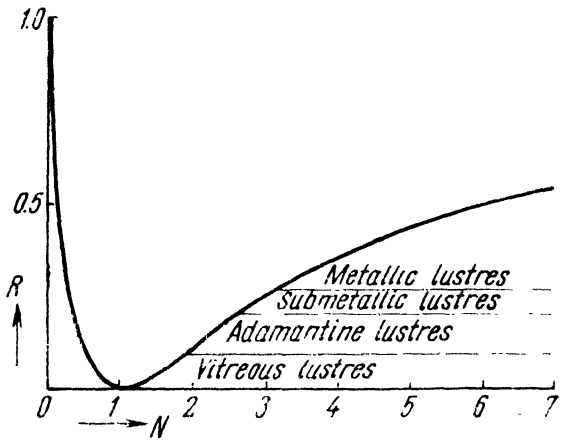


Fig. 20. Dependence of reflective index (R) on the refractive index (n) of minerals.

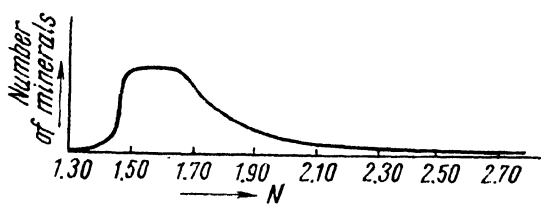


Fig. 21. Relative occurrence of minerals with different refractive indices.

To determine the reflecting power of opaque minerals apart from refractive indices, account should also be taken of the absorption factor (K) of the given medium. In this case, the reflective index (R) will be expressed by the following formula (for optically isotropic sections of the minerals):

$$R = \frac{(n-1)^2+n^2K^2}{(n+1)^2+n^2K^2}.$$

This means that for opaque minerals the values of reflecting indices are, in fact, somewhat higher than those obtained from Fresnel's formula, and also explains the seeming rare exceptions to the above rule. For example, magnetite with a refractive index of 2.42 should have an adamantine lustre, yet, owing to its opacity, i.e., considerable absorption of light, its reflecting index will be somewhat higher passing into the submetallic-lustre region on the graph (Fig. 20).

Should we distribute all transparent and translucent minerals according to the mean refractive index (Fig. 21), we shall notice at once a

wide maximum range for the values of refractive indices between 1.5 and 1.7. It has been established that minerals with a vitreous lustre make up about 70 per cent of all the minerals with a refractive index up to 1.9. Another group of minerals, though less numerous, is characterised by metallic lustre. These metallic lustres, however, are so characteristic of a number of economically important minerals that the names of many of them were derived from this feature (this is still the case in German). Examples: galena (lead glance), chalcocite (copper glance), antimonite (antimony glance), cobaltite (cobalt glance), hematite (iron glance), etc.

As known, the refractive index is a function of ionic refraction, chemical composition, specific gravity and the specific features of the crystal structure. It was observed long ago that in minerals of similar crystal structure, the refractive index and the specific gravity increased with increasing atomic weight of the cation. For instance, whereas in the case of MgO (sp. gr. 3.64) $n=1.73$, in the case of NiO (sp. gr. 6.4) $n=2.23$; or whereas for Al_2O_3 (sp. gr. 4.0) $n=1.76$, for Fe_2O_3 (sp. gr. 5.2) $n=3.01$, etc. It is also known that multivalent ions of Fe^{3+}, Cr^{3+}, Ti^{4+}, V^{5+}, when present in compounds as an isomorphous admixture, materially increase their refractive indices. In isostructural compounds such as NaCl and KCl, an increase in cationic size (Na^{1+} 0.98 and K^{1+} 1.33) causes looser packing and even a decrease in the value of n (1.490 for KCl, and 1.544 for NaCl) with a corresponding decrease in specific gravity, despite the fact that the atomic weight of K (39.0) is higher than that of Na (23.0). The reverse picture with regard to the refractive index is observed in the case of NaF and NaCl compounds where the fluorine anion (at. weight=19.0) is replaced by the chlorine anion (at. weight=35.5); in the case of NaF $n=1.328$, whereas for NaCl it is 1.544, the former compound possessing a much lower n, although the specific gravity of NaF (2.79) is greater than that of NaCl (2.16). This is explained by the very low refraction of fluorine. It is also obvious (as was stated under "Polymorphism") that changes in cationic coordination number caused by the rearrangement of crystal structure affect the specific gravity and hence the refractive index of crystal substances.

Another important factor (independent of the refractive index and the absorption of light) affecting the reflection of light is *the nature of the reflecting surface.*

So far we discussed the lustres of mirror-smooth surfaces of minerals (crystal faces and cleavage planes). But if, upon fracture, a mineral presents cryptotuberous or pitted surfaces, its vitreous or adamantine lustre is somewhat dulled. The reflected light is partly dispersed, loses some of its orderly nature which produces the so-called *greasy lustre.* This phenomenon can be easily observed if one follows the change in the lustre of freshly broken rock salt on exposure to damp air. In a matter of days the brilliant surfaces will seem to be coated with a thin film of grease. This will be especially conspicuous in comparison with

fresh fracture surfaces. The most typical examples of greasy lustre are the fracture surface of native sulphur or the lustre of nepheline touched by decomposition.

Rougher surfaces possess *a waxy lustre.* This is especially characteristic of cryptocrystalline masses and solid light-coloured gels. Common examples are flints, colloidal minerals of the halloysite group, etc.

Lastly, if finely dispersed masses are highly porous, the incident light will be completely and randomly scattered. The micropores "trap" the light, as it were, and the surface is then called *dull* or earthy. Examples are chalk, dry kaolin, various ochres, sooty pyrolusite (MnO_2), finely-porous masses of iron hydroxides, etc.

A phenomenon associated with lustre and peculiar to minerals with a definite orientation of the structural elements in one or two dimensions is called *chatoyancy.*

Minerals of a parallel-fibrous structure (asbestos, nemalite, selenite, etc.) always have a typical *silky chatoyancy.* Transparent minerals of a lamellar crystal structure and hence possessing sharply pronounced perfect cleavage, have a peculiar *pearly chatoyancy* (muscovite, foliated gypsum, talc, etc.). That pearly chatoyancy is associated with lamination may be easily shown by stacking thin sheets of cover slides or window glass and looking through the stack. The peculiar chatoyancy observed will definitely resemble that of pearl.

CLEAVAGE AND FRACTURE

Cleavage is the ability of crystals and crystalline grains to break or split along those crystallographic planes which are parallel to actual or possible crystal faces. This property of crystal media exclusively related to internal structure has nothing to do with external crystal form of

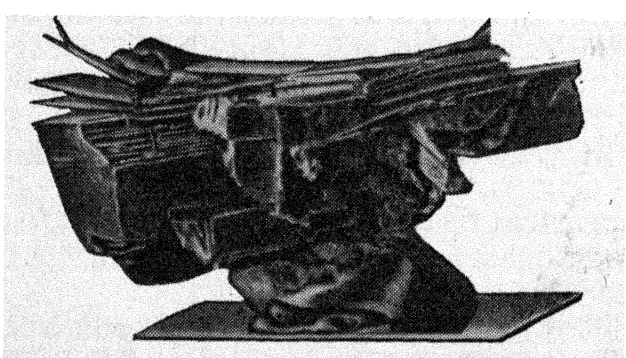


Fig. 22. Eminent cleavage of mica.

one and the same mineral (rhombohedral, scalenohedral, and prismatic crystals or even irregularly shaped crystal grains of calcite always possess the same rhombohedral cleavage). That is why this property, which is very characteristic of any given crystal substance is a very important diagnostic feature for identification of minerals. Character-

istically many minerals are called spars (feldspar, heavy spar, fluorspar, Iceland spar, etc.)*, exactly because of their cleavage. Cleavage is also reflected in the names of minerals like orthoclase (cleavage at right angles), plagioclase (cleavage at oblique angles), etc.

Since it is often important to distinguish the quality of cleavage, the following scale has been adopted.

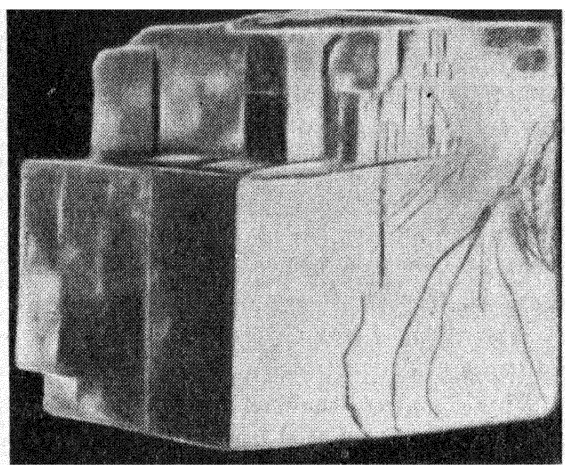


Fig. 23. Perfect cleavage of rock salt.

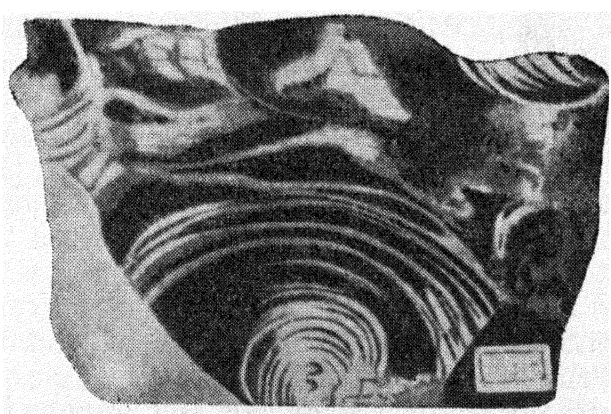


Fig. 24. Conchoidal fracture of obsidian.

1. *Highly perfect* cleavage (micas and chlorites). Crystals readily split into excessively thin sheets (Fig. 22) and it is very difficult to obtain fractures other than along cleavage planes.

2. *Perfect* cleavage (calcite, galena, rock salt, etc.). On striking with a hammer the mineral yields cleavage fragments which strongly resemble its crystals (Fig. 23). Thus, galena breaks into small regular cubes,

* Minerals without metallic lustre but with good cleavage in several directions since long are known as spars (from the Greek "spate" meaning plate).

calcite into regular rhombohedra, etc. It is rather difficult to obtain fractures other than along cleavage.

3. *Distinct* cleavage (feldspars, hornblende, etc.). In mineral fragments both cleavage surfaces and uneven random fractures may be seen.

4. *Imperfect* cleavage (apatite, cassiterite, native sulphur, etc.). It is hardly detectable, and must be looked for in a mineral fragment. As a rule, the cleavage surface is uneven.

5. Cleavage is *indistinct* (*poor*), i.e., practically absent in corundum, gold, platinum, magnetite, etc., and is recognised only in rare cases. Such bodies usually have a conchoidal fracture similar to that of slag or obsidian (Fig. 24). Many sulphides show a conchoidal fracture. Some native metals (copper, silver, etc.) exhibit a splintery or hackly fracture.

Different minerals which possess cleavage have their planes oriented differently according to the type of crystal structure. Thus, in coordination structures with ionic bonding, such as galena (PbS) and halite (NaCl), the cleavage is cubic; rhombohedral in calcite ($CaCO_3$); prismatic in silicates whose complex anions occur as chains extended in one direction, such as pyroxenes and hornblende; pinacoidal in silicates with anionic layers, such as micas and chlorites, etc.

The older concept developed by Bravais was that cleavage planes are parallel to those planar networks of the space lattice which are farthest from each other. Using crystallochemical data G.V. Wulf showed that cleavage in crystals with ionic bonding was due to the anisotropy of the cohesion forces of structural units in different directions. Thus in the crystal structure of sphalerite (ZnS), the planar ionic networks farthest from each other should be parallel to the octahedral faces or, according to Bravais, cleavage should take place along {111}. Actually, cleavage in sphalerite is parallel to the planes of the rhombic dodecahedron {110}, though in this case the distances between the planar networks are shorter. The point is that in the former case, each of the separate planar networks is composed of identical ions, which are, however, differently charged (Zn^{2+} or S^{2-}) which accounts for the chemical bonding of the networks, while in the latter case each network is composed of mutually compensating zinc and sulphur ions and therefore, although they are closer to each other, the bonding between them is weak. Diamond, however, which has the same crystal structure as sphalerite but consists of carbon atoms only, shows octahedral cleavage (Law of Bravais).

Often, the differently oriented cleavage planes of a mineral are not equally perfect. Thus, gypsum which crystallises in the monoclinic system has the following cleavages: highly perfect, parallel to the second pinacoid {010}; distinct, parallel to the rhombic prism {111}; and imperfect, parallel to the first pinacoid {100}. Sometimes the number of cleavage directions is also an important diagnostic feature. For instance, though very similar in external features (colour, hardness, lustre, etc.),

minerals, such as sphalerite, ZnS, and wolframite, (Fe, Mn) WO_4, differ in that the crystals or grains of sphalerite have several cleavage planes parallel to {110}, while wolframite has only one perfect cleavage plane {010} which is parallel to the elongation of the crystals or grains.

In addition to cleavage, some crystals show *parting* due, according to N. Belov, to a submicroscopic "interlayer" of a substance of a different composition, oriented along the planes of closest packing. Unlike cleavage, parting planes are not strictly planar and are usually oriented in one direction.

HARDNESS

Hardness* of a mineral is generally defined as its resistance to external mechanical action such as scratching.

The usual mineralogical practice is to define the hardness of a mineral by scratching it with another, i.e., to establish its relative hardness. Mineralogy uses for this purpose Mohs' scale of relative hardness. Included in the scale are ten minerals, each of which will scratch all those higher in the scale.

The following minerals arranged in the order of relative hardness from 1 to 10 are taken as standards for comparison:

1. Talc—$Mg_3[Si_4O_{10}][OH]_2$
2. Gypsum—$CaSO_4 \cdot 2H_2O$
3. Calcite—$CaCO_3$
4. Fluorite—CaF_2
5. Apatite—$Ca_5[PO_4]_3F$
6. Orthoclase—$K[AlSi_3O_8]$
7. Quartz—SiO_2
8. Topaz—$Al_2[SiO_4]$ (F, OH)$_2$
9. Corundum—Al_2O_3
10. Diamond—C

The hardness of a mineral is estimated by finding out which is the last standard mineral on the scale scratched by it. For example, if a mineral will scratch apatite and will be scratched by orthoclase, its hardness is between five and six.

This simple, though rough, method for determining mineral hardness fully meets diagnostic requirements.

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* The concept of the "hardness of a body" has not yet been strictly defined despite all the studies on the subject. Scratching, drilling, pressing, and grinding hardnesses are recognised. Investigation of all these methods favours the conclusion that in this case we are really concerned with physical phenomena of different nature.

In most minerals the hardness on different faces or cleavage planes is more or less constant, though in some instances it varies depending on the direction in which it is scratched. Thus in disthene (Al_2SiO_5) the hardness is 4.5 along the length of the crystal, but 6 to 7 across the length. Hence the name disthene ("di-" means double in Greek and "sthenos" resistant).

For purposes of research, more accurate hardness tests are made on special apparatuses called scleroscopes using diamond-tipped or metal indenting hammers. Without going into their mechanics, we shall discuss the results obtained in the detailed study of the effects of scratching on crystal surfaces.

In the first place, it is now clear that the hardness of crystalline bodies is a vectorial (anisotropic) property, i.e., it is not the same in different directions. This applies even to minerals in the cubic system. Figure 25 shows a hardness "rosette" on the face of a rock-salt cube.

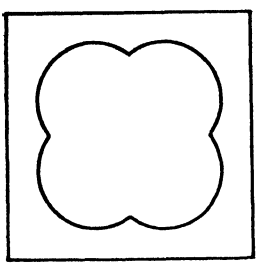


Fig. 25. Hardness "rosette" on the face of a rock-salt cube.

The hardness of a crystal face oriented perpendicular to the cleavage plane is minimum in the direction parallel to this plane and maximum in the direction perpendicular to it.

From the point of view of crystal chemistry the hardness of crystalline solids depends on the type of structure and the strength of the atomic (ionic) bonding. Although information on this particular matter is scarce, some points have been established more or less positively.

A comparative analysis of empirical data suggests that the hardness of ionic crystalline bodies generally is directly proportional to the density of the crystal structures. As the interionic distances in such compounds increase, the hardness diminishes:

	BeO	MgO	CaO	SrO	BaO
Distance AX.....	1.55	2.10	2.40	2.57	2.77Å
Mohs' hardness	9	6.5	4.5	3.5	3.3

It has also been found that in compounds crystallising in the same system with close interionic distances hardness increases with increasing valency, i.e., ionic charges.

It was shown by V.S. Sobolev that the cationic coordination of compounds is also of great importance. Thus, oxides and silicates which have cations with an $r_k : r_A$ ratio corresponding to the lower stability limit of the coordination number, will possess maximum hardness. The hardness of silicates containing aluminium in sixfold coordination will be higher than that of alumosilicates (fourfold aluminium coordination). Hydroxyl ions and water in the composition of compounds tend to reduce hardness.

It should be noted that cryptocrystalline, finely-porous, and pulverulent varieties of minerals may show false low hardness. Example: hematite (Fe_2O_3) in crystal form has a hardness of 6, but when it occurs as red ochre, the hardness is less than 1, which shows that for all practical purposes there is no cohesion between the particles in finely-dispersed hematite.

On the whole the hardness of natural compounds ranges from 2 to 6. Harder minerals are found among anhydrous oxides and silicates, viz., quartz—SiO_2 (hardness 7), cassiterite—SnO_2 (6-7), corundum—Al_2O_3 (9), the spinel group which includes spinel—$MgAl_2O_4$ (8), topaz (8), beryl (7.5-8), tourmaline (7-7.5), and garnets (about 7), etc.

BRITTLENESS, DUCTILITY AND ELASTICITY

These properties, though of secondary importance as diagnostic features, are very characteristic of a number of minerals.

Brittleness is the ability of minerals to powder when scratched with a knife blade. Tetrahedrite (grey ore) in this case produces a dull "dusty" streak edged with dark powder. Chalcosine, however, which is externally similar to tetrahedrite, gives a smooth brilliant scratch indicating plastic deformation, i.e., ductility. This property is displayed even more strongly by native ductile metals (copper, gold, electrum, silver, etc.). Their ductility is also expressed in the fact that grains of these metals can be hammered out into thin plates.

In a number of minerals with weak crystal structures, plasticity is due to gliding, i.e., parallel displacement of the crystal layers in one or more planes. In other minerals plasticity is associated with mechanical twinning (calcite crystals).

Elasticity is the ability of minerals to recover their original shape after being bent, once the forces that caused the deformation have been removed. This property is present, for example, in micas which distinguishes them from the so-called brittle (calcium-bearing) micas which tend to break upon bending. Chlorites, which resemble micas, can be sharply bent, but do not recover their original shape. The asbestos minerals split into thin elastic fibres which can be made into fabrics, a property lacking in fibrous gypsum (selenite).

SPECIFIC GRAVITY

The specific gravity of minerals depends primarily on the weight of the atoms or ions composing a crystalline substance. It also depends, to a great extent, on the ionic radii the increase of which compensates for increase in atomic weight, sometimes to the point when specific gravity even diminishes. For example, although the atomic weight of potassium is 1.7 times greater than that of sodium, the specific gravity of KCl (1.98) is less than that of NaCl (2.17) because the ionic radius of K^{1+} (1.33) exceeds that of Na^{1+} (0.98), which has a pronounced

effect on the volume of these crystalline substances. Furthermore, a change, particularly an increase, in the coordination number in crystal structures results in diminishing volume (see *Polymorphism*), and, therefore, in greater specific gravity. Finally, other conditions being equal, a decrease in cationic valency (or an increase in anionic valency) is also accompanied by an increase in specific gravity.

Minerals vary widely in specific gravity, from less than 1 (natural gases*, liquid bitumens) to 23.0 (some mineral varieties of the osmiridium group).

Most of the natural organic compounds and salts of light metals which are in the upper part of the periodic table, range in specific gravity from 1 to 3.5. Examples are amber, solid bitumens (1.0-1.1), halite—NaCl (2.1-2.5), gypsum—$CaSO_4 \cdot 2H_2O$ (2.3), quartz—SiO_2 (2.65), diamond (3.5), etc. Only a few of these minerals, as corundum and its varieties—Al_2O_3, possess a higher specific gravity (4.0). Barite, $BaSO_4$ (4.3-4.7), is the heaviest of the sulphates as its name suggests ("baros" means burden in Greek).

The compounds of typical heavy metals which occupy the lower part of the periodic table vary in specific gravity from 3.0 to 9. Examples are siderite—$FeCO_3$ (3.9), sphalerite—ZnS (4.0), pyrite—FeS_2 (5.0), magnetite—$FeFe_2O_4$ (4.9-5.2), hematite—Fe_2O_3 (5.0-5.2), anglesite—$PbSO_4$ (6.4), cerussite—$PbCO_3$ (6.5), cassiterite—SnO_2 (7.0), galena—PbS (7.5), cinnabar—HgS (8.0), uraninite—UO_2 (8-10).

Native heavy metals possess the highest specific gravity. Examples are copper (8.9), bismuth (9.7), silver (10-11), mercury (13.6), gold (15-19), native platinum metals (14-20), iridium and osmiridium minerals (17-23).

Two basic methods are used to determine the specific gravity of minerals: (1) the method of displacement of a liquid, i.e., weighing a specimen and measuring the volume of water which it displaces in a vessel, and (2) the method of determining the loss in weight of a mineral immersed in water (the absolute weight of the mineral is divided by the weight lost in water). The specific gravity of fine mineral grains is determined with the aid of a picnometer or by using heavy liquids and the Westphal balance described in special manuals.

Considerable fluctuations in the specific gravity of a mineral are relatively rare and may be caused, apart from isomorphism, by tiny inclusions of other minerals or bubbles of gases and liquids.

Differences in the specific gravity of minerals is taken advantage of in concentration of ores by various gravity methods of separation of non-metallic minerals (quartz, calcite, barite, etc.) from metallic minerals (galena, sphalerite, cassiterite, etc.).

* For natural gases, the specific gravity is determined relative to air.

MAGNETISM

Very few minerals have pronounced magnetic properties. Minerals possessing weak paramagnetic properties are easily attracted by a magnet (low-sulphur pyrrhotite varieties). But there are some minerals which are magnetic in themselves; in other words, they are ferromagnetic and will attract iron filings, pins and nails (Fig. 26). These include magnetite, plessite and certain ferroplatinum varieties. Finally,

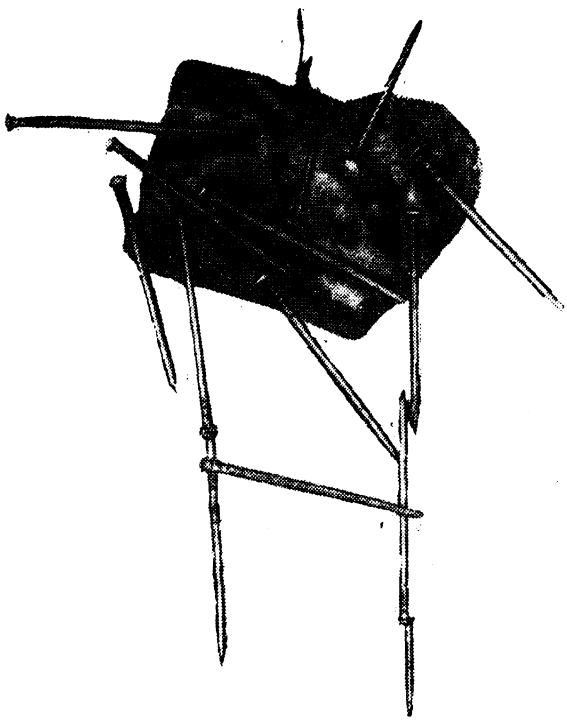


Fig. 26. Magnetite attracting nails.

there are some minerals which are repelled by a magnet (native bismuth) and are said to be diamagnetic.

Since minerals possessing magnetism are few, this property is a very important diagnostic feature. A test for magnetism consists in bringing the specimen close to the poles of a freely suspended magnetic needle.

The magnetism of a mineral may be so weak as to be undetectable by the needle. The difference between these magnetic properties is utilised for the separation of minerals into fractions by means of an electric magnet, in laboratory assaying of the heavy fraction obtained by washing.

RADIOACTIVITY

Of especial interest is the uranium-radium group of radioactive elements which occupy the very end of the periodic table. Radioactivity was discovered by H. Becquerel as far back as 1896. Further study of

this phenomenon resulted in the discovery of the general laws of the structure of the atom and in the development of nuclear physics. As known, the formation of ions, chemical compounds and chemical processes in general are almost exclusively controlled by the structure of the outer electron shells of the atoms and by the energy evolved in the rearrangement of the electrons, in the course of which the atomic nuclei remain intact. Radioactive transmutations, on the other hand, result from processes occurring in the nuclei. It is therefore relevant to recapitulate the structure of atomic nuclei.

It has been established that the atom consists of three principal types of particles: protons and neutrons within the nucleus and electrons which surround the latter. While the number of the protons is equal to the atomic number, and that of the neutrons is equal to the difference between the mass number (which is close to the atomic weight) and the atomic number.

In the first rows of elements in the periodic table (Table 1, pp. 32-34), the numbers of protons and neutrons are usually equal. As the elements become heavier the number of neutrons gradually becomes greater than that of protons (which is essential for achieving minimum energy and, hence, the stability of the nucleus). In the lowest series, the number of neutrons by far exceeds that of protons. For example, the nucleus of heavy U^{238} uranium contains 92 protons and 146 neutrons (238 – 92), while that of the U^{235} isotope has three neutrons less (the number of protons remains the same).

The atomic nuclei of these last elements of the periodic table are not quite stable. As a result, these elements are characterised by so-called radioactive decay, i.e., *continuous emission of*:

(1) α-particles, i.e., atomic nuclei of helium with atomic number 2 and mass number 4; they are emitted with tremendous velocity and ionise the air, i.e., make it electroconductive; the emission of the particles results in the transmutation of the atoms of the given element into those of lighter elements, the atomic number diminishing by 2 units and the mass number by 4 units upon the emission of each particle;

(2) β-particles, equivalent to electrons; the emission of each such particle naturally *increases the nuclear charge* by one unit (the mass number remains constant); hence the atomic number of the transmutation product will also gain one unit;

(3) γ-rays, which constitute electromagnetic radiation similar to X-rays.

This continuous transmutation of atoms which is accompanied by the evolution of tremendous energies does not depend upon temperature or pressure. The end products formed as a result of successive emission of α- and β-particles are stable isotopes of lead. The decay time of the intermediate atoms formed in the process ranges from fractions of a second to thousands of millions of years. The time it takes for half the atoms in an isotope to decay is termed *half-life* and is constant for each given isotope.

Three series of successive radioactive transmutations are known: (1) the uranium series beginning with I U^{238} uranium (Fig. 27), whose intermediate products of decay include radium with a half-life of 1,600 years; (2) the actinium series beginning with U^{235} (another uranium

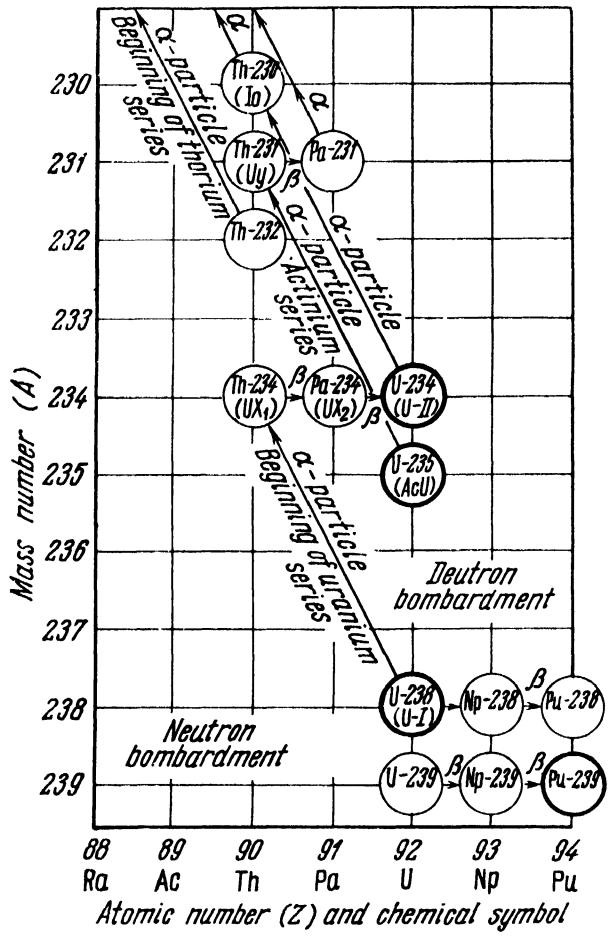


Fig. 27. Initial portions of three series of natural radioactive transmutations and artificially obtained transuranium elements: neptunium and plutonium.

isotope), which includes actinium among the intermediate decay products; and (3) the thorium series beginning with the Th^{232} isotope.

The radioactivity of minerals is determined by the ionisation which they produce in air, using such instruments as electroscopes, ionisation chambers and various types of counters. Uranium minerals, which emit chemically active radiations, strongly affect a photographic plate and enable so-called autoradiographs to be obtained. A polished ore specimen is placed upon a photographic plate and left for some time in a dark room or in a box. The radiations induce chemical changes in the photosensitive emulsion. Upon development, black spots will indicate the presence of uranium minerals. A print made on photographic paper

will show radioactive minerals as light spots and non-radioactive minerals as dark spots.

The processes of radioactive decay which are taking place over very long periods of time are used for absolute dating of rocks in which radioactive minerals had once formed. This is possible, first, because the rate at which a radioactive substance disintegrates remains constant despite temperature variations or chemical reactions, and, second, because the content of helium and lead which are the end products of decay is in direct proportion to the time that has passed since the radioactive mineral was formed.

OTHER PHYSICAL PROPERTIES

Of the many other properties possessed by minerals (heat and electrical conductivity, piezoelectricity, pyroelectricity, semiconductivity, fusibility, solubility, etc.) we shall discuss those which are most useful as diagnostic features or as a means of verifying previous identification. We shall also mention some properties that are used by field prospectors.

Since the investigation of such properties as *solubility*, *fusibility*, *coloration of flame* and *borax beads*, etc., needs special equipment and these properties are treated in detail in manuals on blowpipe analysis, they will not be discussed here. We shall deal with some of those properties which are used sometimes by prospectors.

The *odour* which minerals sometimes give off, when struck or broken, may be indicative of certain elements which are present in the minerals. Thus, native arsenic, arsenopyrite (FeAsS), and other metal arsenides, when struck, give off a characteristic garlic or "arsenic" odour which intensifies on heating or ignition. Petroleum gases often have the unmistakable smell of hydrogen sulphide. The same odour is often a guide to hydrogen sulphide springs. Sometimes vein quartz, which is associated with rare-metal minerals, emits a peculiarly unpleasant odour on breaking which in practice often indicates the presence of the rare mineral. Some minerals are known for their "clayey" odours, etc.

Certain minerals, especially when in pulverulent forms, may be recognised by *touch* or *feel*. For example, common talc feels greasy, and this distinguishes it from the otherwise similar pyrophyllite; the pulverulent varieties of jarosite, $KFe_3[SO_4]_2[OH]_6$, on rubbing between the fingers feels oily and greasy, in contrast to the ochreous masses of limonite, $HFeO_2 \cdot aq$, which are similar in colour, but which feel hard and gritty.

Taste is sometimes relied upon as a means for determining the nature of certain minerals such as common salt, artesian drinking water, etc.

And finally, in mining practice *acoustic* effects may be of some help. Thus a mass of cerussite ($PbCO_3$) when dropped on the floor sounds

like falling glass. During sloping rocks and ores of different strength produce different sounds when struck by a pick or hammer—distinctions are so subtle that they can be grasped only by a very experienced ear. In some miners this ability is developed to an amazing degree. Thus, in practice, all the senses (eyesight, touch, smell, and hearing) are used for identifying minerals, but it is, of course, eyesight and visual memory which develop with experience that are most important.

Chapter III

METHODS FOR DETAILED STUDY OF MINERALS

In order to learn to identify by simple methods minerals widespread in the earth's crust one has to deal with rather large crystals or homogeneous mineral masses. For this purpose the *external* diagnostic features described in Chapter II are used generally. Many minerals, especially those that are likely to contain valuable metals, require for positive identification additional investigations including blowpipe and qualitative chemical analyses.

However, minerals which occur seldom or which cannot be identified by simple methods depend for positive recognition upon more complicated techniques. Such detailed studies with a view to gain deeper knowledge of the composition of natural compounds are undertaken: (1) in petrographical study of rocks needed to compile geological maps; (2) in developing a deposit when the elemental composition of ores must be investigated comprehensively so that all their constituents could be utilised; (3) in the course of specific investigations in some locality which is interesting from the mineralogical point of view; (4) in solving geochemical problems for which purpose mineral substances must be more closely investigated, etc.

These detailed studies generally involve crystallochemical, X-ray, crystallooptical, thermal and chemical analyses, together with spectral, and sometimes X-ray-spectral analyses, etc. For a more detailed account of these methods special manuals should be referred to. In the present work we shall confine ourselves to the principles and applications only.

Crystallochemical analysis, which has been developed by Soviet scientist Fyodorov, is used, as the term implies, in studying crystals. Besides measuring the interfacial angles, the method consists in determining, as far as possible, the internal crystal structure from the external forms, since the most developed and frequently occurring faces usually correspond to the planes of the closest packing of the structural units. Not only the crystal system and the symmetry class, but also the chemical composition of a mineral can be determined by this method. Y.S. Fyodorov is the author of *The Kingdom of Crystals* (1920), a comprehensive treatise containing tables for crystallochemical analyses.

X-ray analysis* to identify a substance by comparing photographs may be effected by various techniques, the most common of which are: the rotation method (Poliani); the X-ray goniometer method (Weissenberg), and the powder method (Debye).

The first two methods are applied to monocrystals. In the rotation method, the crystal is rotated in monochromatic X-radiation. In contrast to this, in the Laue method, the crystal remains stationary and is exposed to a continuous X-ray spectrum. Examples of X-ray photographs are shown in Fig. 28. The more common Weissenberg method involves both the rotation of the crystal and the forward movement of a cylindrical film parallel to the rotation axis of the crystal, i.e., perpendicular to the X-rays. The photographs obtained by the Weissenberg method are peculiar in that the interference pattern consists of curves (Fig. 29) which enables a comparatively easy (geometrical) calculation of indices.

An important advantage of the Debye method is that it may be applied to aggregate mineral masses, including *cryptocrystalline* and *finely dispersed* substances and therefore is widely employed for identification of minerals. The X-ray photographs (Fig. 29) are obtained in a special camera on a photosensitive film which, on development, shows curves of varying intensity (arcs of circles formed by cones of X-rays that have been reflected from the closest-packed planes of the powdered crystal). Comparing the X-ray photographs (with regard to intensity of lines and the calculated interplanar distances) with X-ray photographs of other known substances, externally similar to the mineral in question, it is possible to identify it positively, having the results of spectral analyses and at least some optical constants. Another advantage of this method is that as little as 5 mm^3 of the powder is sufficient to obtain a powder photograph. This is especially important when not enough of the substance is available for a complete chemical analysis. However, very finely dispersed substances yield poorly defined powder photographs, while amorphous bodies proper do not reflect X-rays at all.

In this connection, mention should be made of the electron photoraph method for studying thin films, not exceeding a few millimicrons in thickness, or very finely dispersed colloids. The method is based on the property of electrons to scatter in a regular pattern on impinging on regularly spaced atoms, similar to what is observed in the case of X-rays. The difference is that X-rays penetrate deep into a crystal substance, whereas a beam of electrons penetrates only to a depth of 0.01μ (i.e., 0.00001 mm). Electron photographs have essentially the same appearance as powder photographs.

Crystallooptical analysis may be defined as microscopic determination of certain optical constants peculiar to the mineral being studied.

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* Not to be confused with X-ray structural analysis which is used in the study of crystal structure.

Transparent minerals of rocks and ores are studied in thin polished sections (up to 0.02 mm thick) or in the form of powders. The constants to be determined are the refractive index n (for optically isotropic minerals) and the principal refractive indices n_x, n_y and n_z (for anisotropic

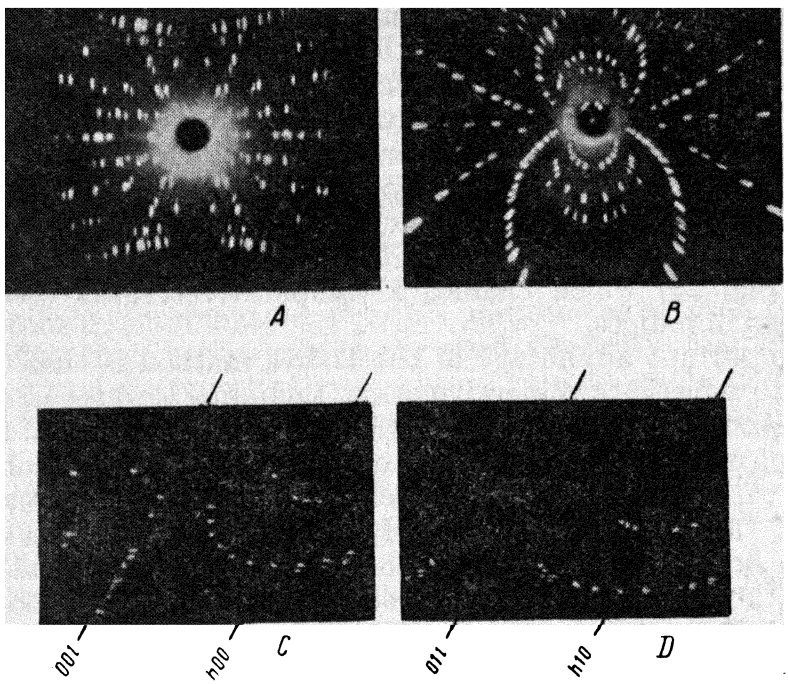


Fig. 28. Top left (*a*): X-ray photograph of a rotating crystal in monochromatic X-rays; right (*b*): Laue-photograph of a stationary crystal in the continuous X-ray tube spectrum. Bottom: Weissenberg X-ray photographs of chromium mica (fuchsite); (*c*): resolution of zero layer line (*h*0*l*), and (*d*) resolution of first layer line (*h*1*l*).

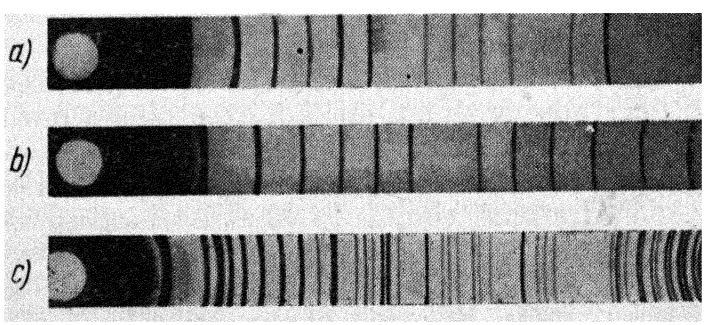


Fig. 29. Typical X-ray powder patterns.
a – sylvite, KCl; *b* – halite, NaCl; *c* – quartz, SiO_2.

minerals). This is carried out by means of specially selected immersion liquids or, more accurately, by means of a microrefractometer. Other constants to be determined include double refraction n_x-n_z, the optic

sign (for anisotropic minerals), the angle $2V$ of optic axes (for anisotropic biaxial minerals), etc. A method for the identification of transparent minerals in *transmitted light* by using the polarising microscope has been greatly improved, especially for plagioclases which are examined on Fyodorov's stage (Fig. 30), or rather on the model improved by Zavaritsky. This method can be used for identification of most minute

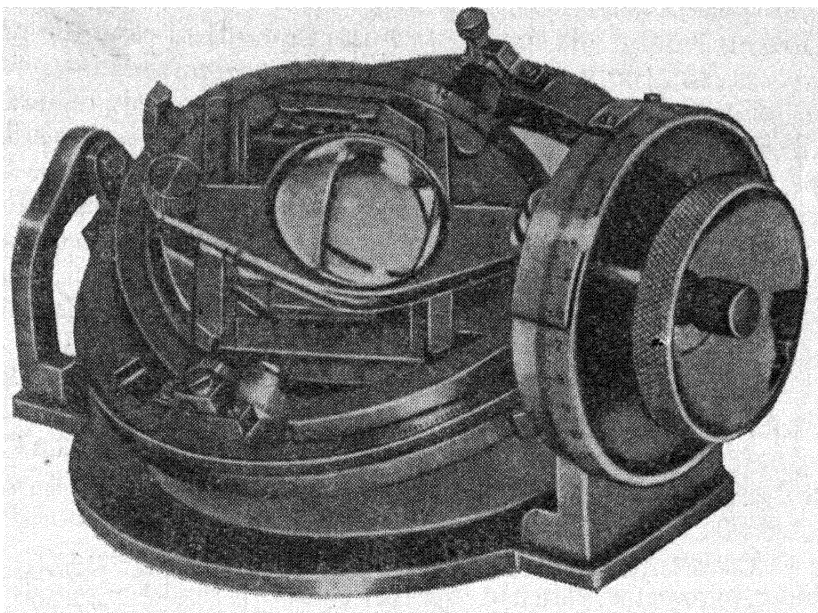


Fig. 30. Fyodorov's universal stage.

crystal grains (a few hundredths of a millimetre in diameter) which are visible as inclusions in transparent polished sections. This is a great advantage, all the more that tables are available for the determination of transparent minerals by microscopic examination. The tables are widely used by petrographers in the microscopic study of rocks. However, work with the polarising microscope and the use of special research techniques require proficiency acquired by practice.

Opaque minerals, chiefly those of bulk metal ores as well as metal ores occurring as minute inclusions in rocks are examined in mirror-polished sections under the microscope in the *reflected light* from an opaque-illuminator. In this case the optical constants are reflective index R (the ability of a mineral to reflect incident light in quantities measurable by a microphotometrocular or photoelectric cell) and the principal reflective indices (*Rg*, *Rm*, *Rp*) and double reflection (*Rg-Rp*) in the case of anisotropic biaxial minerals. Although methods for determining the optical constants of anisotropic, and particularly, biaxial minerals, have not yet been sufficiently developed, the determination of reflective indices combined with the study of other properties of minerals (hardness, colour, reactivity, etc.) is very helpful in the microscopic study of ores in reflected light. In this way it is often possible

to identify inclusions of ore minerals a few thousandths of a millimetre in diameter.

Thermal analysis which was introduced by Soviet Academician N.S. Kurnakov consists in obtaining thermal-analysis (heating or cooling) curves for the substance analysed in order to establish the endothermal or exothermal effects induced in that substance by physicochemical changes with increasing temperature (water evaporation,

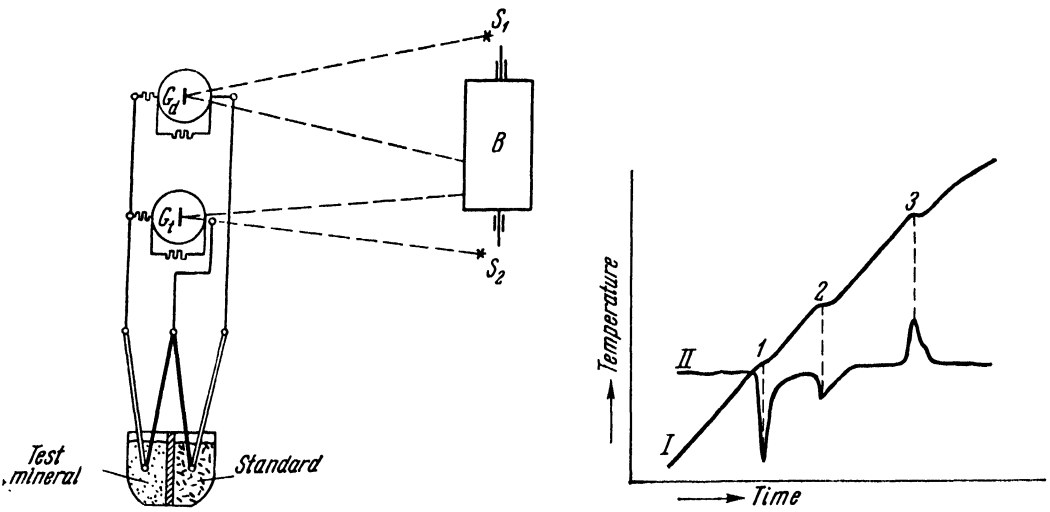


Fig. 31. Left—differential and temperature thermographs recorded with a self-recording pyrometer designed by Kurnakov (U.S.S.R.): S_1 and S_2—light sources; B—drum; G_d and G_t—galvanometers of the differential and simple thermocouples. The continuous solid line stands for platinum-rhodium wire, the double line for platinum wire, and the thin line for copper wire. Right—thermographs: *I*—recorded by a simple thermocouple; *II*—recorded by a differential thermocouple.

oxidation, reduction, conversion to a different polymorphous modification, etc.).

The thermal-analysis curves are usually recorded automatically by a pyrometer actuated by a conventional thermocouple connected in series with a differential thermocouple, both immersed in a two-compartment crucible (Fig. 31, left). One compartment holds the test mineral, while the other is packed with a thermally inert material taken as a standard (MgO, Al_2O_3, etc.). Both circuits are connected to mirror galvanometers (G_t and G_d), each of which throws a luminous spot onto photosensitive paper on drum B* which is slowly rotated by a clockwork.

In the course of heating, the galvanometer of the conventional thermocouple records the temperature curve (Fig. 31, right, curve *I*) on which any changes in the heated substance are reflected as changes in its slope at certain points (1), or as horizontal flats (2), which correspond to endothermal effects (heat absorbed), or as sharp peaks (3)

* The records are made and developed in the dark as conventional photographs.

which correspond to exothermal effects (heat evolved). The galvanometer which is connected to the differential thermocouple will record only the difference between the two thermo-electromotive forces, i.e., the difference between the temperatures of the test mineral and the standard when they are heated simultaneously. The differential curve therefore (Fig. 31, right, curve *II*) will have sharp downward inflections (endothermal effects) or sharp upward inflections (exothermal effects) indicating changes in the test mineral. Hence the importance of obtaining differential thermal-analysis (heating or cooling) curves.

In mineralogical practice, this method is usually reserved for cryptocrystalline and finely-dispersed masses for which it is difficult to carry out visual (or any other) analysis. A number of minerals (kaolin, alumohydrates, iron hydroxides, carbonates, chlorites, etc.) have characteristic heating curves which facilitate the identification of the mineral species.

The number of minerals for which this method yields characteristic data of diagnostic significance constitutes a relatively low percentage of the total number of minerals occurring in nature and includes mainly chemical compounds containing water, hydroxyl ions, and carbon dioxide. The method is further limited to the analysis of the predominant mass of the substance investigated. With a few exceptions, mechanical impurities in quantities up to 5-10 per cent of the total mass, which are of principal interest to the analyst, usually escape detection.

Often a more exhaustive knowledge of mineral properties may be necessary, especially when the mineral has practical uses. Thus, it may be important to determine its behaviour on heating. The obtaining of heating curves alone is not sufficient, and the products of each transformation of the substance require chemical analysis, the study of optical properties and X-ray investigation.

The temperatures at which these transformations occur must be measured very accurately. The thermographs do not always answer this requirement, since usually there is a lag in the recording of the transformations, the difference being as much as 60° to 100°. Hence, in the case of minerals containing water and hydroxyl ions much more precise and reliable data can be obtained from *dehydration curves.* These curves are obtained as follows: 1-2 grams or more of the test substance are weighed together with a platinum crucible and heated in an electric furnace successively at definite temperatures (usually at temperature steps of 50°); when the loss in weight, as against the previous weighing, becomes less than 0.03-0.05 per cent, the temperature is raised a step further. The resulting dehydration curves clearly show temperatures at which transformations within the substance begin.

Figure 32 shows two dehydration curves: for kaolinite – $Al_4[Si_4O_{10}][OH]_8$ and halloysite – $Al_4[Si_4O_{10}][OH]_8 \cdot 4H_2O$. While for kaolinite (curve *I*), which contains hydroxyl ions and no water, considerable changes occur at temperatures ranging from 500° to 550°, for halloysite (curve *II*) molecules of crystallisation water are liberated at temperatures up to

150° (the first upward inflection of the curve) and hydroxyl ions are liberated at temperatures between 450° and 500° (the second higher inflection). Upon losing its hydroxyl ions, the crystal lattice in these minerals breaks down and the refractive index falls sharply, as shown by X-ray examination.

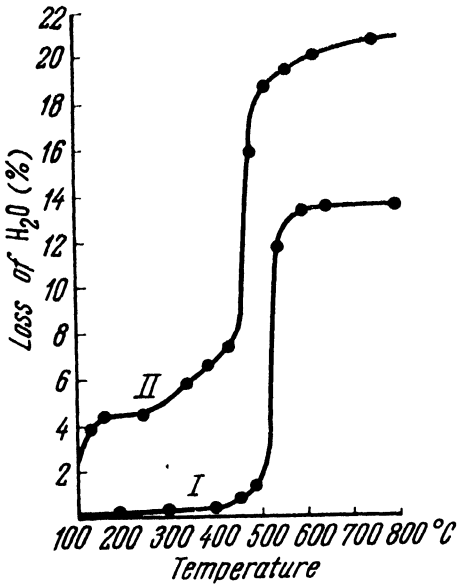


Fig. 32. Dehydration curves for kaolinite (*I*) and halloysite (*II*).

Chemical analysis is relatively laborious and expensive. Therefore, full chemical analyses are used only when a new variety or a new mineral is found which with regard to a number of properties differ from those already known, or when it is necessary to determine the variety of a mineral of a variable composition, or finally, when the mineral is one of the rare compounds for which very few full chemical analyses have been made, etc.

The minimum quantity of a pure uncontaminated substance required for the chemical analysis is 1-2 g, a quantity which is not always available, especially when the mineral is a rare one or is disseminated in rocks and ores as fine crystals or grains.

If the test mineral occurs as small crystal druses in cavities, it is first extracted by some method, e.g., with a steel needle set into a wooden handle. The mass thus obtained is carefully sorted with the aid of the same needle under the binocular lens, so as to collect the mineral in a quantity sufficient for chemical analysis and other tests. If the mineral is disseminated in a rock in a considerable quantity, the whole piece of rock is repeatedly crushed and screened each time through a sieve of 0.5 to over 1.0 mm mesh (depending on the size of the impregnated mineral grains). The mineral in question is similarly hand-picked under the binocular lens.

In the case of accessory, i.e., most sparsely disseminated, minerals, mechanical concentration methods have to be used. These methods are based either on the differences in specific gravity (gravity concentration), magnetism (magnetic separation) or upon the reaction of the mineral with flotation reagents (flotation), electricity (electrostatic methods), etc.

The simplest of the numerous gravity concentration methods consists in separating the mineral grains in heavy or viscous liquids (methylene iodide, bromophorm, etc.). In large quantities a mineral may be conveniently concentrated either in laboratory-type hydraulic classifiers consisting of a cylindrical glass tube in which water rises in a spiral stream, or on small laboratory-type concentration tables. Prior to

concentration in these devices, the crushed material is graded into several sizes on specially selected screens. Heavy minerals are roughly graded by washing the crushed material in a prospector's pan or trough.

Earthy finely dispersed masses are subjected to elutriation in glass jars or separated into fractions of different specific gravity on a centrifuge filled with a liquid or viscous medium.

Chemical analysis of the test material should be preceded by spectral analysis in order to find out what chemical elements the mineral contains in general and which can be determined by chemical analysis. It should be noted that these preliminary spectrograph determinations are made quickly and yield certain quantitative ratios of the elements.

The data of a complete chemical analysis in percentages by weight have to be recalculated in terms of atomic (molecular) quantities, which is necessary for deducing the chemical formula of the mineral. For this purpose, the quantities by weight obtained for each element (or oxide) are divided by its atomic weight ("molecular weight" of an oxide)*. The quotients indicate the ratio of the elements (or oxides) entering into the composition of the mineral. Due to the limited accuracy of analyses or to some other reasons, the proportions of the constituents obtained by chemical analysis are never exact multiples. Two examples are given below.

(1) Chemical-analysis data for bournonite (Nagolny ridge):

	Weight percentages	Atomic weights	Atomic proportions	Relative amounts
Pb	42.75	207.2	0.204	1
Cu	12.77	63.6	0.201	1
Sb	24.76	121.8	0.206	1
S	19.40	32.0	0.606	3
Total	99.68			

Thus the chemical formula of the mineral is $PbCuSbS_3$.

(2) Chemical-analysis data for rhodonite (Kyzyl-Tash, the Southern Urals):

	Weight percentages	Molecular weights	Molecular proportions		Relative amounts
SiO_2	46.06	60.1	0.767		1
Al_2O_3	0.11	101.9	0.001		—
Fe_2O_3	nil	—	—		—
FeO	1.83	71.8	0.025		
MnO	44.76	70.9	0.630	0.772	1
CaO	6.59	56.1	0.117		
Total	99.35				

* Atomic weights are taken from the periodic table. Molecular weights of oxides are the sum totals of the atomic weights of the elements, e.g., for SiO_2 it will be $28.1 + 2 \times 16.0 = 60.1$.

The chemical formula of the mineral may be written as follows: (Mn, Ca) $O \cdot SiO_2$ or (Mn, Ca) SiO_3.

In some cases it is not possible to collect a mineral for analysis so that it would be absolutely free of impurities. Provided the quantity of the impurities is small and the mineral composition is known, the calculation of the chemical composition from the data of the chemical analyses has to be done approximately, with reference to the results of microscopic examination. If the impurities are considerable, the recalculations of the mineral composition will not be always accurate.

Spectral analysis has come into such wide use by mineralogists at the present time that in many cases it has replaced the blowpipe method, especially in the laboratory. This method of determining the chemical elements in a mineral depends on the property of each element to emit, when heated, rays of a specific wavelength which are measured with a spectroscope. The main advantages of spectral analysis are the accuracy and speed with which metal cations in the mineral are determined, a very important point when dealing with such rare metals as tin, molybdenum, indium, germanium, gallium, cadmium, etc. Furthermore, techniques have been devised to determine approximately the relative amounts of a number of metals. The fact that a few milligrams of a material are enough for spectral analysis is another major advantage of this method.

X-ray-spectral (X-ray-chemical) **analysis** is based on the fact that when a mineral is placed on the surface of an anticathode and exposed to cathode radiation, it emits X-rays of definite wavelengths corresponding to each of the elements present in the mineral. This procedure is similar to spectral analysis. It is important, however, that the voltage applied to the X-ray tube electrodes should be high enough to induce visible rays peculiar to each particular element. X-ray spectral analysis is best used for quantitative determination of the rare earths (Y, Nb, Ta, Hf, Re) in minerals, since the determination of these elements by conventional chemical methods is a very laborious proposition.

The use of luminescence. Some minerals glow or become luminescent when heated (e.g., fluorite), pounded, occasionaly when dissolved (and also during crystallisation of certain compounds) and, finally, when exposed to ultraviolet, cathode and other rays of short wavelengths. The last case mentioned is the most important for mineralogists.

Luminescence can be observed only in the dark*. Minerals possessing this property fluoresce on exposure to ultraviolet or other rays and appear to be coloured, sometimes very brightly. The true nature of luminescence still remains obscure. One thing is clear, however, namely that due to some kind of temporary disturbances of the electrostatic equilibrium within the crystal structure, the exciting invisible

* Ultraviolet rays are emitted by a mercury-quartz lamp or a spark gap, and cathode rays by cathode-ray tubes using either a hot or cold cathode. In the latter case luminescence appears in a vacuum.

light of short wavelength is transformed into visible reflected light of greater wavelength. More minerals luminesce in cathode rays than in ultraviolet rays.

In this way it is most easy to detect, in a rock, mineral impregnations which the eye often misses. Thus upon exposure to ultraviolet rays such an important mineral as scheelite ($CaWO_4$) glows brightly with beautiful blue (more rarely greenish) tints which distinguishes it from other minerals; diamond will fluoresce with a light-blue or yellowish-green colour, fluorite (CaF_2) produces a bright blue glow, etc. Very spectacular is the fluorescence displayed by uranium minerals, bitumens of different composition, etc.

This method of detecting minerals is not foolproof. Some varieties of scheelite or diamond do not respond at all to ultraviolet or cathode rays. Other minerals are luminescent because of infinitesimal inclusions of foreign matter. It is known that in artificial luminescent compounds the colour of luminescence changes when admixtures of different composition are present in the substance. The colour may be extinguished altogether (e.g.,the glow caused by the presence of copper is extinguished by bismuth). Interesting, though not as yet fully understood, is the fact that the same mineral from different deposits produces a glow of a different colour (e.g., calcium carbonate).

Pan test is based on the following principle. The weathering of rocks on the earth's surface leaves weathering products consisting of chemically inert minerals such as quartz, magnetite (Fe_3O_4), zircon ($ZrSiO_4$), tourmaline, rutile (TiO_2), occasionally cassiterite (SnO_2), gold, platinum, etc. These minerals are transported by running water and accumulated as placers in river valley deposits and along marine coasts. Washing the samples of these loose sediments by simple equipment (a pan, a trough, a trommel, a gold washer) yields a concentrate of the heaviest minerals, which is appropriately called *heavy concentrate.*

Prior to the identification and quantitative analysis of minerals in heavy concentrates, an average sample (10 to 20 grams by weight) is graded by grain sizes with standard sieves. Next, a magnetic fraction is extracted from each fraction through paper with a conventional horseshoe magnet. The non-magnetic remainder is divided into fractions according to magnetic permeability with an electromagnet (at different currents), after which the minerals are further separated according to specific gravity in heavy liquids (bromophorm, Thoulet solution, etc.) by means of either separating or conventional chemical funnels.

After being still further separated by external features (grain forms, transparency, lustre, colour, hardness, etc.), the fractions are subjected to binocular examination, and then, the optical constants are determined in immersion liquids with appropriate refractive indices. If necessary, qualitative microchemical tests, spectrographic, fluorographic, and other analyses are performed. Microscopic examination of opaque ore minerals in reflected light requires the preparation of polished sections using bakelite varnish or other bonding material.

A quantitative determination of all the minerals composing a heavy concentrate is very laborious (involving the weighing of both the total and the individual samples, the calculation of the percentage by volume and the specific gravity of each mineral, etc.). Therefore the usual practice is to calculate the most important components of the concentrate, such as cassiterite (SnO_2), scheelite ($CaWO_4$), etc.

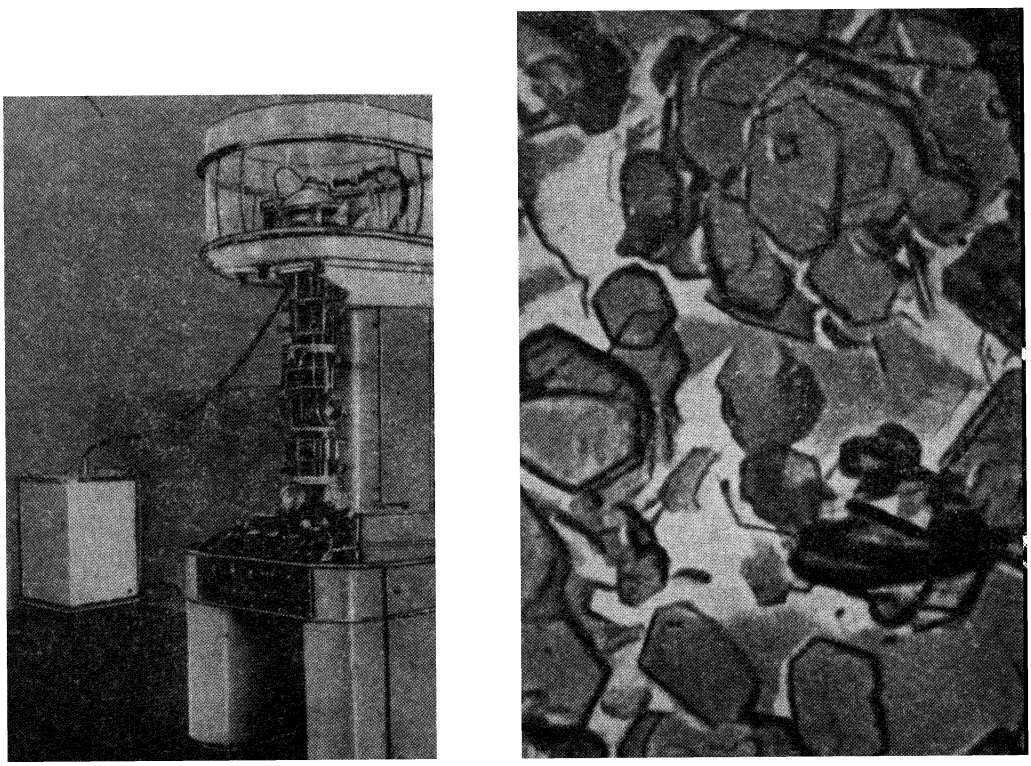


Fig. 33. Left – general view of electron microscope. Right – electron photograph of kaolinite precipitated from a suspension. ×2500.

The same procedure is followed for heavy concentrates which are obtained from crushed samples of massive rocks in order to find out whether they contain minerals which may be useful as guides to ore deposits. This investigation is usually carried out during geological surveys. The study of haloes of dispersion of valuable components in loose deposits and bedrocks, as well as of the transportation of heavy minerals by running water is highly important in prospecting for mineral deposits.

Electron microscope. The resolving power of a microscope largely depends on the wavelength of the incident light (the shorter the waves, the smaller the particles that can be discerned). The resolution of a conventional optical microscope is relatively moderate: in white light the smallest particles that can be seen are those of 0.5 μ in diameter. Microphotography in ultraviolet light, which is shorter in wavelength,

using immersion objectives with large apertures, results in reducing the minimum size of the particles resolved to 0.2μ. And finally, using an ultrashortwave beam of electrons (in the electron microscope) makes it possible to discern particles as small as 0.002μ. Thus with the aid of an electron microscope it is possible to investigate specks of smoke and dust precipitated on metal gauze, clayey matter suspended in water (for this purpose a drop of the suspension is dried on a slide), and other finely dispersed matter.

Unfortunately, electrons have limited penetrating ability, (particles of a material which are transparent to rays of light are usually opaque to electrons). It is impossible, therefore, to get anything but a general idea of the shape and size of the particles which are studied under the electron microscope (Fig. 33).

Compact samples may be studied by the "method of replicas", i.e., by obtaining from them thin colloidal, quartz-polystyrol, or other films which reproduce all the finer relief characteristics on the faces of crystals or of the polished planes of minerals, etched or unetched.

Experimental investigation (both chemical and physico-chemical) is mainly concerned with the artificial preparation of compounds under laboratory conditions, which correspond in composition and form to natural minerals. In this way it is sometimes possible to obtain compounds which both in form and composition exactly reproduce those occurring naturally and thus shed light on the conditions of the formation and crystallisation of minerals in nature. Hence the interest with which mineralogists follow the research and experimental work done at chemical and physico-chemical centres, conducting research into the problems of utilisation of economic minerals.

Chapter IV

FORMATION OF MINERALS IN NATURE

1. GENERAL

Formation and growth of crystal phases. A crystalline solid may form in different ways: (a) by the crystallisation of *liquids* (melts or solutions); (b) by the deposition of crystals on walls of openings from the *gaseous* products of sublimation, and (c) by the recrystallisation of *solids* (e.g., colloids). The crystalline formations occurring in nature are overwhelmingly the products of crystallisation of silicate melts and aqueous solutions. This includes the enormous masses of igneous crystalline rocks, the vast majority of commercial mineral deposits, and the crystalline precipitates of saline basins.

Theoretically the crystallisation of a cooling melt should begin at a definite temperature corresponding to the melting point of a given substance. In the same way a solution should crystallise at the point when the solvent is saturated with the solute. Actually, however, the crystallisation of liquid phases begins at certain *supercooling* or *supersaturation**.

The degree of supercooling or supersaturation required for the crystallisation to begin depends on the chemical composition and, to some extent, on pressure. Pressure variations play a much more important role when the crystals are formed out of condensing vapours.

The process of the growth of crystals in both a supercooled melt and in a supersaturated solution is exactly the same. The initiation of crystals may be *compelled*, if some fragments and specks of a solid which act as primers, due to their crystallochemical properties, are already present in the liquid; it may also be *spontaneous*, in the absence of any primers in a supersaturated solution or supercooled melt.

In the case of spontaneous crystallisation at different points of the melt or solution there appear so-called *crystallisation centres* or crystal seeds. At the beginning of crystallisation (e.g., in a single-component liquid), regular crystals will grow unimpeded around the crystallisation centres until they impinge on one another, thus obstructing the

* Both in nature and in the laboratory the supercooling of a liquid is quite a common phenomenon. On the other hand, the superheating of a crystal substance (beyond the melting point) is very difficult to obtain. This is equally true of the supersaturation of a solution and the retention of a soluble solid phase in a dilute solution.

further development of crystallographic forms (Fig. 34 *a* and *b*). Further crystallisation takes the form of struggle for the remaining space, and the end product is an aggregate of irregularly-shaped crystal grains (Fig. 34 *c* and *d*). Sometimes the grains show a crystalline zonality, as evidence of their gradual growth.

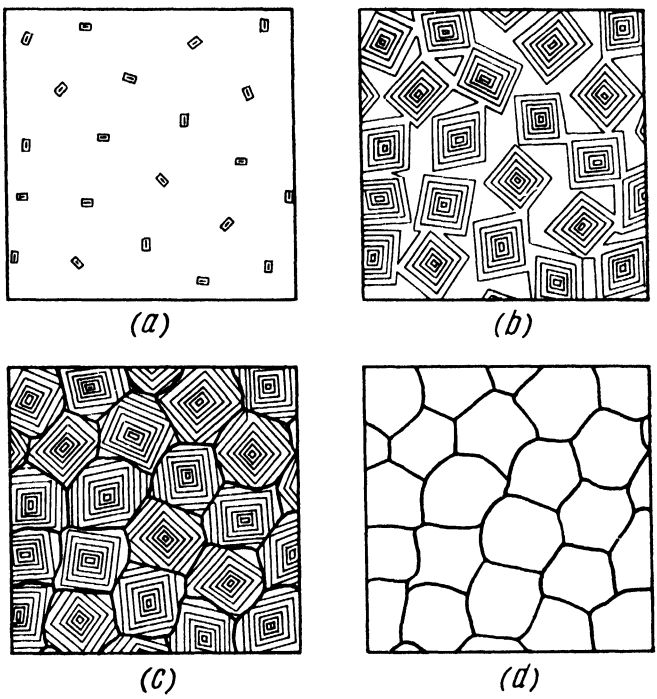


Fig. 34. Diagrammatic representation of the crystallisation of a homogeneous liquid.

There is a direct relationship between the degree of supercooling or supersaturation and the number of crystallisation centres which spontaneously develop when solidification begins: the *more* supercooled or supersaturated is the liquid, the *greater* will be the *number* of crystallisation centres in a given volume per unit of time (Fig. 35), and hence the smaller will be the crystal grains on final solidification (Fig. 36).

If crystallisation begins at relatively low supersaturation of the solution k_1 (Fig. 35), the number of developing crystal nuclei will be comparatively small and the resulting aggregates will be relatively coarsely crystalline (Fig. 36 *a*). If crystallisation begins at greater supersaturation (or supercooling), e.g., at k_2 (Fig. 35), the natural result will be finely-crystalline aggregates (Fig. 36 *b*). Upon crystallisation of an extremely supersaturated solution, cryptocrystalline substances or colloids will be formed.

According to experimental data, initiation of crystals in a liquid depends on a variety of factors, such as the chemical character of the material, the presence of impurities which may accelerate or delay the

development of crystal nuclei, mechanical influences (shaking of the solution or its friction against walls of the vessel), occasionally the effects of light or sound.

Experiments also show that concentration currents develop around crystals growing in an unrestricted environment: where the supersaturated solution contacts the crystal it imparts to the latter the excess solute, becomes lighter and rises, yielding place to fresh portions of the supersaturated solution. The more supersaturated is the solution, the quicker is crystal growth.

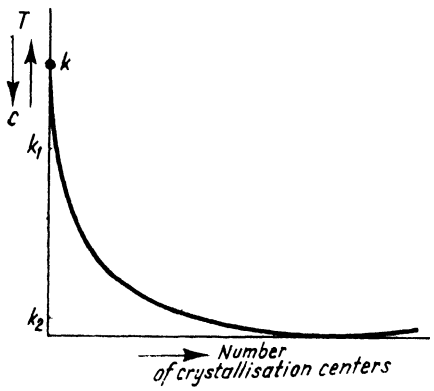


Fig. 35. The dependence between the number of crystallisation centres(n.cr.c.) and supercooling or supersaturation.
T – temperature; *C* – concentration.

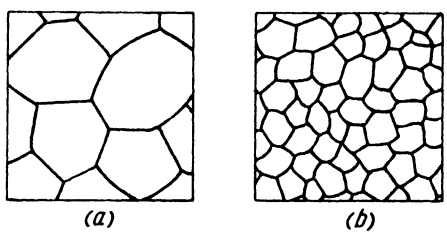


Fig. 36. Influence of the number of crystallisation centres on aggregate structure.
a – coarse-grained aggregate; *b* – fine-grained aggregate.

As long as the conditions of growth for each crystal face remain unchanged from the moment of initiation the shape of the crystals does not change during growth. However, the rate of growth of each crystal face is often uneven, which results in fewer faces. Dissolved impurities also greatly affect the shape of the crystals. Thus sodium chloride, which normally crystallises as cubes, will crystallise in octahedra in solutions containing $CaCl_2$ and $MgSO_4$.

Rapid crystal growth produces irregular shapes. This chiefly occurs when the uniform influx of the feed solution is disturbed (e.g., in case of an increase in the viscosity of the environment, in colloidal solutions, etc.). In this case the best supplied are the apexes and edges of the growing crystals, i.e., the areas of crystal structures least saturated with valencies. This results in the curving of the crystal faces and the formation of funnel-shaped indentations and not infrequently to the overgrowth of crystals on one another (at their apexes). As a result, *crystalline skeletons* or *dendrites* with an ordered arrangement of branches are formed. Often the branches grow thicker at the ends with the development of more regular and larger crystal individuals. This is probably due to the decreased supersaturation in the adjoining areas and hence to the more normal conditions for crystal growth.

Crystals may grow not only in liquid media, i.e., through the diffusion of supersaturated portions of the solution to the crystal, but also in air or gaseous media, when fed by the saturated solution through

capillary channels. The following experiment is a good illustration. If a hygroscopic cotton thread is immersed in a saturated solution of table salt (Fig. 37), the part of the thread exposed to air will develop a crystalline aggregate fed by the saturated solution rising by capillary action. In the air, the solution becomes strongly supersaturated through evaporation, which results in the crystallisation of the solute on the cotton thread.

If the solvent evaporates slowly, well-developed crystals may form in this way. The student may remember seeing ice needles growing from damp soil after a clear frosty night. Similar needles grow in the air from slowly drying damp powders of salts which are readily soluble in water, e.g., calcium chloride. This may be the mechanism of the formation of long acicular crystals of many minerals found in cavities.

Crystals may also form in a gaseous medium without being fed by a liquid solution, when a substance transmutes directly from a vapour into a solid at certain temperatures (below the melting point) and pressures. One example is the formation of snow flakes in the air in the form of stellate crystals. Another example are the various minerals deriving from volcanic sublimation.

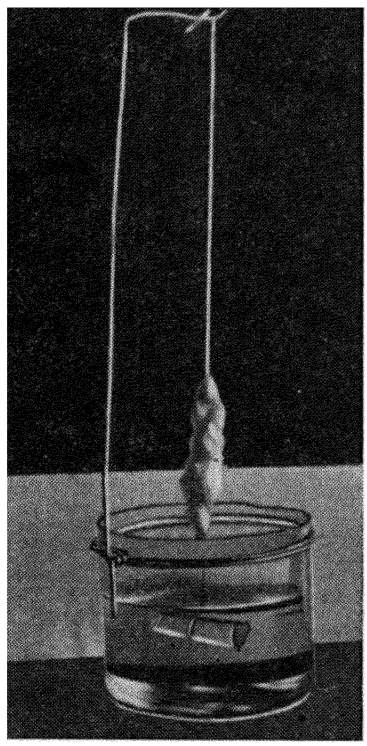


Fig. 37. Crystalline formations of NaCl in the air on a thread immersed in a saturated solution. The thread is weighted with a glass rod.

Frequently, crystals and crystal grains contain tiny inclusions of foreign matter (solid, liquid and gaseous). These inclusions for the most part make the crystals appear dim or opaque. They can be readily seen upon microscopic examination in polished sections. Only when a mineral is uniformly opaque it is rather difficult to discern the liquid or gaseous inclusions.

The study of the spatial distribution of these foreign substances shows that they were apparently mechanically entrapped by the rapidly growing crystals. Inside the crystals they are often oriented in crystallographic directions. Examples of this are the inclusions of volcanic glass (solidified magma drops) in crystalline-banded plagioclases, mother liquors of the salts of K, Na, Ca, etc., gas bubbles which are usually mixed with a liquid in dim crystals of quartz, calcite, topaz, and other minerals.

It is curious that gas-liquid inclusions, when heated to a definite temperature, usually become a homogeneous liquid (the gas dissolving

in the liquid) and, when cooled, the gas bubble separates again. This is important because in this way one may determine the approximate temperature at which the mineral crystallises and captures the minute drops of the solution.

Some of the gas-liquid inclusions may even contain a third, solid phase (e.g., tiny NaCl crystals). On heating these crystals are the first to dissolve in the liquid, followed by the gas bubble.

In addition to primary gas-liquid inclusions, the crystals may have later, secondary inclusions which are associated with "healed" cracks in the crystals. It will be noted that in the secondary gas-liquid inclusions the gas bubbles in the drops of liquid will disappear upon heating earlier than in primary inclusions. On further heating the crystal mass will decrepitate in either case (so great is the pressure of the expanding liquid inclusions).

If a solution impregnating a rock enters into an exchange decomposition reaction with it, this, as a rule, results in neocrystallisation involving either all of the rock or some of its constituents. This process known as *replacement* or *metasomatism*, is exemplified in the replacement of calcite by gypsum upon reaction with water containing sulphuric acid:

$$\underset{\text{calcite}}{CaCO_3} + H_2O + H_2SO_4 = \underset{\text{gypsum}}{CaSO_4 \cdot 2H_2O} + CO_2$$

or in the replacement of sphalerite by covellite upon reaction with copper-sulphate solution:

$$\underset{\text{sphalerite}}{ZnS} + \underset{\text{solution}}{CuSO_4} = \underset{\text{covellite}}{CuS} + \underset{\text{solution}}{ZnSO_4}$$

In the case of selective metasomatism (when only some of the minerals in a rock are replaced) the resulting mineral, which retains not only the external shape but sometimes also the peculiar internal structure of the original mineral, is called a *metasome*. In many cases when the constituent replaced is a crystal there develops a *pseudomorph*, i.e., a crystal form which is quite foreign to the new mineral. When organic remains, such as wood, are replaced by colloids like opal or iron sulphides, their peculiar structure often remains intact.

Quite common in nature are well-formed crystals developed through metasomatism in solid environments (rocks). Such formations, or *metacrystals*, occur in a limited number of minerals. An example are the well-formed cubic crystals of pyrite in schists, marbles and other rocks. Metacrystals often contain remnants of unreplaced minerals of the enclosing rock. Not infrequently they occur along hardly detectable hair cracks in rocks, which definitely points to their later origin.

Recrystallisation and other transformations of minerals in *solid* media occur as a result of material changes in the physico-chemical equilibrium, in particular in conditions of so-called regional metamorphism.

Solution and decomposition of minerals. It has already been stated that many minerals undergo diverse transformations because of changes in the environment, sometimes dissolving completely or decomposing into insoluble products of chemical reactions.

The beginning of *solution* is easily detected in individual crystals by the following characteristic features:

(1) whereas during the growth of a crystal it is the apexes and edges that tend to grow faster, during solution they also dissolve faster, and therefore the crystal becomes somewhat rounded;

(2) whereas during the growth of a crystal the slowly growing faces of a crystal are the most stable, on solution of a crystal fragment or a sphere made out of a crystal the first to appear will be the faces that dissolve most rapidly;

(3) the slowly growing faces usually have brilliant and smooth surfaces; on solution the slowly dissolving faces often appear lustreless;

(4) at the initial moments of solution, the faces often develop very shallow polyhedral solution pits or etch figures.

Decomposition of minerals in nature, either complete or incomplete, is mainly associated with oxidation and reduction processes. This is especially true of minerals containing elements which under natural conditions are capable of forming several ions of different valencies (e.g., Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{3+}, Mn^{4+}, S^{2-}, S^{6+}, etc.).

When a mineral, which originally contained lower valency cations, finds itself in oxidising conditions (e.g., the weathering zone of rocks and ores) these cations will naturally tend to pass into ions of higher valency. During this process the cations diminish in size with the subsequent disintegration of the crystal structure. Thus, in an oxygen- and water-rich environment, the divalent iron cation in FeS (pyrrhotite) readily becomes trivalent with the formation of poorly soluble iron hydroxides, whereas the divalent sulphur anion oxidises into a hexavalent cation with the formation of a complex $[SO_4]^{2-}$ anion, which, on reacting with hydrogen ions, finally yields sulphuric acid, which goes into solution. In this way, a new substance with completely different properties is formed in place of pyrrhotite. In the same way, a carbonate of divalent manganese ($MnCO_3$) readily forms hydroxides of tetravalent manganese.

If iron and manganese hydroxides, in the course of geological processes, find themselves deep in the earth's crust where a reducing environment prevails, the higher valencies of the cations of elements often change into lower valencies, which is accompanied by the dehydration of the compounds. New minerals are formed under these new conditions: hematite (Fe_2O_3) or magnetite ($Fe{\cdot\cdot}Fe_2{\cdots}O_4$), braunite ($Mn{\cdot\cdot}Mn{\cdot\cdot\cdot\cdot}O_3$), hausmannite ($Mn{\cdot\cdot}Mn_2{\cdots}O_4$), etc.

Many examples of this kind will be cited in Part Two.

Generations of minerals. The generations of a mineral, as the term implies, are its differently aged formations in a particular mineral association, differing also in size, appearance, and specific features of

chemical composition. Observations of the occurrence of minerals, especially in ore deposits, often point to the existence of several generations of the same mineral developing within a single stage of mineral genesis. In some instances (Fig. 38) younger generations of finer crystals overgrow older and larger crystals of the same mineral. In other instances, one observes older coarse-grained generations and younger fine-grained crystalline formations along thin cracks of other minerals, or, as micro-inclusions discernible only under the microscope, etc. Detailed microscopic examination of ores shows that almost *every ore-forming mineral* comprises *several generations*, which indicates the complexity of the processes of ore-genesis. This complexity must not be ignored in studying the paragenesis of minerals.*

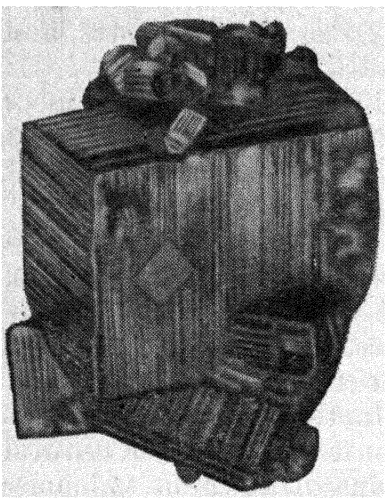


Fig. 38. Two generations of pyrite (FeS_2) crystals.

Mineral aggregates. The crystallisation and solidification of a solution or melt gives rise to a mixture of intergrown grains called a mineral aggregate.

Aggregates may be *monomineral* consisting of crystal grains of a single mineral (e.g., marble or magnetite) and *polymineral*, consisting of several minerals of different properties and composition (e.g., granite or copper-zinc sulphide ore).

Mineral aggregates occur in a wide variety of forms and structures, some of them being so characteristic that they are designated by special terms. The main morphological feature of a mineral aggregate is the degree of its crystallinity. With regard to crystallinity, minerals fall into two clearly distinct groups: (1) phanerocrystalline aggregates, and (2) cryptocrystalline and colloidal masses.

The principal types of mineral aggregates are the following:

1. *Granular aggregates* composed of crystal grains sometimes occurring together with well-developed crystals of some minerals. This type is the most widespread in the earth's crust. Examples: holocrystalline igneous rocks, numerous sulphides and other ores.

With regard to grain size, aggregates are classed as (1) coarse-grained, with grains over 5 mm in diameter; (2) medium-grained, with grains

* Generally speaking, the term *generation* applies not only to individual minerals, but also to whole mineral complexes such as rocks and ores. Thus, veins of diabases or quartz porphyrys not infrequently have several generations as the intersections of rock veins show. Another example: veins of coarse-granular quartz containing coarsely crystalline molybdenite (MoS_2) may include more recent generations of molybdenum ores (occurring as veinlets or cementing material between the fragments), i.e., fine-granular quartz and abundant cryptoscaly molybdenite.

1 to 5 mm in diameter, readily distinguished by the naked eye; and (3) fine-grained, with grains less than 1 mm in diameter.

The structure of cryptocrystalline aggregates can be established only under the microscope in thin polished sections.

The shape of the grains comprising the aggregate is reflected in the morphological features of the aggregate as a whole. If an aggregate consists of roughly equidimensional grains, it is simply called *granular*.

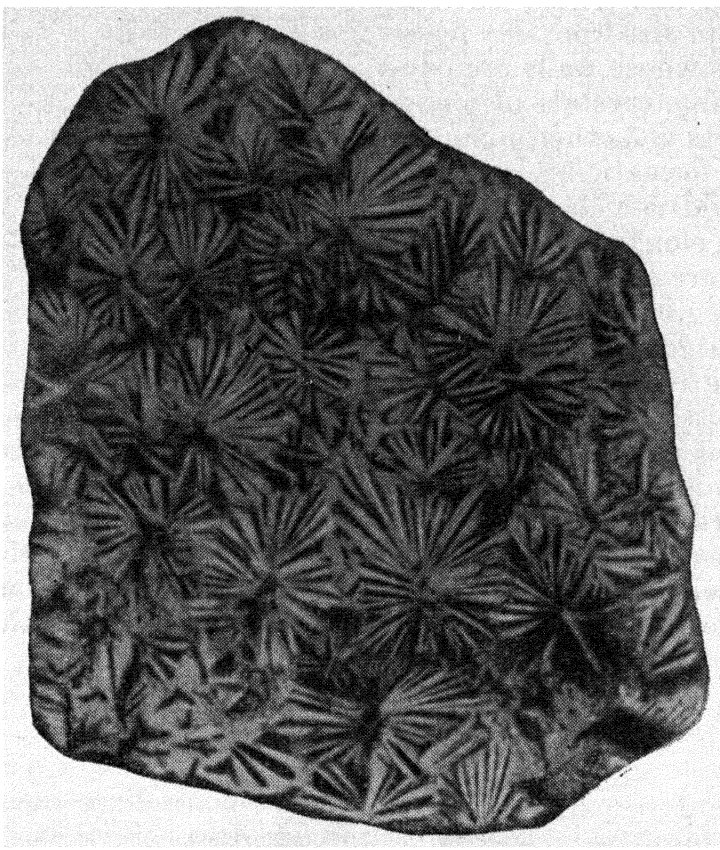


Fig. 39. Radially-fibrous aggregates of pyrophyllite.

If the grains are lamellar in habit, the aggregate is called *foliated* or *scaly*, depending on the size of the grains. Aggregates with grains elongated in one direction, sometimes radiating or diverging (Fig. 39) from a common centre are called *columnar*, *acicular*, or *fibrous*. Also widespread are aggregates composed of minerals of different forms, such as mica schists with isometric garnet crystals, granular masses of quartz with columnar tourmaline crystals, etc. (Fig. 40).

An aggregate may be compact or friable. An example of the latter are crystalline formations at the bottom of drying salt lakes.

2. *Druses* are intergrowths of well-developed crystals on the walls of cavities. An example are the common druses of quartz crystals (Fig. 41). Druses are interesting not only crystallographically but also because they often slow the sequence of segregation of different minerals

crystallising from the last portions of a solution.

The very fact that druses contain well-developed crystals indicates that they have formed in free space, that is, in some primary cavities, hollow cracks, fractured rocks, etc. These cavities may range in size from tiny pores to big caves whose walls are covered with large crystals of transparent quartz and other minerals.

Mineral formations, in which the crystal individuals are in close contact and elongated parallel to each other, are referred to as *comb* or *drusy* aggregates. Evidently, the close contact between the crystals forming on the walls of cavities allowed them to develop only in a direction perpendicular to the walls. This group also includes *crystalline crusts*, composed of fine, closely intergrown crystals.

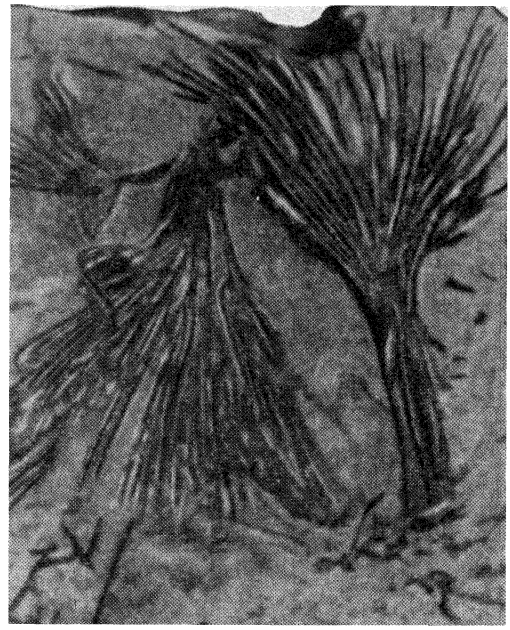


Fig. 40. Sheaf-like tourmaline aggregates in sericite-chlorite schist.

It has been demonstrated that in these cases the numerous original crystal nuclei develop in random directions. However, in the process of growth, fewer and fewer crystal individuals will survive in the competi-

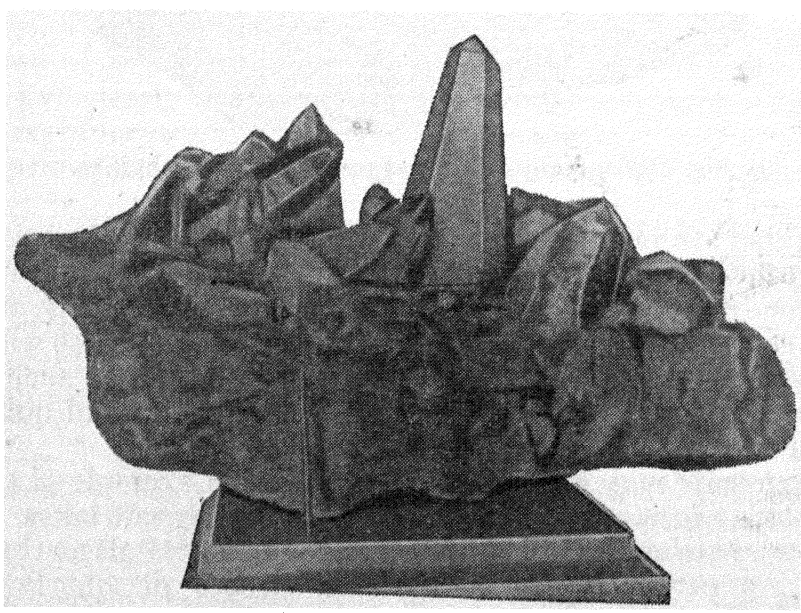


Fig. 41. Druse of quartz crystals.

tion for available space, and it will be those growing perpendicular to the surface of initial crystal that will have the greatest chance of survival ("geometrical selection"). If the surface is concave, the result will be converging radiated aggregates. If the surface is convex, diverging acicular or columnar crystalline masses will form.

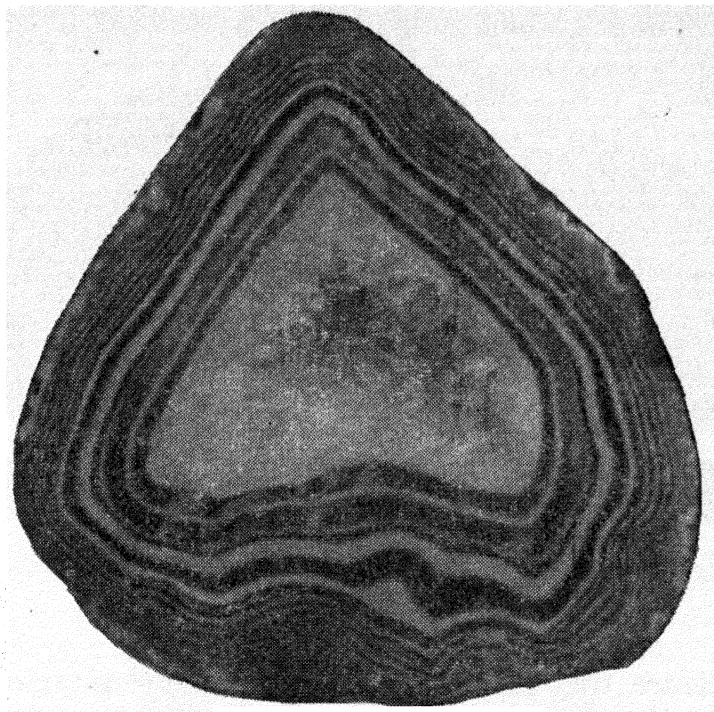


Fig. 42. Geode.

3. *Secretions* are formed when an irregularly-shaped, but generally spherical cavity is filled with crystalline or colloidal material. A peculiar feature of many secretions is a concentrical deposition of mineral matter from the walls of a cavity towards its centre. The layers thus deposited frequently vary in colour and sometimes in composition.

Small openings or cavities are usually completely filled with mineral matter. Sometimes the central part is filled with radially-fibrous aggregates of some mineral, e.g., zeolite. Large cavities often have a hollow centre with druses or sinter formations lining its walls.

Smaller secretions (up to 10 mm in diameter) are termed *amygdules*, while bigger ones are called *geodes* (Fig. 42).

4. *Concretions* are globular or irregular spherical formations and nodules (Fig. 43) which develop in unconsolidated sedimentary rocks, mostly in clays, sands, and in the earthy products of rock weathering. They vary widely in size, from a few millimetres to tens of centimetres and sometimes even metres in diameter. As they expand and coalesce, the concretions form large bodies of complex configuration.

Often, though not as a rule, concretions develop around foreign bodies, usually organic remains. In polished sections the sandy concretions of phosphorite and marcasite show a banded arrangement of sand particles which corresponds to the banded structure of the rock as a whole. This shows that the concretions were formed, at least partially, later than the enclosing rock. In all probability they first appeared as colloidal clots or gels which subsequently crystallised. When fractured

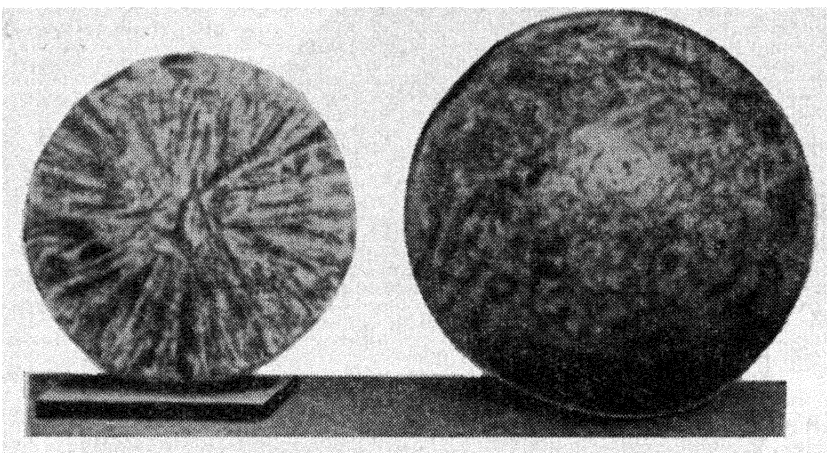


Fig. 43. Phosphorite concretions (left-hand concretion shown on fracture).

across the centre, they often display a radially-fibrous texture (Fig. 43). Occasionally the mineral mass displays indistinct concentric banded structure.

Thus, the origin of concretions differs materially from that of secretions. In contrast to the latter, concretions grow out radially from a centre.

The minerals found most often as concretions are phosphorite, pyrite, marcasite, sometimes siderite, barite, etc.

5. *Oölites* form in almost the same way as concretions. They also are spherical formations, but somewhat smaller in size (from tenths of a millimetre to 5-10 mm), developing in an aqueous environment around suspended foreign matter, such as sand particles, fragments of organic remains, and even gas bubbles. A characteristic feature of oölitic formations is their distinct, rather regular concentric banded, occasionally conchoidal, structure. Formations analogous in shape, but lacking concentric banding are so-called pseudo-oölites .

Recent calcareous oölites are formed from suspended matter in running water, and when they attain a certain size, they settle to the bottom. Sedimentary rocks composed of cemented pea-sized oölites are called pisolites (Fig. 44).

6. *Sinter forms* of minerals originate from colloids or gels. Like crystal druses, they are found in cavities. When slowly migrating colloidal

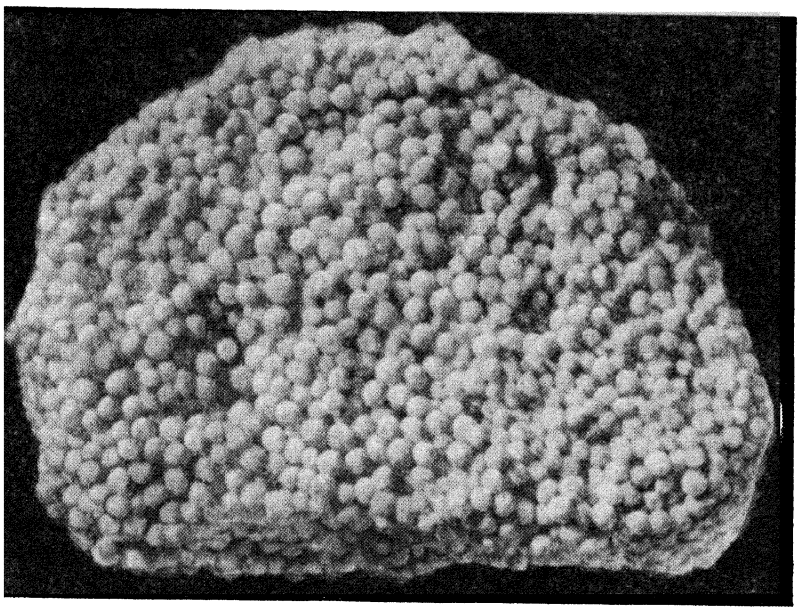


Fig. 44. Oölitic concretion of $CaCO_3$.

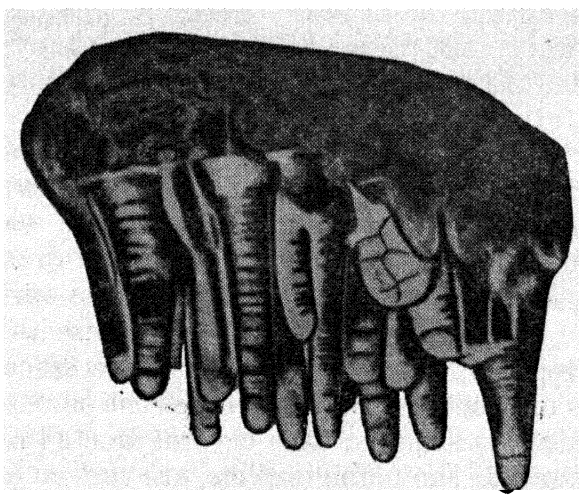


Fig. 45. Limonite stalactites.

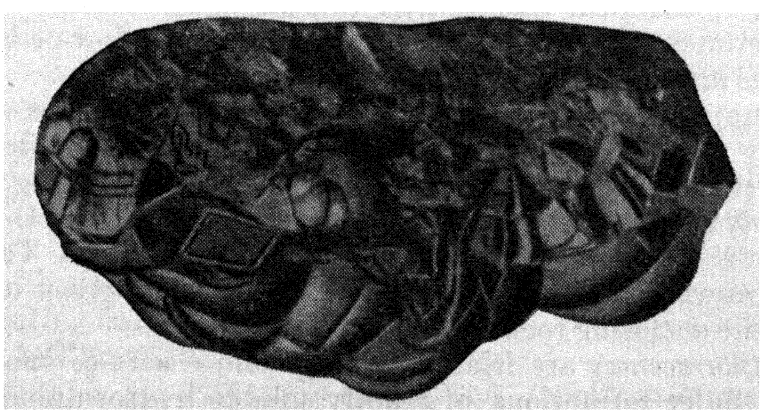


Fig. 46. Reniform hematite mass.

solutions enter a cavity, they coat its walls. Gradually losing water (dispersion medium) which evaporates into the empty space inside the cavities, the solutions thicken and under the action of gravity form *stalactitic* (Fig. 45), *reniform* (Fig. 46), *botryoidal*, and other shapes which finally solidify. Falling colloidal drops may deposit tapered *stalagmites* on the floors of cavities.

Such formations range widely in size, from microscopic to huge, pillar-like stalactites and stalagmites of aragonite and calcite ($CaCO_3$) in large caves.

Most diverse minerals may appear in the forms of sinters: iron hydroxides (limonite, goethite), manganese hydroxides (psilomelane group), opal, malachite, gypsum, aragonite, calcite, sulphides of different metals, etc.

Examination of sinter masses (in cross sections) often reveals a concentric zonal structure. This is due to alternation of zones of the same minerals which are differently coloured or possess different physical properties (malachite, limonite, etc.) or much more rarely because the zones consist of minerals of different composition (limonite, chalcedony, and malachite; limonite and native copper, etc.). The differences in the mineral composition of the concentric bands reflect changes in the composition of the solutions which produced the sinter forms.

It has been stated earlier that colloidal formations or gels crystallise rather easily. Since the process takes a different course with different minerals, the resulting crystalline aggregates will also differ in structure. For instance, limonite sinter formations, while fully retaining their external shape, turn into an aggregate of diverging fine fibres of goethite or hydrohematite perpendicular to the surface of the individual concentric layers. Other minerals crystallise into coarser radiated fibrous aggregates, which nevertheless show traces of the original concentric layers on fracture. In this process the smooth surface of sinter formations becomes studded with crystal facets (marcasite).

7. *Earthy masses*, as the name implies, are soft mealy formations in which no crystallinity is detectable even with a hand lens. Usually they are found as crusts or accumulations which are most often the products of chemical weathering. Depending on colour, such masses are sometimes called *sooty* (black) or *ochreous* (yellow or brown accumulations and crusts).

Examples are variously coloured nickel hydrosilicates which occur as earthy mineral formations; sooty manganese hydroxides; ochreous iron hydroxides, and other residual products of weathering.

8. *Coatings and selvages* which sometimes occur as thin films on crystal surfaces may consist of most diverse substances. These include films of brown iron hydroxides on rock crystals; the green or blue selvages on the enclosing rocks of copper deposits, etc.

9. *Efflorescences* are friable coatings and crusts or sporadic moss-like and fluffy formations of readily soluble hydrosulphates or other salts appearing periodically on the surface of ores, rocks, dry soils and

in cracks. They usually disappear during the rainy seasons to reappear with dry weather.

Another type of efflorescences are the very common dendritic growths of manganese hydroxides on the surface of rocks along thin cracks (Fig. 47).

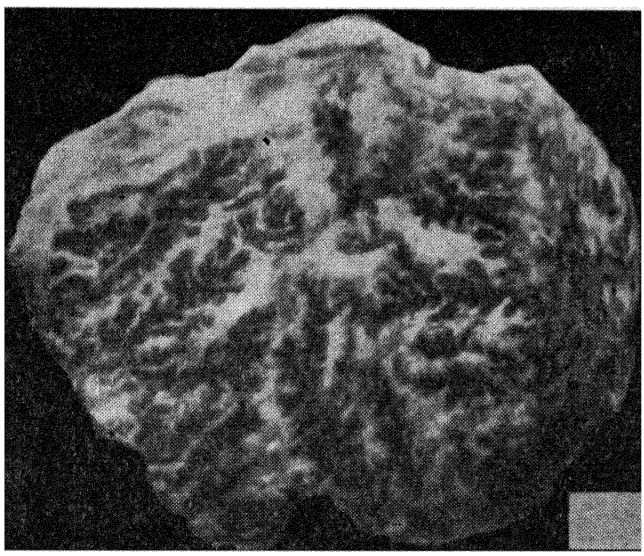


Fig. 47. Dendritic manganese hydroxides on a fissure surface in altered albite rock.

10. *Liesegang rings and spirals.* This term denotes regularly alternating banded formations which result from the intermittent deposition of compounds in the course of diffusion in gels, very similar to the concentric rings and spirals obtained by R. Liesegang (Fig. 48). Essentially, his experiment consisted of the following: microscopic $Ag_2Cr_2O_7$ crystals were formed around an $AgNO_3$ drop on gelatin impregnated with $K_2Cr_2O_7$. The crystals at first moved with the solution, but later as they grew larger, were retained in the gelatin pores and deposited at regular intervals to form concentric rings. Structures of this kind are sometimes found in agates (Fig. 42) and jaspers. Very similar formations develop in finely porous rocks, in the course of weathering processes. Examples are the periodic rings, bands and hyperbolas stained by brown iron hydroxides found in limestones, sandstones, and other rocks. In this case the staining matter apparently is deposited from sols in the form of a gel when the dispersed phase or the electrolyte reaches the critical concentration point. If this process goes parallel with the leaching of a rock, the end result will be concentric conchoidal formations in which bands of compact gel alternate with earthy bands. Ores with alternating bands of sphalerite and ankerite (Fig. 49) or magnetite and calcite belong to this type of formations.

Sometimes, in place of rings and spirals, dendritic formations are found, such as iron and manganese hydroxide inclusions in opal

("moss" agates). They can also be readily reproduced artificially in a gelatinous medium.

Paragenesis of minerals.* This term which was understood as "the simultaneous occurrence of minerals", was introduced into geology in 1849 by Breithaupt. Long before Breithaupt, however, V. M.

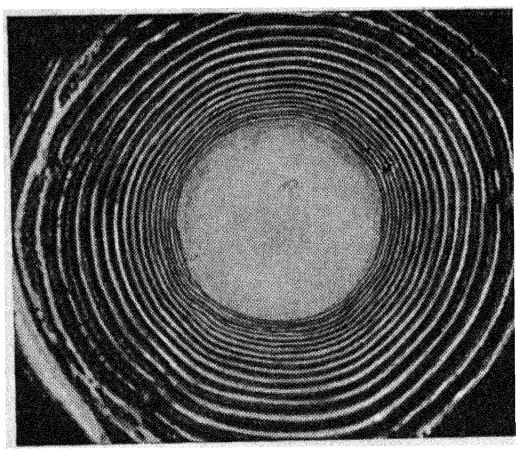


Fig. 48. Liesegang spirals.



Fig. 49. Banded ore.
Dark bands--sphalerite, ZnS; light-coloured bands—carbonate (ankerite).

Severgin (1798) in Russia had used the term "contiguity of minerals", which is another way of saying the same thing. In 1923 Vernadsky coined the term "mineral association" for the simultaneous occurrence of several minerals in the same mineral body, in distinction from the term "paragenesis" to which he attached a different meaning.

He believed that this idea had its beginnings in the observations of early miners who looked for accessory minerals as guides to ores and gemstones. "Though not aware of that, they were in fact studying mineral associations." Thus, it has long been known that galena (PbS) which is often associated with silver, as a rule, occurs together with sphalerite (ZnS). Similarly, in many deposits gold is associated with quartz, and cinnabar (HgS) with antimonite (Sb_2S_3). The vast amount of empirical evidence which has already been collected in this field is a great aid to geological prospecting and exploration.

By "paragenesis" Vernadsky meant "all the mineral associations known for a given mineral or chemical element", and he suggested that this should embrace the mineral bodies in which the given mineral is found, its mineral associations and generations (*History of Minerals in the Earth's Crust*, vol. 19, 1923, p. 153). Unfortunately, Vernadsky

* "Para" is the Greek for near, close to; "genesis" means formation, origin.

did not cite concrete examples to illustrate his concept. Elsewhere in his work, however, Vernadsky stressed the need for "studying the dependences governing the combination of minerals or their paragenesis" (ibid., p. 11). Viewed in this context the problem acquires special interest to mineralogy.

The vast amount of mineralogical data collected in Soviet times in the process of detailed study of various rocks and ores has greatly furthered research in these directions. Soviet scientists have established that definite paragenetic associations, that is, *groups of minerals formed together* in a given mineral body develop in the process of mineral genesis, depending on the physico-chemical conditions and the interaction of solutions with the environment, at each stage of the process. Characteristically, each such group reflects the particular conditions under which the minerals had formed. The following example will illustrate this point.

Often one and the same ore specimen may have among its constituents *two or more groups of minerals which differ in the time of their formation and origin.* Thus limonite (iron hydroxide) and malachite (copper carbonate) often occur together with semi-decomposed copper and iron sulphides (pyrite—FeS_2 and chalcopyrite—$CuFeS_2$). Geological data always show, however, that the sulphides formed earlier under one set of conditions, while the iron hydroxides and copper carbonate formed later under entirely different conditions (in conditions of weathering). The two groups are spatially associated only because they had a common source of the chemical elements entering into their composition (iron and copper). Hence, in this mineral association we have *two groups of minerals differing in the conditions of their formation.*

This approach to mineral associations enables conclusions to be drawn about the *dependences, important both theoretically and practically, governing the alteration of paragenetic associations of minerals with time* and bearing evidence to changes in the physico-chemical conditions in the course of mineral genesis. Soviet scientists developed a geometrical method for the analysis of different mineral associations occurring in nature which makes it possible to reveal many details and facts which generally elude the student when other methods are used.

Knowledge of typical paragenetic associations is very important in mineralogy. Apart from its value as an aid to the identification of minerals occurring together, it is an important guide to economic minerals. Thus, if the easily identifiable minerals pyrrhotite (FeS) and chalcopyrite ($CuFeS_2$) are found in a *basic* magnesial igneous rock, one must look for a third, nickeliferrous mineral, pentlandite, which is not as readily indentifiable but is very important economically.

In nature, minerals occur in most diverse paragenetic associations. This depends not only on the initial composition of the crystallising solutions or the enclosing rocks which react with them, but also on such factors as temperature, pressure, depth of the formation or transformation of the minerals, etc. Some minerals develop at very specific

environmental factors, while others may form under various conditions. Thus gypsum ($CaSO_4 \cdot 2H_2O$) under some conditions occurs in association with chlorides and sulphates in salt beds formed as a result of the drying of salt lakes and lagoons. In other instances it is the product of chemical weathering (in areas with scarce precipitation) in association with iron hydroxides and the argillaceous products of disintegration. Mining experience shows that it disappears quite rapidly with depth. Furthermore, gypsum has been found as crystals in fissures, in decomposed and discoloured lava and igneous rocks in the vicinity of solfataras where it might have derived from calcareous minerals through the action of hot waters containing sulphuric acid, etc.

The diversity of paragenetic mineral associations is often further complicated by the fact that superimposed on a group of minerals formed in one process may be mineral associations formed through other processes, the later minerals not infrequently deriving partly from those of the earlier group. Hence the importance, in such cases, of taking *separate* account of each *group of contemporaneous minerals*, since *each* process of mineral formation, and consequently each group, has *its own* dependences governing its mineral associations. The very fact that one process is superimposed on another is evidence of a change in the physico-chemical equilibrium of the mineral phases. Owing to this, at least some of the earlier formed minerals become unstable under the new conditions and are therefore either altered or replaced by other minerals.

As far as typical *associations of chemical elements* in separate minerals are concerned, this problem, in the case of crystalline bodies, is solved entirely on the basis of the laws of crystal chemistry. The combination of the different elements within a crystalline body depends upon the chemical properties, i.e., on the structure of atoms or ions, as well as on their sizes and properties. The replacement of some atoms or groups of atoms by others likewise depends on their sizes. In ionic compounds the condition is added that the sum total of positive and negative valencies must be balanced.

Typomorphic features of minerals. It has long since been noticed that some minerals have crystal forms typical of a given deposit or rock. Thus calcite ($CaCO_3$) which occurs as crystals usually in cavities occurs in different deposits as scalenohedral, obtusely or acutely rhombohedral, platy, fine rod-like, etc. Attempts were made to establish a connection between these different crystal forms and the temperature of their formation. In the end, however, it was found that the morphology and sizes of the crystals depended not so much on temperature, as on the concentration of the constituents in solutions, the presence of certain dissolved impurities, and the degree of supersaturation.

At the present time not only the crystal forms, but any typical features of minerals such as colour, admixtures of chemical elements, types of twinning, etc., are regarded as "typomorphic" features. There is no question that the characteristics of a particular deposit are relat-

ed to the specific features of the solutions, from which its minerals have crystallised, as well as to temperature, pressure and other factors of mineral formation. Some examples are given below.

It has been noted that cassiterite (SnO_2) from high-temperature or pegmatite formations (in distinction from that of hydrothermal deposits) often contains as impurities such metals as columbium, tantalum, iron, etc. Therefore, if found as rounded grains in unconsolidated deposits of gullies and river valleys, the specific features of its composition give a rough indication of the type of deposit it has come from.

It has been also established that large quartz crystals from Alpine clefts, unlike quartz from other deposits, are characterised by certain features of crystal form, specific paragenetic association and the presence of relatively large monocrystal blocks inside crystals which are usually twinned according to the Dauphiné law.

Native gold is characteristically richest in silver (isomorphously admixed) when found in deposits which have formed in the upper part of the earth's crust, i.e., at relatively low temperatures and pressures. Argentiferous gold (electrum) differs from ordinary native gold in physical properties as well (lower specific gravity and lighter yellow colour). Sulphur compounds of silver, such as argentite (Ag_2S) and proustite (Ag_3AsS_3), etc., are often paragenetically associated with electrum.

The vast majority of ore deposits of a complex origin show a great variety of typomorphic features, which necessitates very detailed research to establish their true dependences as the basis for positive conclusions. Be that as it may, paragenetic associations remain important criteria in the study of mineral deposits.

2. THE GEOLOGICAL PROCESSES OF MINERAL FORMATION

To establish the genesis (origin) of a given complex of mineral it is essential not only to know the way they have formed, but also the geological processes that occur in the earth's crust and give rise to rocks and ores of most diverse composition. Since these problems are thoroughly covered by special courses of petrography and deposits of economic minerals, the question of mineral genesis will be dealt with here only in general terms, so far as it is necessary for the understanding of terms used in Part Two.

All mineral masses which are formed as a result of some geologic process fall into two basic genetic groups, depending on the source of energy to which they owe their formation:

(1) *endogenous* (born from within) formed in the course of processes which depend on the internal thermal energy of the earth; the minerals of this group are the products of magmatic activity (in the broad sense of the term); rocks and economic mineral deposits result from the crystallisation of the magma itself and from different segregations from the

latter; mineral forming processes occur at different depths and at different, though usually high, temperatures;

(2) *exogenous* (born from without) depending for their formation on the energy of the sun; the source of the mineral matter are outcropping and disintegrating rocks and ores of different origin; mineral formation processes occur in the uppermost part of the earth's crust at low temperatures and pressures close to atmospheric, in the conditions of interaction between the physical and chemical agents of the atmosphere, hydrosphere, and biosphere.

After their formation, both the endogenous and exogenous mineral masses undergo transformations under conditions of altered environment (metamorphism). Particularly profound transformations, both in composition and structure, occur in the course of *regional metamorphism* when the rock masses and the associated deposits are moved by tectonic dislocations from their zone of formation to the deeper zones of the earth's crust.

ENDOGENOUS PROCESSES OF MINERAL FORMATION

Modern knowledge of endogenous processes is based on the concepts of the activity of magmatic hearths or chambers situated in the lower parts of the earth's crust. These processes occur at great depths, and cannot be observed directly. Only in the vicinity of active volcanoes can we obtain certain data indicating the nature of the processes occurring in the interior of the earth. Moreover, knowledge of the composition, structural features, occurrence, and interrelation of various igneous rocks and mineral deposits spatially associated with them enables some idea to be formed (in agreement with the physico-chemical laws) of the dependences governing the endogenous processes of mineral formation.

According to this concept magmas are silicate melts of complex composition containing also some volatile constituents.

When for some reason or other large masses of magma fail to reach the surface, they cool slowly in the upper part of the earth's crust under high external pressure. At the same time magma differentiation takes place, and its products crystallise into different igneous silicate rocks. In the course of these processes heavy metals (Sn, W, Mo, Au, Ag, Pb, Zn, Cu, etc.) which are present in the magma in negligible quantities, and volatile constituents (H_2O, S, F, Cl, B, etc.) combine into readily soluble compounds, and on crystallisation of the magma, concentrate in the upper parts of the magmatic hearths. Sometimes the metals take part in the formation of residual silicate solutions the crystallisation of which gives rise to pegmatites containing minerals with F, B, Be, Li, Zr, occasionally with rare-earth elements. In other instances they emanate from the magmatic hearth in the form of gaseous products which have vigorous contact effects on the enclosing rocks with which they react chemically. Finally, as aqueous solutions (hydrotherms) they are

carried through fissures into the roof of magmatic masses, where they often form rich deposits of metalliferous economic minerals.

Only a few heavy metals remain in the magma, and in the course of differentiation, concentrate in some of the rocks within the magmatic masses.

When the magma erupts to the surface as lava, the volatile constituents escape into the atmosphere.

In accordance with the above sequence of development of the magmatic cycle, the following stages of endogenous processes of mineral formation are distinguished: (1) the magmatic stage proper; (2) the pegmatitic stage, and (3) the pneumatolytic-hydrothermal stage.

1. Magmatic processes had occurred during all geological eras and have given rise to tremendous masses of igneous rocks.

According to the conditions of their formation these rocks fall into two principal groups: (a) *effusive* (extrusive), i.e., those that reached the earth's surface as lava or rapidly solidified in direct proximity to the surface under low external pressure, and (b) *intrusive*, i.e., those that solidified at great depths under high pressure in the form of large mushroom-like, sheet-like or irregularly shaped blocks. Effusive rocks solidify rapidly, before crystallisation is completed and therefore contain varying quantities of volcanic glass. Often (in vesicular lavas) they also contain numerous spherical cavities formed through the evolution of gaseous products upon a sharp decrease in the external pressure. Intrusives, on the other hand, are holocrystalline (completely crystallised) rocks.

Magmatic differentiation, as was stated earlier, gives rise to rocks differing in chemical and mineral composition as well as in specific gravity. Depending on the content of silica and other constituents, igneous rocks are classed as:

(a) *ultrabasic*, rich in MgO and FeO, but poorest in SiO ($<45\%$), e.g., dunites, pyroxenites in intrusive complexes, and pycrites in effusive complexes;

(b) *basic*, richer in SiO_2 (45-55%), rich in Al_2O_3 and CaO, but poorer in MgO and FeO, e.g., gabbro, and norites in intrusive complexes, and basalts and diabases in effusive complexes;

(c) *intermediate* acidity rocks, SiO_2 content (55-65%), poorer in CaO, but richer in alkalis: diorites, quartz diorites in intrusive complexes, and porphyrites, andesites, etc., in effusive complexes;

(d) *acid*, rich in SiO_2 ($>65\%$), still richer in alkalis, but poorer compared with the preceding ones in CaO, FeO, and MgO: granodiorites, granites, etc., in intrusive complexes, and liparites, quartz porphyrys, etc., in effusive complexes.

Figure 50 shows graphically the difference in the content of certain oxides in the principal igneous intrusive rocks (ultrabasic, basic, intermediate, and acid).

Somewhat apart stands the family of quartzless nepheline syenites (about 55 per cent of SiO_2), which are richer in alkalis and Al_2O_3 than

granites, as well as of phonolites, leucitophyres, and other effusive complexes.

In a number of intrusive blocks where the differentiation of the magma was more complete, acid rocks are found at the top, while the ultrabasic and basic rocks, whose specific gravity is higher, in the deeper parts of the blocks.

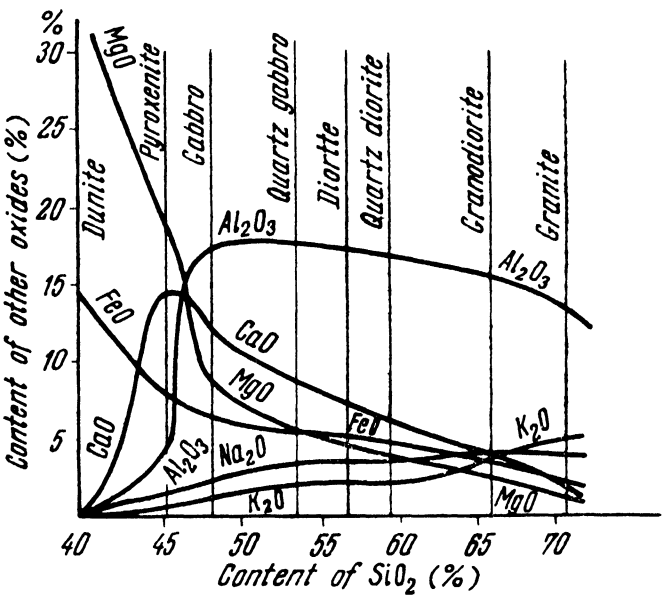


Fig. 50. Graph of chemical composition of principal intrusive igneous rocks.

Ore deposits of magmatic origin are found only in ultrabasic and basic igneous rocks. This includes deposits of Cr, Pt, and other metals of the platinum group, as well as Cu, Ni, Co, Fe, Ti, etc.

Alkali-rich intrusives (nepheline-syenites) may be associated with deposits of rare earths, such as columbium, tantalum, titanium, zirconium, and non-metallic mineral deposits, e.g., phosphorus (apatite), aluminiferous rock (nepheline), etc.

2. Pegmatite-forming processes take place in the upper marginal parts of deep-seated magmatic blocks (several kilometres from the surface of the earth) where external pressure is high enough to keep in solution the volatile magma constituents, which react with the earlier crystallised rock.

Pegmatites as geological bodies* occur as veins or irregularly-shaped deposits, occasionally as stocks distinguished by unusually coarse-

* This concept of pegmatite should not be confused with the purely structural idea of "pegmatite" which is a regular intergrowth of quartz and feldspar in a definite quantitative ratio ("graphic granite", "jewstone"). Such forms occur for the most part in granitic pegmatites.

grained texture of the mineral aggregates. The pegmatite veins may be several metres thick, and on the strike they generally extend for tens, more rarely for a few hundred metres. For the most part pegmatite bodies are enclosed in the parent igneous rocks, but sometimes occur in the form of vein-like bodies in the invaded rocks.

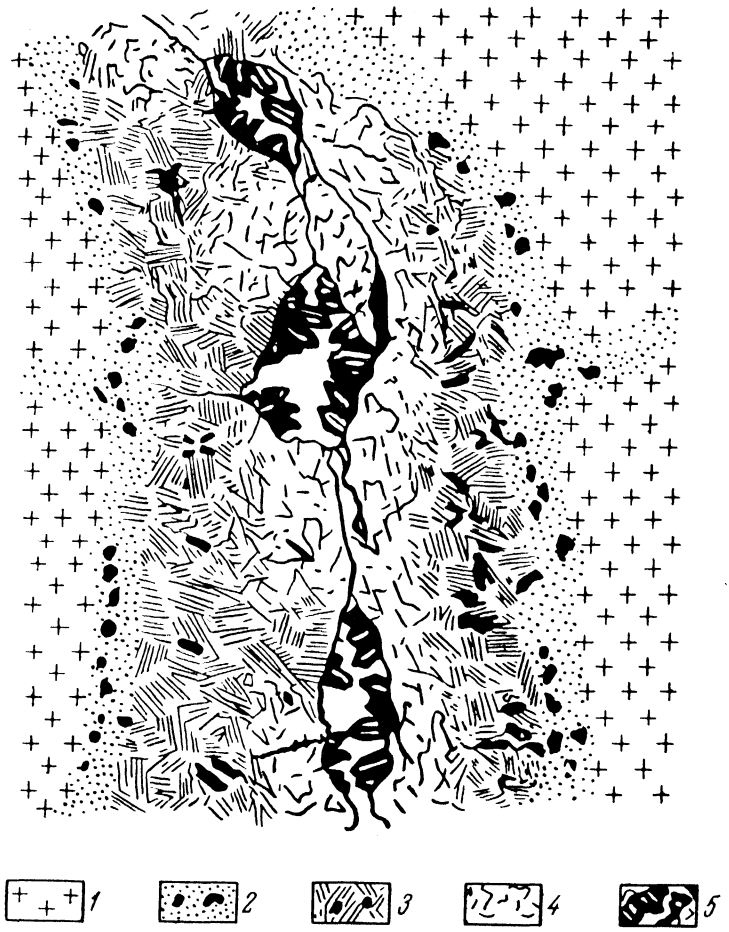


Fig. 51. Structure of the Murzinka pegmatite dike.

1 – granite; *2* – aplite zone; *3* – graphic granite; *4* – coarse-crystalline masses of feldspar and quartz; *5* – vug (cavity with crystal druses).

It should be pointed out that pegmatite formations are found in intrusive rocks of most diverse composition, from ultrabasic to acid. Most commonly, however, pegmatites occur in acid and alkaline rocks. Those found in basic rocks are of no commercial importance.

In composition, pegmatites differ very little from parent rocks, being composed mainly of the same rock-forming minerals. Only minor (quantitatively) minerals which are not found in every type of pegmatites substantially differ in composition, since they contain valuable rare chemical elements often in association with minerals containing

volatile constituents. Thus, besides the principal rock-forming minerals (feldspar, quartz, micas) granitic pegmatites contain minerals of fluorine and boron (topaz, tourmaline), beryllium (beryl), lithium (lithium micas), occasionally rare-earth minerals, columbium, tantalum, tin, tungsten, etc.

Many pegmatite formations show a zonal structure and rather regular distribution of minerals. For instance, in the pegmatites of the Murzinka area in the Urals (Fig. 51) the outer pegmatite zones at the contact with the enclosing granites are composed of light-coloured close-grained rock (aplite). Towards the centre, they are replaced by "graphic granite" zones (intergrown quartz and feldspar) followed by zones of coarse-crystalline feldspar and quartz. In the central zone of the pegmatite vein there are cavities ("bags") whose walls are lined with druses of large, well-formed crystals of rock crystal, topaz, and other gemstones.

The pegmatites which penetrate into intrusives very rich in alkali earths (MgO, CaO) sharply differ in mineral composition from pegmatites in the parent rocks. In that case, mineral paragenesis gives an indication of the vigorous reactions that have taken place between the solutions and the enclosing rocks. In such cases there are established mineral associations in which not only the elements of the magma (Si, Al, alkalis, etc.) take part but also the elements of wall rocks (MgO and CaO) which, at the contact with the pegmatites, also undergo sharp changes. Such pegmatites are referred to by A.Y. Fersman as "hybrid" pegmatites, as opposed to "pure-bred" pegmatites discussed above.

The origin of pegmatites has not yet been completely deciphered. According to A.Y. Fersman, they are the product of crystallisation of residual melts enriched in volatiles. Recently Soviet scientist A.N. Zavaritsky, proceeding from physico-chemical considerations, suggested the possibility of formation of coarse-crystalline masses through crystallisation of parent rocks under the influence of gases accumulating in the residue of the crystallisation of the magma. However, in all cases the pegmatites are formed towards the end of the magmatic process proper and, as such, occupy an intermediate position between plutonic magmatic rocks and hydrothermal ore deposits.

3. Pneumatolytic-hydrothermal processes are essentially postmagmatic, i.e., they occur when the main process of magma crystallisation in a deep-seated block is over in the main.

Pneumatolysis (*pneuma* is the Greek for gas) may occur when melts saturated with volatile constituents, crystallise under the conditions of relief of external pressure. Therefore at a certain pressure the residual melt boils up, as it were, passing into gas which interacts with the formed earlier solid minerals. In other words, there occurs the process of sublimation. Processes of this kind occur when magmas solidify at great or medium depths.

In this case the volatiles chemically react with the enclosing rocks, which gives rise to *contact metamorphism*. This is accompanied by chem-

ical reactions in the wall rocks (the roof) *impregnated with solutions.* The degree of metamorphism and the composition of the resulting products depend not so much on temperature, as on the chemical activity of the solutions and the composition of the rocks with which they react. The most profound changes are observed in *limestones* and other

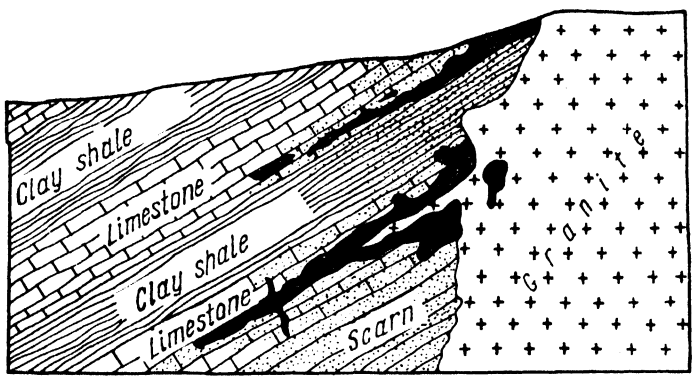


Fig. 52. Section of a contact-metasomatic deposit. Ore bodies (magnetite ores) are shown black.

calcareous rocks contacting the magmatic masses. Chemical reactions, involving the mechanism of replacement or metasomatosis, give rise to so-called *skarns* (Fig. 52) which are mainly composed of silicates of Ca, Fe, Al, etc. Their chemical composition indicates that skarns have derived both from the wall rocks (limestones, dolomites, etc.) and the magma constituents. It should be noted that the intrusives which have already solidified by the time the process under consideration takes place, also alter along the contact. In this process the minerals of magmatic rocks are replaced by new formations whose composition shows that an influx of elements (Ca, Mg) from the carbonate strata had taken place. Skarns are often associated with deposits (Fig. 52) of iron, occasionally of tungsten, molybdenum, and other metals.

When the magmas erupt to the earth's surface, enormous quantities of volatiles are discharged into the atmosphere. However, in the fissures of cold lavas, on the walls of volcano craters, and in other enclosing rocks one often observes sublimation products such as native sulphur, ammonium chloride, borates, etc. Some metasomatic reactions are also observed, but they are less pronounced than in the previous case.*

Hydrothermal processes occurring at great depth develop in the roof, at some distance from the direct contact with igneous rocks. The residual vaporous solutions which move through a network of fissures developing in the roof of the magmatic hearths in the course of mag-

* These processes of mineral formation of course cannot be classed with pneumatolytic processes proper, since they occur at very low external pressure.

matic intrusion (Fig. 53) gradually condense into hot aqueous solutions or hydrothermas.

Conditions for hydrothermal processes are most favourable at low and medium depths (3 to 5 km) from the surface of the earth. The majority of hydrothermal formations are spatially and genetically associated with acid intrusive rocks (granites, grandiorites, etc.). The range of circulation of the solution extends sometimes from the upper parts of magmatic hearth right to the earth's surface. In areas of recent volcanic activity one still finds hot mineralised springs depositing siliceous material with substantial amounts of sulphides of Hg, Sb, As, Pb, Cu, etc.

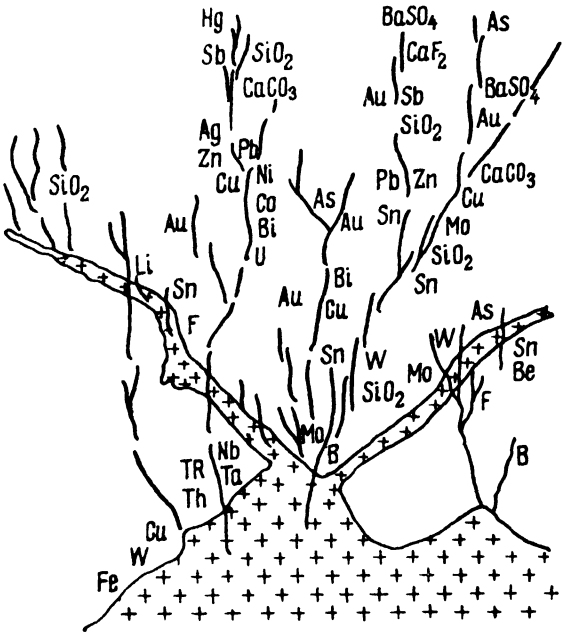


Fig. 53. General diagram of hydrothermal formations.

Crosses denote igneous rocks.

Farther away from the magmatic hearth, the hydrothermal solutions enter an environment which is gradually enriched in oxygen. At the same time there is a decrease in external pressure and temperature, the latter diminishing from approximately 400° to a few tens of degrees. These factors, naturally, influence the course of chemical reactions and the mineral composition of the hydrothermal solutions. By the token of the prevailing mineral associations, these formations are tentatively classified as high-, medium-, and low-temperature ones. This does not mean, of course, that high-temperature formations cannot be found among mineral associations crystallising at lower temperatures. Even in pegmatites and contact-metamorphic formations there are invariably found lower-temperature minerals of hydrothermal origin. These, however, reflect the final stages of the process of mineral deposition which began at high temperatures.

The formation of hydrothermal solutions continues for a very long time, evidently as long as the magmatic hearth exists. Soviet scientist S.S. Smirnov deduced from an analysis of the correlation of different deposits forming a single ore complex that the movement of the mineralising solutions must have been intermittent due to repeated resumption of fracturing processes. This is borne out by the frequent indications of superimposition of later mineralisation stages on earlier ones.

The shape of the mineral bodies depends on the configuration of the cavities filled by them and, to some extent, on the composition of the rocks through which the solutions had circulated. When fissures had been filled, this results in interrupted veins (Fig. 54) the roots of which

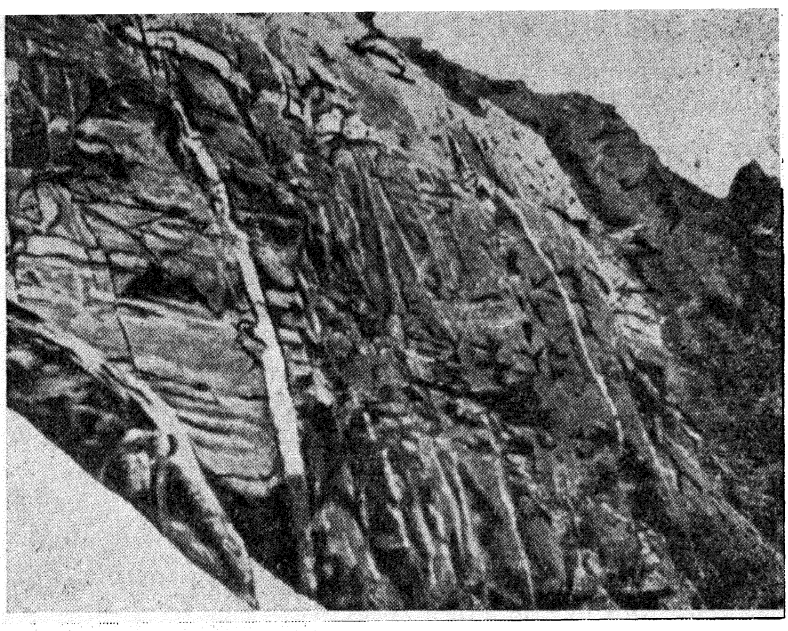


Fig. 54. Series of thin scheelite-bearing quartz veins showing on a scarp.

White at left—snow.

sometimes go down to the upper parts of the magmatic masses. Deposition of minerals in tiny pores and openings produces *impregnations.* The passing of the solutions through chemically reactive rocks (e.g., limestones) gives rise to *metasomatic deposits* which often are irregularly shaped. Should a solution suddenly encounter a large opening, the sharp pressure relief causes intense evaporation of the solvent (water) and hence, at least initially, considerable supersaturation of the solution and the precipitation of colloids. Indeed, metacolloidal formations on the walls of veins are quite common, particularly when the processes were associated with shallow-seated intrusives. Also very common are cavities lined with druses of different crystals.

The mineral composition of hydrothermal deposits is extremely varied. The veins in the vast majority of cases are composed of quartz containing diverse minerals, mostly metal sulphides. It should be noted that it is hydrothermal deposits that produce most of the ores of rare (W, Mo, Sn, Bi, Sb, As, Ng, sometimes Ni, and Co), non-ferrous (Cu, Pb, Zn), precious (Au and Ab), and radioactive (U, Ra, Th) metals.

EXOGENOUS PROCESSES OF MINERAL FORMATION

Processes occurring on the earth's surface which derive their energy from the heat of the sun are more accessible to observation than endogenous processes.

On dry land, atmospheric agents (oxygen, carbon dioxide, water) and bacterial activity give rise to a powerful chemical process known

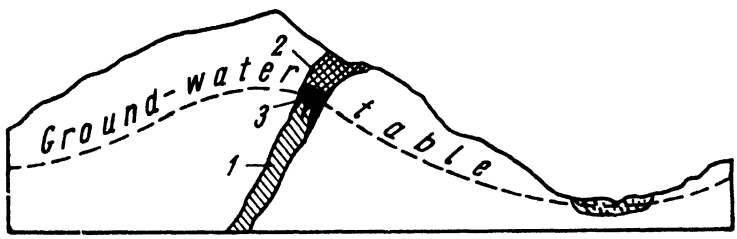


Fig. 55. Section of a sulphide deposit outcropping to the daylight surface.

1 —primary copper-sulphide ores; *2* —gossan; *3* —zone of secondary copper enrichment (black).

by the general name of *weathering*. It consists in the physical and chemical disintegration of everything that had been formed by the endogenous processes and at the same time gives rise to products which are stable in the new conditions on the surface of the earth.

In part, these products are transported by running surface waters either in solution or in suspension and deposited wherever the current becomes more sluggish, in river valleys, or in lacustrine and marine basins. The latter become the site of specific processes of mineral formation resulting in the deposition of sediments in the form of beds on the bottom of the basins. This is known as the *sedimentary* process.

1. Weathering in the first place takes the form of mechanical destruction of rocks and ores caused by temperature fluctuations, as well as by the action of water freezing in cracks and pores, and by other factors. All this results in the disintegration of rock and ore minerals which possess different expansion factors. Much more important, however, is the chemical weathering of minerals by rain and surface waters which contain dissolved oxygen, carbon dioxide and other gases, and therefore possess rather strong oxidising and dissolving properties. Percolating to the ground water table (Fig. 55), these waters gradually lose their oxygen in the course of reactions of oxidation, hydration, and carbonation.

The leaching-out of the soluble compounds thus formed leads to the formation of pores, caverns, and sometimes even great chambers (karsts). The walls of such chambers are often covered with colloidal sinter formations or crystal druses of exogenous minerals, or else may be coated with earthy ochreous matter. Where intense leaching of more or less readily soluble rocks takes place, the soil over them sags

forming sinks and sometimes swallow holes or even great caves (in gypsum and limestone series).

Vegetation and various organic compounds which pass into solution intensify considerably the chemical weathering of ores and rocks.

Chemically inert minerals (quartz, gold, platinum, etc.) and also recent formations of low solubility accumulate in the residual products at the surface in the form of clayey masses of different light and dark shades, but most often stained brown by iron hydroxides.

Accumulating at or near the surface, the insoluble products of chemical weathering form the so-called *residual deposits* composed predominantly of hydroxides and hydrosilicates. Examples are the numerous deposits of clays, kaolins, and bauxites, as well as of iron, nickel, and other ores, formed in the course of intense disintegration of rocks of corresponding composition. These deposits have a vast areal extent.

The chemical weathering of economic mineral deposits gives rise to residual formations called *caps* (iron, manganese, gypsum, and others). In the case of iron, they are known as iron hats or gossans. Because certain constituents are leached out, the concentration of residual economic minerals in these caps is generally much higher than in the undecomposed primary ores, i.e., those lying below the ground-water table. It should be noted that the leached-out metals, especially copper, and also silver and zinc which percolate in aqueous solutions down to the lower part of the zone of oxidation, i.e., to the ground-water table, react with primary ores or with the chemically active wall rocks (limestones). Thus, a zone of *secondary* sulphide enrichment with a much higher concentration of copper in the ores (Fig. 55) develops in copper-sulphide deposits.

Climatic factors (mean annual temperatures and precipitation) greatly affect chemical weathering. Low humidity and high mean annual temperatures accelerate the oxidation and concentration of chemical compounds. Topography is also an important factor. In mountainous regions intense erosion carries away the products of chemical weathering before they can form large accumulations. A different picture is observed in flat country.

The deposits formed by weathering commonly have somewhat irregular pocket- or sheet-like shapes which are more or less parallel to the daylight surface. Along large fissures, zones of crushing, and the contacts of physically and chemically different rocks, i.e., where the surface weathering agents penetrate to greater depth, steep ore bodies of surface origin, pinching out with depth, may develop.

2. Sedimentary processes occur in aqueous environment: rivers, lakes, and seas. In sea basins these processes through geologic time gave rise to the formation of series of sedimentary rocks of enormous thickness. Sedimentary rocks may be divided into mechanical and chemical.

Mechanical sediments are formed as a result of the erosion of the weathering products and the re-deposition by running water of the

chemically inert minerals and rock fragments such as pebbles, gravels, sands and sand clays in river valleys and aquatic basins. If the eroded products of weathering contain chemically inert valuable minerals, they are re-washed and redistributed in river valleys in accordance

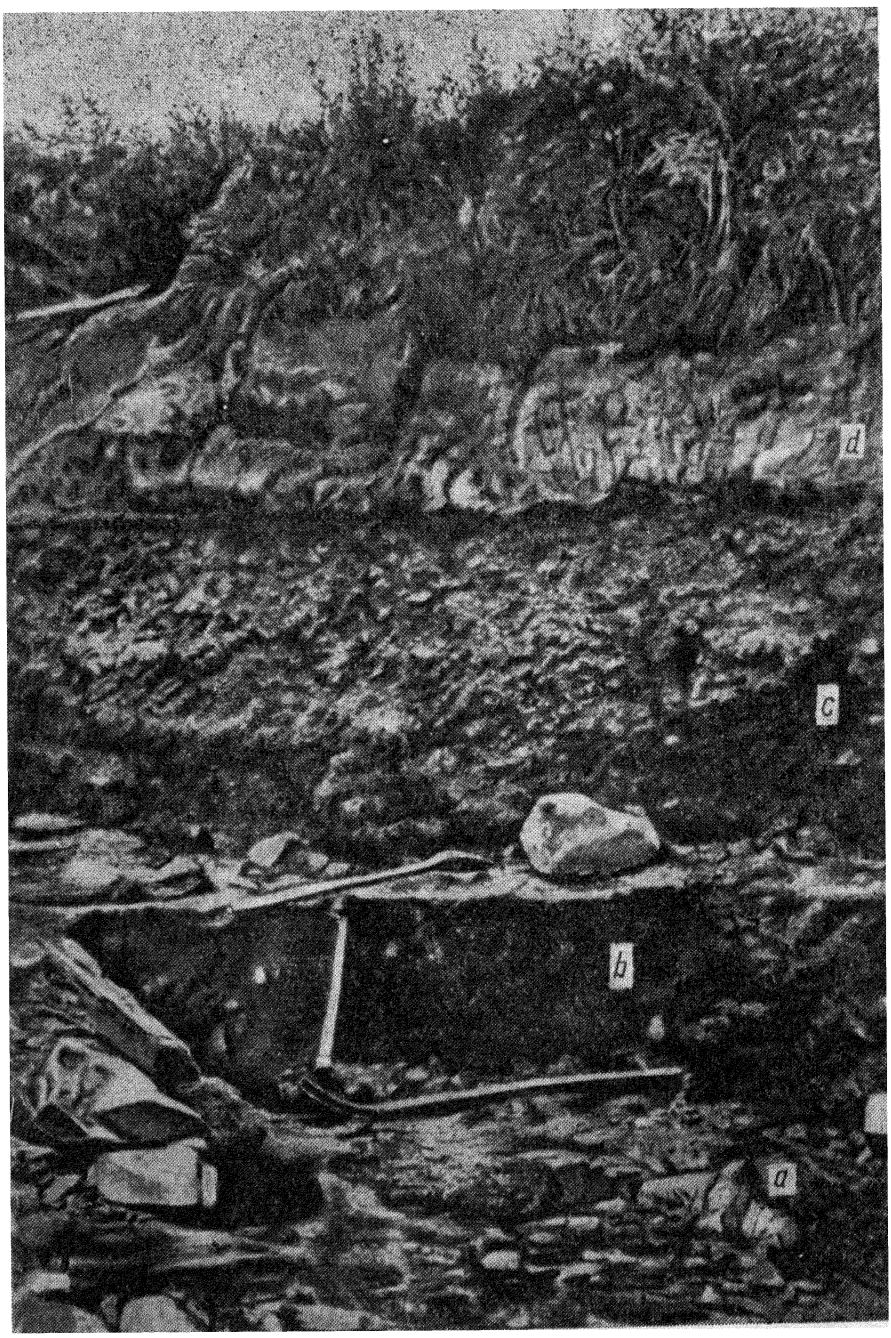


Fig. 56. Sectional view of a platinum placer.

a – bedrock outcrops; *b* – platinum-bearing gravels; *c* – layered bench gravels; *d* – clays covered with vegetation.

with their specific gravity, forming *placer deposits* which often are of commercial importance (Fig. 56). Such are the gold, platinum, diamond, and some other placers.

No new minerals are formed in the process of accumulation of mechanical sediments. Only in the case of ancient placers does one observe later chemical alterations in the clastic material.

Chemical sediments are mostly limited to lacustrine and marine basins. They are formed by crystallisation of saturated salt solutions, by deposition of coagulating colloids in the form of gels, and finally, by accumulation of the products of activity of the organic kingdom and of the organic remains themselves.

(1) The formation of *crystalline* sediments occurs in many drying lakes in regions with an arid and hot climate where surface evaporation prevails over influx of fresh water.

Crystallisation begins at a certain supersaturation of the aqueous solutions. The order of the segregation of minerals with progressive evaporation of water depends on the two main factors of the equilibrium of the system: the composition of the solutions or, to be more precise, the ratio of concentration of the components forming the system, and the temperature of the solutions at which crystallisation takes place. The equilibrium conditions of sulphates and chlorides of Ca, Mg, K, and Na in sea water have been thoroughly investigated for different concentrations and temperatures by N.S. Kurnakov and many others.

(2) The formation of *colloidal* sediments in lacustrine and marine basins is much more complex, and some of its aspects are still obscure. Thus, certain compounds which result from weathering are transported by running water, not only in true solutions but also in colloidal solutions or sols which are stable in fresh water. When these solutions are transported by surface waters into marine basins, they are coagulated by the abundant electrolytes present in sea water in the form of ions of the dissolved salts. This is the case with colloidal solutions of iron, manganese, silica, and other oxides.

The gels, thus formed, together with the clayey and fine detrital particles brought by fluvial waters as well as the remains of marine life are deposited at the bottom of the near-shore zone, either as intercalations or thicker and more regular beds. With time, these sediments undergo alteration (diagenesis) turning into compact masses.

Sedimentary manganese deposits offer a good example of the dependences governing the alteration of paragenetic associations of minerals due to the physico-chemical conditions in which the sediments are formed at the bottom of basins. Tetravalent manganese compounds which are the richest in oxygen are prevalent in shallow near-shore zones. Farther away from the coast they are replaced by divalent manganese carbonates accompanied by rare iron sulphides. Sedimentation in the shallow zones apparently took place in the presence of the oxygen, which down to a certain depth is dissolved in sea water, whereas in the deeper zones, in conditions of oxygen deficiency, the carbonates

and the accompanying sulphides apparently formed through the action of carbon dioxide and some hydrogen sulphide evolved in the course of decomposition of organic remains. Hence there emerge the so-called *facies* of ores of different composition (oxides and carbonates). A similar relationship between sediments of different composition apparently exists in deposits of iron ores, for which facies of oxides, silicates, and carbonates have long been known.

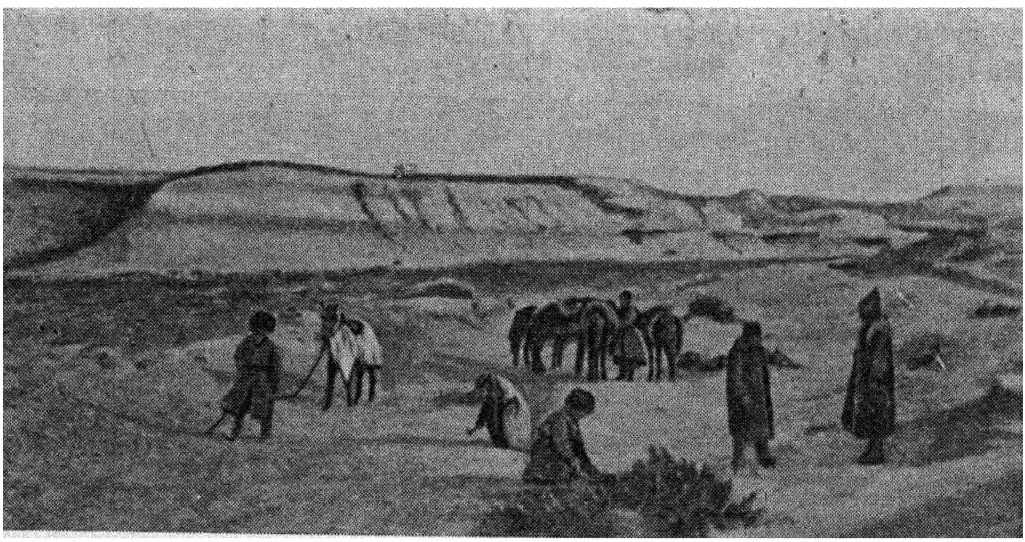


Fig. 57. Outcrops of horizontally-stratified Tertiary sedimentary rocks with a horizon of calcareous clays, marls rich in remains of algae and coquina, intercalated with gypsum and native sulphur.

As to the processes occurring in deeper parts of marine basins and oceans, our knowledge is still very scarce.

(3) Organogenic or *biogenic* sediments which are formed as a result of a very complex biological process include limestones consisting of skeletons of marine animals, diatomites consisting of siliceous skeletons of diatoms, and caustobioliths (*caustos* means combustible in Greek) formed chiefly from vegetal and partly from animal organisms (fossil coals, shales, oils, combustible gases, solid bitumens, etc.).

Organogenic sediments may develop through the accumulation of the skeletons of dead animals (coquina) or from the tissues of higher or lower plants (peat, sapropel). They also may result from the life activity of the organisms themselves, e.g., the decomposition by anaerobic bacteria of organic remains or sulphates, giving rise to sulphur deposits (Fig. 57). Finally, laboratory experiments with ferrobacteria have shown that the latter may give rise to nodular formations.

On subsequent transformation, some of these sediments turn into inorganic products (limestones, phosphorites), while others remain organic (coals, etc.).

REGIONAL METAMORPHISM AND RELATED MINERAL FORMATION PROCESSES

The most profound changes both in endogenous and exogenous formations occur in the process of so-called regional metamorphism when as a result of tectonic displacement whole areas of the upper parts of the earth's crust sink to great depths, finding themselves in the conditions of high temperatures and pressures or the conditions of powerful orogenic processes.

In this new environment, the mineral and chemical composition, physical properties and external appearance of the rocks and ores undergo substantial alteration. Exogenous water-rich compounds become partially or completely dehydrated, (e.g., opal changes to quartz, limonite to hematite or magnetite, etc.). This is accompanied by recrystallisation (organogenic limestone, for instance, turns into marble with the obliteration of its former structural characteristics). In many rocks, including igneous ones, a complete rearrangement of the constituents occurs with the formation of new minerals. Some minerals, for instance, gypsum, native sulphur and rock salt never occur in metamorphic series. Under the action of high temperature and pressure, chemical reactions tend to produce minerals of smaller volume and higher specific gravity. Mineral paragenesis depends not only on the composition of the rocks undergoing metamorphism but also to a large extent on the depth at which this occurs, i.e., on the thermodynamic conditions.

The rocks themselves under high dynamic stress change to schists (Fig. 58) which readily split into plates (clay shales, slates, mica schists, gneisses, etc.). If metamorphism affects finely laminated sedimentary rocks so that the stress applied roughly coincides with the direction of lamination, the laminations will be crumpled into numerous fine folds as is shown in Fig. 59.

There is no doubt that such constituents as H_2O, CO_2, and other mineralisers which promote not only recrystallisation, but metasomatosis and even re-deposition of the minerals play a large part in the rearrangement of mineral matter. In this case H_2O and CO_2 originate either from magmatic rocks or rocks undergoing metamorphism. Some, especially sedimentary rocks, in the course of their recrystallisation into aggregates of anhydrous minerals should release large quantities of water and some carbon dioxide. Under high temperatures and pressures, the metamorphic water should acquire all the properties characteristic of hydrothermas which are genetically associated with magmatic intrusion, i.e., higher dissolving capacity and ability to carry and re-depose minerals either along fissures or through metasomatosis. This, however, does not exclude the possibility of the impregnation of metamorphosed rocks with magmatic water vapours, especially in regions of great intrusions of acid igneous rocks.

Among economic mineral deposits occurring in metamorphosed rocks the following genetic types are identified: (a) *metamorphosed*

deposits which existed before metamorphism began (e.g., sedimentary deposits of iron and manganese), and (b) *metamorphic* deposits, i.e., those produced in the metamorphic process.

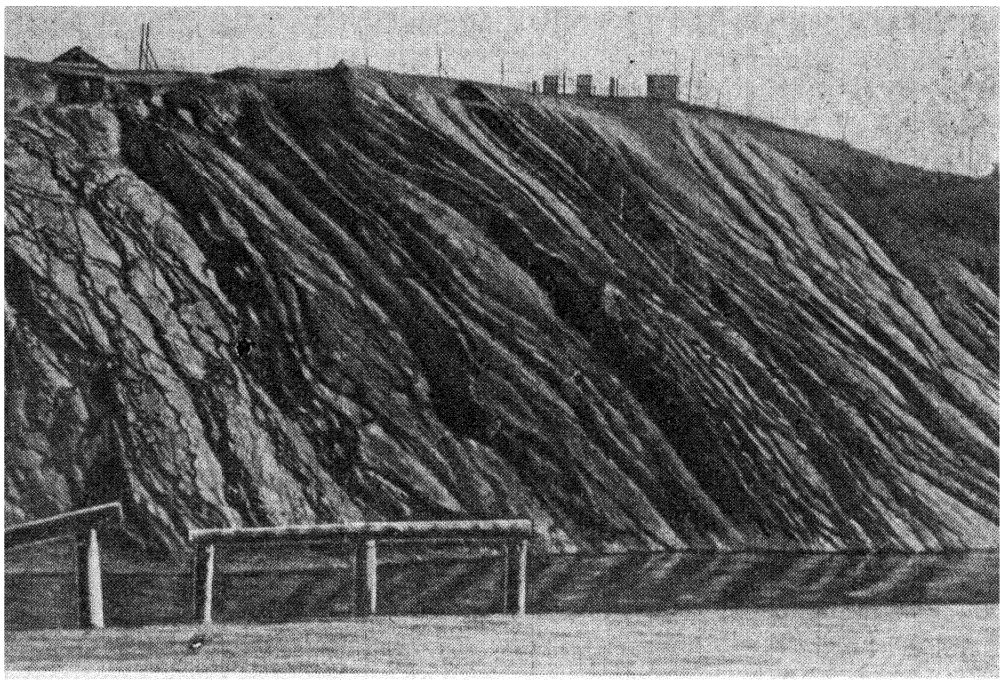


Fig. 58. Outcrop of schistose rocks on a river bank.

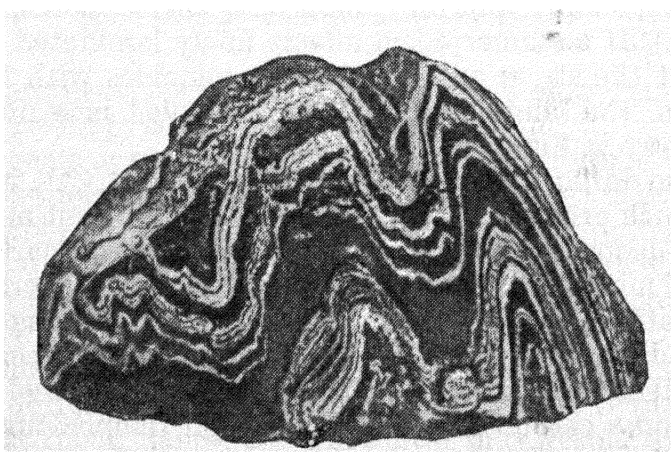


Fig. 59. Plicated thinly-lamellar quartz-magnetite rock.
¼ natural size.

The latter type is exemplified in the formation of graphite in metamorphic rocks from organic remains. Sometimes cryptocrystalline graphite is found, bearing the imprints of plants deriving from coal seams (in metamorphic series of the eastern slope of the Urals mountains). The graphite, in this case, is no longer a combustible substance

due to a radical change in its original properties and the loss of its volatile constituents.

This genetic type also includes the so-called *Alpine* clefts (the name referring to the place of its discovery) which are very interesting mineralogically. The veins have long since attracted the interest of mineralogists because of the beautiful druses of crystals of different minerals found in them. They are associated with fissures in metamorphic

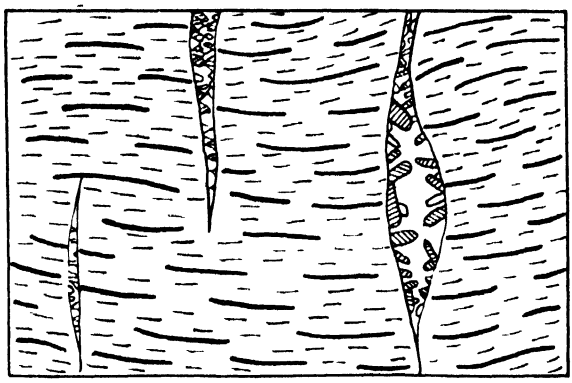


Fig. 60. Diagrammatic structure of Alpine clefts.

rocks, usually across the bedding plane (Fig. 60). The important feature of their composition is that the minerals crystallising in them are exactly the same as those which form in the course of metamorphism in the *enclosing* rocks. They are also found in approximately the same quantitative ratio. Only the more soluble rare minerals containing Ti, P, Cl and B are present in fissures in greater quantities than in the wall rocks. Another important feature is that these fissures generally do not contain chemical elements or minerals that might point to any genetical relationship with the hydrothermal activity of acid magma intrusions (e.g., minerals of gold, silver, lead, zinc, antimony, tin and tungsten), although the possibility is not excluded that magmatic water too takes part in these processes.

Thin cracks in metamorphic rocks are completely filled with mineral matter, examples being the veins of white calcite in grey limestones, of milk-white quartz in red jaspers, etc. It should be noted that the crystal grains in these veinlets are always larger than those in the host rock.

Part Two

CLASSIFICATION OF MINERALS

Principles. During the past five or six decades all the leading textbooks and handbooks on mineralogy have generally adhered to the chemical classification of minerals based on Mendeleyev's periodic law.

For this reason, the basic division of all minerals into classes, according to the types of chemical compounds, with slight variations, has become fundamental in the modern classification of minerals. But the subdivision of classes into subclasses and groups of minerals has changed essentially, especially in the last 30-35 years, due to outstanding advances in the study of crystalline substances.

X-ray structural analysis of crystals on the basis of Y.S. Fyodorov's 230 regular arrangements of points in space has proved the existence of an interrelation between chemical composition and crystal structure, and this has led to the more accurate determination of the chemical formulas of many complex compounds. In this way it has been established that such compounds as the minerals of the spinel group, titanates, and columbates-tantalates heretofore regarded as separate classes, are actually complex oxides. Similarly our concepts of the chemical nature of silicates underwent profound change when complex anions of most diverse form and structure were found within their crystal structures.

These advances have led to the discovery of a functional dependence of not only the external shape of the crystals, but also of their optical, electrical, and mechanical (hardness, cleavage, elasticity) properties on the specific features of their crystal structure. These properties of minerals proved to be functionally related both to the spatial arrangement of the structural units (ions, atoms, molecules) at a definite ratio between their sizes, and on the type of bonding between them, as well as the properties of the ions and atoms themselves determined by their position in the periodic table and, therefore, by their structure.

Furthermore, a knowledge of the dependences governing the combinations of chemical elements in the course of the formation of minerals has deepened our understanding of mineral genesis. This knowledge also helped to understand the sequence and order of the "selection" and combination of particular ions in the course of the formation of crystals segregating from a solution or melt, depending on the physico-

chemical factors of the equilibrium of the system (temperature, pressure, and the concentration of the chemical components). In this way it is also possible to account for the regularities in the distribution of the chemical elements and types of chemical compounds in various successive magmatic products (igneous rocks, pegmatites, hydrothermal formations) or in the products of exogenous processes which result in the formation of the crust of weathering and of chemical sediments in aqueous basins.

All this indicates that a new page is opening in the history of mineralogy. It is no longer possible to understand the properties of minerals out of context of chemical composition and without analysing their crystal structures. And vice versa, even when we do not know yet the crystal structure of a mineral, we may, on the basis of its physical and chemical properties, form an idea of the particular structural type of compound to which it belongs.

Therefore, *the classification of minerals should be crystallochemical and based on the knowledge of the interrelationship of all the properties of natural chemical compounds and their chemical composition and crystal structure.*

The principles of mineral classification adopted in this textbook may be summarised as follows.

All natural formations comprising the subject of mineralogy, as well as artificial substances in chemistry, are divided into two big independent groups:

(i) *inorganic minerals* which, apart from rarely occurring native elements, include natural compounds (except organic compounds) of all the chemical elements;

(ii) *organic minerals* comprising diverse compounds of carbon (except carbonates and carbides which are classed with the inorganic compounds).

Organic compounds, as known, differ materially from inorganic compounds not only in chemical properties but also in crystal structure and the type of bonding between the structural units. While the present state of knowledge of inorganic minerals is quite advanced, the mineralogy of organic minerals is almost rudimentary.

Twenty years ago such natural substances as peats, coals, lignites, resins and petroleum were regarded as independent minerals. However, recent investigations, particularly of solid inorganic substances, by means of new techniques established beyond doubt that these substances are nothing but widely heterogeneous mixtures of a number of organic minerals the true nature of which has only now become the object of study.

The classification of *inorganic* minerals is based on the following principles. Since minerals are basically crystalline products of chemical reactions, for our purposes it is best to classify them according to chemical composition and crystal structure. It is these features that are related to the most important chemical and physical properties by

which minerals are identified and the conditions of their formation determined.

All the minerals of inorganic nature are first divided by the chemical criterion into large classes which differ in the *type of chemical compound* and in the type of chemical bonding between the structural units.

A special position is held by *native elements*, mostly metals, with the characteristic metallic bonding between the atoms. Intermetallic salt-like compounds are also classified with these.

An independent division is formed by *sulphides* and similar compounds, which with regard to a number of their properties occupy an intermediate position between typical metals and compounds with ionic bonding. The so-called sulphosalts, about which little is known structurally, tentatively are put into this division.

Next comes a characteristic type of chemical compounds with typically ionic bonding, the *halides*, i.e., compounds of metals with fluorine, chlorine, bromine, and iodine.

These are followed by *oxides* and *hydroxides* (simple and complex compounds of metals with oxygen or a hydroxyl).

Finally, there is the class comprising numerous *salts of oxygen acids*, i.e., compounds of metallic cations with different oxygen-containing complex anions.

According to the type of anions, some of these divisions must be further divided into *classes* and *subclasses*. The latter are further subdivided into *groups* by the token of similarity of crystal structure and specific chemical features which, in the main, depend on the cations entering into their composition.

Thus, a classification of inorganic minerals may be presented as follows (without subdivision into groups):

Division I. Native elements and intermetallic compounds.
Division II. Carbides, nitrides, and phosphides*.
Division III. Sulphides, sulphosalts, and similar compounds.
Class 1. Simple and binary sulphides and similar compounds.
Class 2. Sulphosalts.
Division IV. Halides.
Class 1. Fluorides.
Class 2. Chlorides, bromides, and iodides.
Division V. Oxides.
Class 1. Simple and complex oxides.
Class 2. Hydroxides.
Division VI. Oxygen Salts.
Class 1. Iodates*.
Class 2. Nitrates.
Class 3. Carbonates.

* These compounds are not considered in the present course.

Class 4. Sulphates and selenates.
Class 5. Chromates.
Class 6. Molybdates and tungstates.
Class 7. Phosphates, arsenates, and vanadates.
Class 8. Arsenites*.
Class 9. Borates.
Class 10. Silicates.

A. Silicates with isolated tetrahedra of the SiO_4 anion.
B. Silicates with isolated groups of SiO_4 tetrahedra.
C. Silicates with continuous chains of SiO_4 tetrahedra.
D. Silicates with continuous sheets of SiO_4 tetrahedra.
E. Silicates with continuous three-dimensional networks of SiO_4 and AlO_4 tetrahedra.

To avoid repetition, the dependence of the main properties of minerals on composition and crystal structure will be given in the introductions to each respective division, class, subclass, and group, inasmuch as it is this dependence that serves as a basis for classifying them. In describing separate minerals, only those additional properties will be given which depend on their particular structure and composition.

Mineral species and varieties. The basic classification unit of natural chemical compounds is a *mineral species* generally possessing a definite chemical composition and a definite crystal structure.

Thus, polymorphous modifications of one and the same crystal substance constitute separate mineral species (graphite and diamond, α-sulphur and β-sulphur).

When two isostructural substances form a continuous series of solid solutions (e.g., Au—Ag, $MnWO_4$—$FeWO_4$, $NaSi_3AlO_8$—$CaSi_2Al_2O_8$), physico-chemically we have a single phase. In mineralogical practice, however, it is customary to designate by several names not only the end members of the series but also the intermediate forms of an isomorphous series (for instance, gold—electrum—silver; huebnerite—wolframite—ferberite; albite—oligoclase—andesine—labradorite—bytownite—anorthite).

What is meant by *varieties* are minerals which are either identical or almost identical in crystal structure, and only slightly differ in:

(1) chemical composition, one of the chemical constituents of the mineral being isomorphously replaced in part by another constituent; e.g., cobalt-pyrite, (Fe, Co)S_2, a variety of pyrite which may be distinguished from the latter only by chemical analysis;

(2) certain physical properties, though the minerals are exactly the same in regard to composition and structure; e.g., amethyst differs from colourless quartz by its violet colour; or a sooty variety of pyrolusite (MnO_2) which differs from its crystalline individuals (polyanite) only in the degree of dispersion and in false low hardness;

* These compounds are not considered in the present course.

(3) both in composition and physical properties, e.g., a strongly ferruginous variety of sphalerite (ZnS) differs from the common light-coloured species by being almost black, and in certain other features.

Each mineral species of a definite chemical composition has a name of its own. The majority of polymorphous modifications also have either specific names or the same name prefixed by Greek letters, α, β, γ.... As to mineral varieties, formerly it had been the custom to give them separate names, even when the difference in composition was negligible. By now many of these names have been abandoned, the only exceptions being gemstones (emerald, ruby, sapphire, amethyst, citrine, morion, etc.). Mineral varieties differing in composition are usually called by the names of their species with either an adjective or a prefix indicating some of their properties (magnesiomagnetite, strontium-aragonite).

NATIVE ELEMENTS AND INTERMETALLIC COMPOUNDS

General. Thirty-odd native elements mostly metals are found in the earth's crust. Also classed with these are a number of gases and very few elements occurring in the liquid state (mercury and some amalgams).

The total weight of the native elements in the earth's crust is very small (less than 0.1 per cent of the total mass). Of this about 0.04 per cent falls to the share of nitrogen and 0.01 to 0.02 per cent to the share

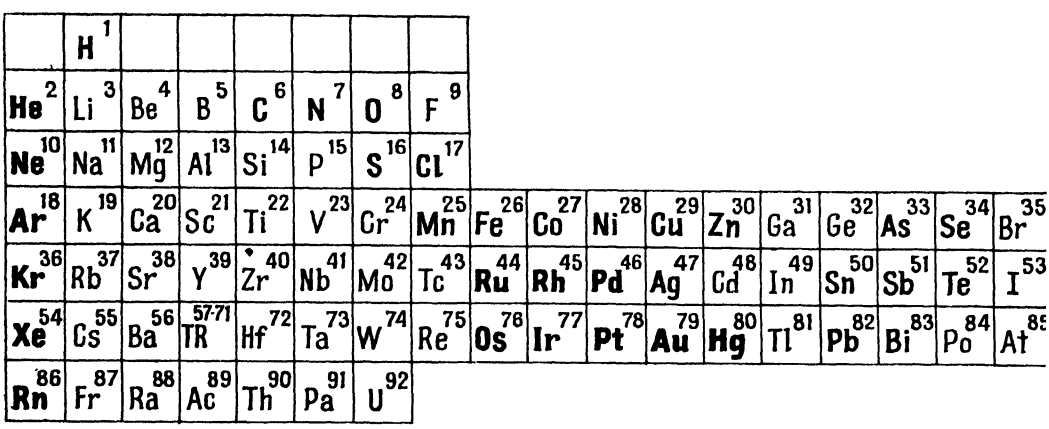


Fig. 61. Elements occurring native (bold and medium type).

of oxygen. The remainder of the native elements therefore constitute not more than 0.05 per cent. They are represented by hydrogen, argon, helium, carbon, sulphur, gold, elements of the platinum group, copper, and bismuth.

Some chemical elements are found in nature almost exclusively in the native state, and are called *noble* elements. In the table (Fig. 61) they are shown bold type.

In the first place these are the noble gases He, Ne, Ar, Kr, Xe, and Rn outstanding for their chemical inertness, i.e., inability to form compounds with oxygen, hydrogen, and other elements. This property of the noble gases is explained by the fact that their atoms have stable outer shells of two or eight electrons.

A special position in the table is held by the group of noble metals (Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au). These are found in the fifth and sixth long periods of the periodic table. In these periods, the atomic radii are almost identical in the vertical groups (the phenomenon known as lanthanidic contraction of atomic volumes). This circumstance plays a very important role in the chemical affinities of these elements in natural conditions, especially in the formation of isomorphous mixtures of noble metals. The metals of the platinum group which form solid solutions are always found together in deposits. The triads of Fe, Co, and Ni in the composition of these minerals usually hold a subordinated place. Isomorphism is even more pronounced in the case of Au and Ag, but Cu rarely occurs in them in solid solution.

Of the other native metals found in the subperiods on the right-hand side of the table, the so-called semimetals (As, Sb, and Bi) are the most widespread. Despite some similarity in chemical properties, these elements occur in nature in different conditions. Only arsenic and antimony occasionally form the intermetallic compound AsSb.

Of the native nonmetals, free hydrogen containing impurities of other gases, is often found in rocks and economic minerals. Nitrogen and oxygen, as known, are the principal constituents of the atmosphere. Carbon usually occurs in two modifications which differ in crystal structure. Native sulphur is for the most part the product of partial oxidation of H_2S and, less often, of the reduction of SO_2, as well as of certain sulphates and sulphur-rich organic compounds.

As many as 80 mineral species and varieties are classed under this division by the criterion of their chemical composition. This greatly exceeds the number of their constituent elements. Some of the elements occur in two or more *polymorphous* modifications (diamond, graphite, α-sulphur, β-sulphur, etc.). Other elements which occur in the native state, may also form *solid solutions* with each other, e.g., electrum (Au, Ag) and palladic platinum (Pt, Pd).

Also common are *intermetallic* compounds which have stoichiometric formulas and are distinguished by specific features of crystal structure (e.g., algodonite—Cu_3As, stibiopalladinite—Pd_3Sb, discrasite—Ag_3Sb, etc.). Along with compounds of a definite composition there are others the composition of which is variable, e.g. (Pt, Fe), (Pt, Cu), etc. The number of intermetallic compounds that are obtained artificially is truly enormous.

Crystal structure and the physical properties of minerals. Native elements occurring in the solid state have different crystal structures. As far as the type of atomic linkage is concerned, predominant are the most closely packed structures with metallic bonding, occasionally with features of bonding which is transitional between heteropolar bonds and van der Waals forces. Some essential common properties of native metals depend upon these characteristics.

Of all natural substances, native *metals* are the best conductors of heat and electricity. When polished, all of them possess a strong me-

tallic lustre, i.e., high reflecting power. The refractive indices on which lustre depends are of the highest order. Only in the case of gold, silver and copper are the refractive indices less than 1.0, but high enough to make them highly reflective (Fig. 20). The indices of absorption of light of these metals are also exceptionally high.

The overwhelming majority of native metals are silver- or tin-white. The striking exceptions are gold and copper. These elements may display valencies higher than one would expect from their position in the periodic table ($CuCl_2$, $AuCl_3$). Probably the selective reflection of light is caused by the specific features of the structure of the nuclei of these elements.

Of all known minerals, native metals possess the highest specific gravity (especially in the platinum group of minerals). Those metals whose structure has a coordination number 12 and which have no directive bonds, are highly malleable, have no clearly expressed cleavage and their hardness is low. The only exception as far as hardness is concerned is iridium and minerals containing a high proportion of iridium.

The malleability and plasticity of metals chiefly depend on the number of directions to which the most closely-packed sheets are at right angles. In media with cubic closest packing, there are four such directions, whereas in the hexagonal structure there is only one. Therefore, the metals with structures of cubic packing have greater plasticity than those of hexagonal structure.

Owing to the lanthanidic contraction of atomic volumes, noble metals are more inert chemically. This is why gold and metals of the platinum group are widely distributed in valley placers.

The *semimetallic* group (arsenic, antimony, bismuth), whose cubic structures are, so to speak, partially distorted, differ somewhat from typical metals in physical properties. The smallest distortions in crystal structure are observed in bismuth, which has the strongest lustre and the lowest brittleness and hardness in this group. All the three metals have common morphological features and cleavage directions, which strictly follows from the specific features of their crystal structure.

The metalloids are entirely unlike typical metals in their crystal structures and properties depending on them. They will be characterised in detail in the descriptions of individual minerals.

1. GOLD GROUP

This group includes typical native metals, such as copper, silver, and gold, and their varieties in terms of chemical composition.

Of these elements, gold occurs in nature mostly in the native state and rarely in the form of tellurides. Silver frequently occurs in the form of sulphides and halides. Copper in the native state occurs much more rarely than in compounds with sulphur, oxygen and other elements.

All these metals crystallise in the cubic system, forming crystal structures of the same type. Gold and silver, the unit cells of which are

almost equal in size, form solid solutions, whereas copper, whose unit cell is smaller, forms solid solutions with gold only at high temperatures and these disintegrate on cooling. For the silver-copper system, the limits of their solubility in one another are extremely narrow.

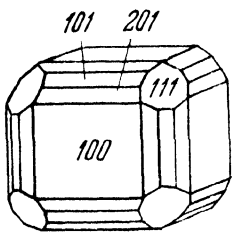


Fig. 62. Native copper crystal.

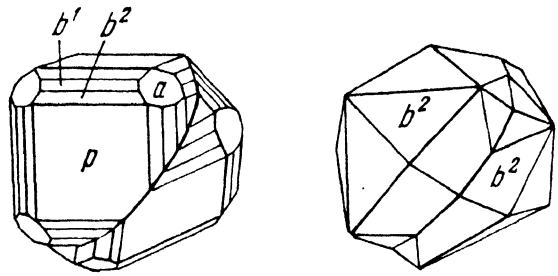


Fig. 63. Twins of native copper crystals, on {111}: *p* {100}, *a* {111}, b^1 {101}, b^2 {201}.

COPPER, Cu. **Chemical composition.** Usually chemically pure. Sometimes contains impurities: Fe (up to 2.5%), Ag (often as inclusions of native silver), Au, rarely as a 2-3% solid solution (*auric copper*).

System, cubic; symmetry, hexaoctahedral $3L^4L_6^3 6L^2 9PC$. Space group $Fm3m(O_h^5)$. $a_0 = 3.6077$. **Crystal structure** of the simplest type is a face-centred cube with the closest packing of atoms. Cu atoms are distributed at the apexes of the cube and at the centre of each unit cell face.

Habit. Regularly-shaped crystals are rare (Fig. 62). Chief forms: {100}, {111}, {110}. Penetration twins occur on (111) (Fig. 63), sometimes in the form of crystalline dendrites (Fig. 64). **Aggregates.** Irregular platy dendrites are observed often. Less frequently there are found whole plates formed in the course of exogenous processes in fissures in rocks. Solid masses weighing as much as several tons have been discovered in the upper parts of deposits (the oxidation zone).



Fig. 64. Native copper dendrite.

Colour, typically copper-red, often tarnished. **Streak,** metallic, shiny. **Lustre,** typically metallic.

Hardness, 2.5-3. Malleable. Hackly fracture. **Cleavage,** none. **Specific gravity,** 8.5-8.9. **Other properties.** Excellent conductor of electricity. Conductivity 99.95 (100 for silver).

Diagnostic features. Easily recognised by its colour, malleability, and high specific gravity. Fusible in the blowpipe flame (melting point 1080°). Readily soluble in dilute HNO_3. Soluble with difficulty in HCl, yielding copper chloride. Aqueous solution in ammonia is characteristically blue in colour.

Genesis and occurrence. Native copper is formed in reducing conditions in the course of different geological processes.

Typical *hydrothermal* deposits of economic importance are very rare. An example are the large native copper deposits in the region of Lake Superior (Michigan, U.S.A.), where copper impregnations are associated with zeolites, calcite and other minerals.

Native copper is often observed as microinclusions in basic igneous rocks altered by hydrothermal processes, in which it may be the product of decomposition of copper sulphides.

Native copper most often occurs in the lower parts of *oxidised zones* of copper sulphide deposits, in association with cuprite (Cu_2O), malachite, occasionally chalcocite (Cu_2S), and other copper minerals. It is found as plates or irregular platy dendrites in fissures in host rock in the immediate vicinity of the deposits. Huge tabular slabs of native copper are exhibited at the Leningrad Mining Museum and the Moscow Geological Institute. These came from some old mines in the *Degelen Hills* (Kazakhstan) where masses weighing several tons had been found.

Copper also occurs in *sedimentary* rocks, mostly sandstones, as binding material between the sand particles, or as irregularly-shaped concretions, occasionally associated with cuprite, malachite, azurite, etc., without an apparent association with primary copper deposits. The genesis of such deposits still remains obscure. Of definite interest are the accumulations of irregularly-shaped copper concretions in the sandstones of the *Naukat* deposits in Central Asia.

Remarkable twins and dendrites from the upper levels of the well-known *Turya* copper mines (Northern Urals) were described in 1837 by G. Roze.

Finally, there is the so-called cement copper (Fig. 65) which is found precipitated on iron objects (cramps, bolts, rails, etc.) in abandoned mine workings flooded with water carrying copper sulphates in solution. The ability of metallic iron to precipitate copper from solution is used for obtaining the latter commercially. Iron filings are placed in special concrete reservoirs which are periodically filled with cupriferous mine waters.

When exposed to oxygen, native copper oxydises on the surface. Exposure to water and air results in the formation of hydrocarbonates (malachite, azurite).

Pseudomorphs of native copper occur after cuprite, chalcocite, and occasionally after organic remains (usually fragments of wood).

Uses. The numerous uses of copper as a metal are well known (electrical engineering, machine building, various instruments, utensils, etc.). The process of extracting native copper from its ores is quite simple (by gravity concentration). Therefore, such ores are regarded as economic at much lower tenor than in the case of sulphide and oxidised ores (down to 0.5 per cent for large deposits).

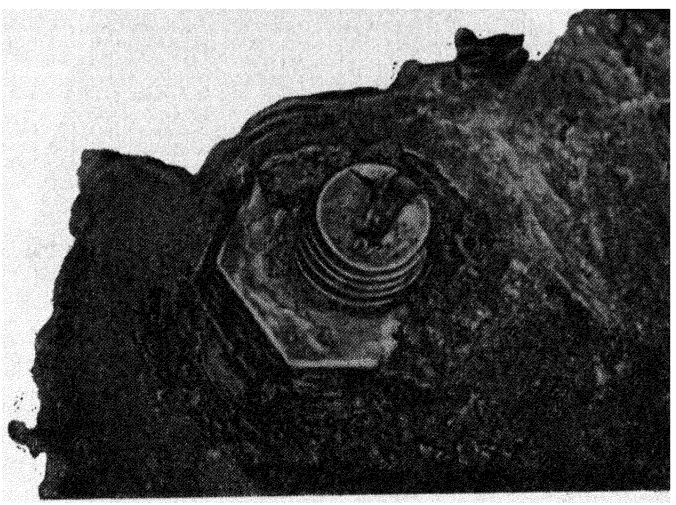


Fig. 65. Cement copper on an iron bolt.

SILVER, Ag. Native silver is not as common in nature as copper, and incomparably rarer than gold.

Chemical composition. Apart from chemically pure silver, there are varieties: *küstelite* containing up to 10% and more of isomorphously admixed gold, *copper* silver, *dyscrasite*, etc.

System, cubic; symmetry, hexoctahedral $3L^44L_6^36L^29PC$. Space group $Fm3m(O_h^5)$. $a_0 = 4.0772$. **Crystal structure.** Face-centred cube. **Habit.** Regularly shaped crystals are rare. Forms {100}, {111}. Twins on (111). **Aggregates.** Sometimes as typical pinnate dendrites (Fig. 66), thin irregular plates and scales. Also typical are mossy, hair-like (Fig. 67), and wire-like forms (Fig. 16). Most common are irregularly-shaped grains, and larger nuggets.

Colour, silver-white on freshly broken surface. Often tarnished black. **Streak,** metallic. **Lustre,** typically metallic.

Hardness, 2.5. Highly malleable. May be beaten into very thin sheets. Fracture, hackly. **Cleavage,** none. **Specific gravity,** 10.1-11.1. **Other properties.** The best conductor of heat and electricity.

Diagnostic features. Recognisable by colour, typically hackly fracture, malleability (easily scratched with the point of a knife), and by specific gravity. Distinguished from platinum by lower hardness and specific gravity. Argentite, Ag_2S, a common accessory of native silver, is darker, lead-grey or black in colour.

Fusible in the blowpipe flame. Soluble in nitric acid giving on addition of hydrochloric acid a curdy precipitate of AgCl. Blackens on contact with H_2S.

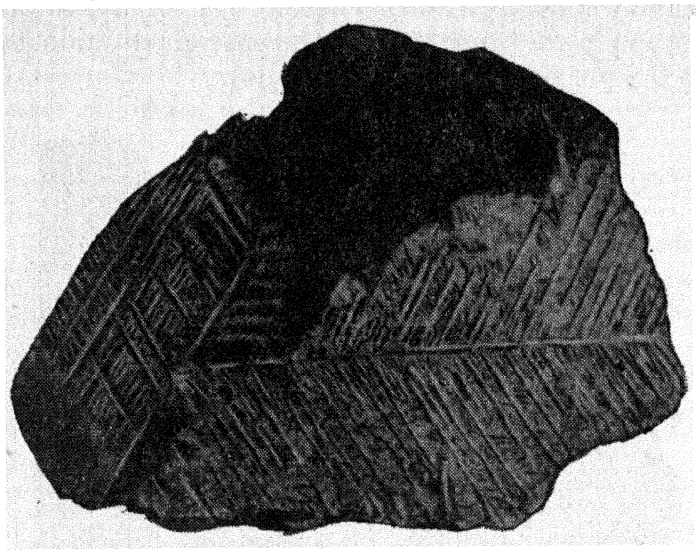


Fig. 66. Native silver in platy dendrites.

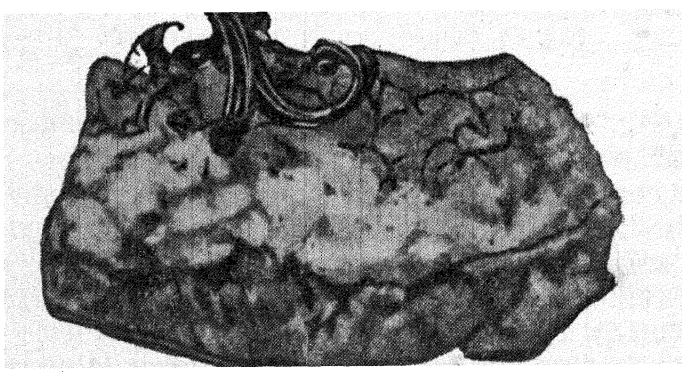


Fig. 67. Twisted filiform and capillary native silver growths on calcite.

Genesis and occurrence. Native silver forms in nature very much like copper. Together with other argentiferous minerals, it occurs in *hydrothermal* vein deposits in association with argentite (Ag_2S) and calcite (Kongsberg, Norway), sometimes with complex sulphides, arsenides and antimonides of various metals, including nickel and cobalt.

Under exogenous conditions, native silver, just as native copper, occur in the *oxidised zone* of sulphide and arsenic-antimony ore deposits, being the product of decomposition of the latter or of reduction from surface solutions by various organic compounds. Native silver thus formed is often in the shape of dendrites, plates, and mossy, and filiform aggregates. It was shown experimentally that fine filiform and

dendritic formations, which sometimes appear in fine patterns, are precipitated from solution on lumps of coal, especially in the presence of soluble organic compounds.

Under surface conditions, native silver is less stable than gold and is often coated with black gouges or films. In localities with a hot arid climate it frequently alters to stable halides (AgCl, etc.).

Uses. The chief uses of silver are in alloys with copper to make silverware, coinage, and for other purposes. Pure silver is used for filigree work, in the manufacture of crucibles for fusing alkalis, in silver plating, for obtaining chemical compounds, and many other purposes. Eighty per cent of the world's silver production comes as a by-product from silver-rich lead-zinc, gold, and copper ores.

GOLD, Au. The most widely distributed member of the group of native elements; gold has been known to man from time immemorial.

Chemical composition. Chemically pure gold occurs very rarely. The so-called native gold nearly always contains an isomorphous admixture of silver (usually 4 to 15 per cent by weight). Some varieties containing more silver are classed as a separate mineral species (see "Electrum").

The varieties include *copper* gold (cuproaurite) with a Cu content of up to 20% (by weight); *porpezite*, palladium gold, with a Pd content of 5 to 11% and up to 4 per cent of Ag; *bismuth* gold (bismuthaurite) containing up to 4% bismuth in solid solution.

System, cubic; symmetry, hexoctahedral $3L^44L_6^36L^29PC$. Space group $Fm3m(O_h^5)$. $a_0 = 4.0699$. **Crystal structure.** Face-centred cube. **Habit.** Rare crystals are commonly octahedral {111} (Fig. 68), less often rhombododecahedral {110}, and occasionally cubic {100}. Faces generally dull, and uneven, sometimes with combination striations parallel to (111) : (310) and (111) : (110) edges. Intergrowths and twins are common on (111). **Aggregates.** Usually as irregularly-shaped grains in quartz or ore masses. The grains vary greatly in size, but are most often microscopic and sometimes hardly visible, even in polished sections. In valley placers, rounded nuggets are often found weighing several grams, and occasionally tens of kilograms. In the weathering zone of primary deposits smaller dendritic gold nuggets of secondary origin are found occasionally. In the ores of primary deposits dendritic crystalline intergrowths and of reticulate patterns are found occasionally along with small crystals (Fig. 69).

Colour, golden-yellow (pale-yellow in the case of argentiferous varieties). **Streak**, metallic, yellow. **Lustre**, typically metallic.

Hardness, 2.5 to 3.0. Malleable and ductile. May be easily beaten into very thin sheets. **Cleavage**, none. **Specific gravity**, 15.6 to 18.3 (19.30 in the case of pure gold).

Other properties. Good conductor of heat and electricity.

Diagnostic features. Characteristic golden-yellow colour, low hardness (can be easily cut with a knife), high malleability and specific grav-

ity, does not oxidise on exposure to air. Distinguished from similar pyrite, chalcopyrite ($CuFeS_2$), and millerite (NiS) by strong lustre and characteristic tint.

Fusible in the blowpipe flame. Insoluble in acids except aqua regia. Soluble in KCN and reagents evolving free chlorine and bromine. Hot high-sulphur alkalis dissolve gold with the formation of sulphides.

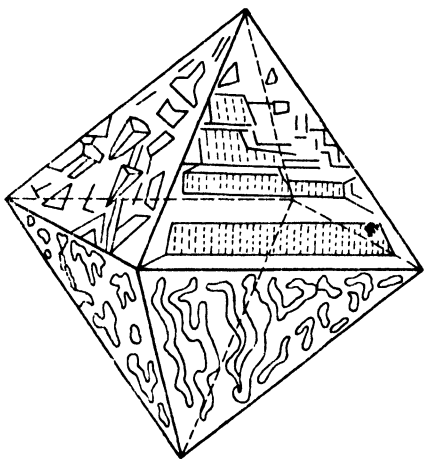


Fig. 68. Octahedra gold crystal.



Fig. 69. Gold dendrite.

Genesis and occurrence. The bulk of gold occurs in typical *hydrothermal* deposits genetically associated with intrusions of acid igneous rocks. Paragenetically, it is most often associated with quartz and sulphides (pyrite, arsenopyrite, tetrahedrite, chalcopyrite, less often with galena and sphalerite) and occasionally with tellurides of gold and silver, etc. So-called "free milling gold" is, as a rule, one of the last minerals formed, often being confined to cracks in the earlier minerals. Besides free milling gold, there is also "bound" gold the presence of which in appreciable quantities in sulphides, mainly pyrite and arsenopyrite (FeAsS), is determined by chemical analyses, only some of it being visible under the microscope. Apparently, a part of it is disseminated in a finely dispersed state, similar to the dispersed phase in crystallosols.

Native gold of recent formation is present in the oxidised zone of sulphide deposits, in association with limonite, azurite, the ochres of lead, bismuth, antimony, etc. The silver present in gold is partly removed by surface weathering, which explains the higher purity of gold on the periphery of the deposits and in fissures. It is an old observation that placer gold contains less silver than gold from primary deposits.

The U.S.S.R. has numerous placer and primary deposits. The biggest nugget in Russian history found in 1842 weighed 35 kg.

Of the deposits in other countries, widely known are the gold fields of Transvaal, South Africa, which accounted for nearly 40 per cent of the world's production of gold. Gold occurs there in metamorphosed an-

cient conglomerates that apparently had formerly been placers. Some of the mine workings there are more than 2 km deep.

Much gold is also produced in the U.S.A. (the Western States and Alaska) and in Canada. The deposits are mostly confined to quartz veins in which gold is generally associated paragenetically with sulphides. Vast gold placer provinces are known in California and Alaska (along the Klondike river, a tributary of the Yukon, and the Seward Peninsula), and in Australia. It was the placers of Victoria (Australia) that yielded the world's biggest nuggets: "Pleasant Stranger" weighing 59.67 kg (1858) and "Desirable" weighing 68.08 kg (1869).

Uses. Gold is the basic metal of currency and coinage. It is also used in jewelry, physical and chemical instruments, dentistry, etc.

The minimum gold content of ore that makes mining a commercial proposition ranges from 1 to 10 g per ton, i.e., from 0.0001 to 0.001 per cent (depending on the size of the deposit and the general economic conditions of its development).

ELECTRUM, (Au, Ag). **System**, cubic. This mineral species embraces varieties of intermediate composition in the isomorphous (Au-Ag) series. Silver content exceeds 15%, usually about 30%, sometimes 40%, and even as much as 50%. Cu, Fe, etc., are present in minor quantities. The physico-chemical properties are likewise intermediate. **Colour**, light-yellow to silver-white. **Lustre**, metallic. Reflectivity very high. **Hardness**, 2 to 3. Malleable and ductile. **Cleavage**, none. **Specific gravity**, 12 to 15.

Occurs almost exclusively in hydrothermal deposits, but much more rarely than native gold and silver. Electrum is typically found in paragenetic association with argentiferous sulphides (argentite, tetrahedrite, proustite, pyrargyrite, etc.). Owing to its high silver content, electrum is lighter than gold and is subject to alteration by weathering: sometimes it is coated with films of halogen and sulphide compounds from which a thin film of native silver is formed under reducing conditions.

2. IRON-PLATINUM GROUP

The group comprises native metals found in the periodic table under Group VIII (except ruthenium and osmium which will be discussed later): Fe, Co, Ni, Rh, Pd, Ir and Pt.

By the criteria of occurrence and crystal chemistry, the group falls into two subgroups: (a) the iron subgroup, and (b) the platinum subgroup.

The minerals of the *native iron* subgroup which occur in the earth's crust are by the token of their origin classified as those of cosmic origin, i.e., iron meteorites, and exceedingly rare telluric (terrestrial) formations.

The minerals of the *native platinum* subgroup comprising a fairly large number of mineral species and varieties are solid solutions of

such metals as Pt, Fe, Ir, Pd and Rh, sometimes of Ni and Cu, rarely of Au, Os and Sn (though sometimes in large amounts) and also of Pb, Zn, Ag, Co, Mn, Mo (up to 0.006%) and Re (0.00008 to 0.002%).

Polyxene and *palladium platinum* are the most common of this latter subgroup. What is loosely called "native platinum" in most cases is polyxene.

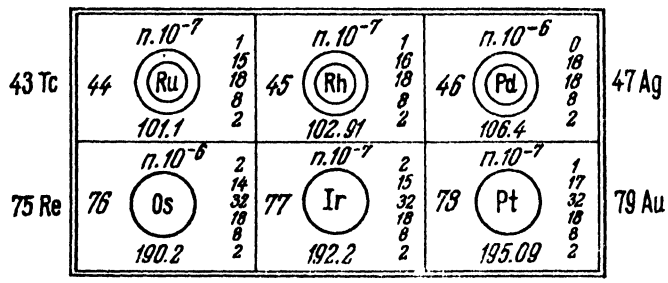


Fig. 70. Triads of platinum-group metals.

A characteristic feature of the minerals of this subgroup is that they do not include isomorphous admixtures of Ru and Os. Although all the six elements of this group have many common physical and chemical features (Fig. 70), they behave somewhat differently under natural conditions. In each triad (Pd and Pt) the elements with the maximum atomic weight on the extreme right of the chart behave very differently from Ru and Os on the extreme left. It is still not known whether these two extreme pairs of elements can isomorphously replace one another, though the minerals in which they are found may be in close paragenetic relationship and not infrequently form intergrowths. The elements Rh and Ir which occupy an intermediate position (Fig. 70) play a dual role: on the one hand, they form chemical compounds of variable composition with Ru and Os, and on the other hand, they often enter into solid solutions with Pd and Pt and less often with Fe, Ni and Cu. It should be noted that the right-hand and the left-hand pairs of the platinum elements are capable in rare cases of forming natural compounds with S, As, Sb, and partly with Te, whereas no such compounds have as yet been found for Rh and Ir. It is no less significant that while the minerals of the Pd-Pt series, as a rule, crystallise in the cubic system (copper-type crystal structure), the minerals of the Ru-Os series clearly appear as compounds of variable composition crystallising in the hexagonal system (in osmium-type crystal structures).

It is because of that the minerals formed by the platinum elements are divided into two parts, one classed with the iron group, and the other (osmium-ruthenium) as an independent group.

IRON, α-Fe. Synonym: ferrite.

Chemical composition. According to chemical analyses, telluric iron is almost pure iron with minor admixtures of: Ni up to 0.6%, some-

times up to 2%, seldom more; Co up to 0.3%; Cu up to 0.4%; Pt up to 0.1%.

System, cubic; symmetry, hexoctahedral $3L^4 4L_6^3 6L^2 9PC$. Space group. $Im3m(O_h^9)$. $a_0 = 2.8607$.

Occurs extremely rarely in very small crystals. Usually as minute irregularly-shaped grains, less often in larger accumulations. **Crystal**

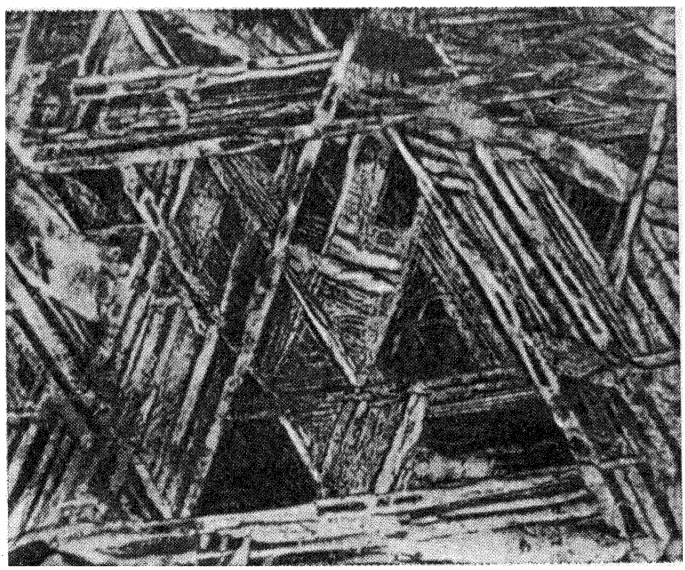


Fig. 71. Widmanstätten figures on a polished surface of an iron meteorite.

structure. Several polymorphous modifications of iron have been established. Of these γ-Fe, a high-temperature modification (above 906°) has the structure of a face-centred cube of the copper-type ($a_0 = 3.63$), and α-Fe, a low-temperature modification, has the structure of a centred cube of the α-Fe type ($a_0 = 2.86$).

Colour, steel-grey, in polished sections metallic white. **Streak**, shiny, steel-grey. **Lustre**, typically metallic on fresh fracture.

Hardness, 4 to 5. Malleable. **Cleavage**, on {100}. **Specific gravity**, 7 to 7.8. **Other properties.** Strongly magnetic.

Diagnostic features. Distinguished from native platinum by solubility in nitric acid, lower specific gravity, strong magnetism and ready oxidation in air. Nickel-poor varieties precipitate metallic copper onto their surface from a solution of copper sulphate. When polished and etched, the surface of meteoric iron usually shows a coarse-latticed structure (widmanstätten figures, Fig. 71), never observed in telluric iron.

Genesis and occurrence. The rare occurrences of telluric native iron are confined to basic and ultrabasic igneous rocks. Larger masses have been found in the basalts at Uifak on Disko Island, Greenland, and near Kassel, Germany. In both localities it is associated with pyrrhotite

(FeS) and cohenite (iron carbide, Fe_3C). It has been repeatedly found as microscopic grains in altered (serpentinised) ultrabasic rocks, also in paragenesis with pyrrhotite, occasionally with magnetite, being the product of the reduction reactions of the latter.

There are also indications of its formation by exogenous processes as impregnations in siliceous schists on the island of Kalimantan (Borneo), in the products of coal fires and in peats.

All these occurrences are of no economic importance.

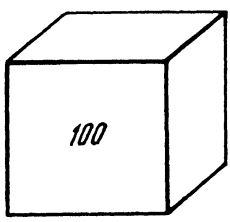


Fig. 72. Cubic crystal of polyxene.

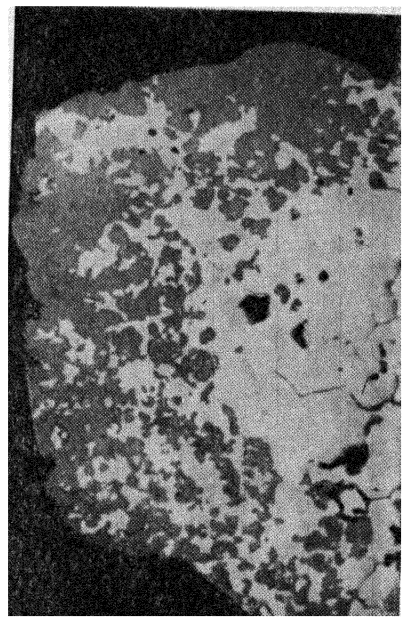


Fig. 73. Half of a cut and polished nugget from a primary deposit. Polyxene (white) and chrome spinellids (grey). × 3.

POLYXENE—(Pt, Fe). The name originates from its numerous isomorphous admixtures; "poly" is the Greek for many and "xenos", foreign. Polyxene is the most widespread platinum mineral in the earth's crust.

Chemical composition. Pt 80 to 88%, Fe 9 to 11%, sometimes diminishing to 4 or 5 per cent or increasing over 11 per cent (with corresponding changes in the Pt content). Isomorphous admixtures: Ir up to 7%—*iridioplatinum*; Pd 0.1 to 1.0%, sometimes up to 7% and more—*palladium platinum*; Rh 0.1 to 0.5%, sometimes as high as 4 to 5%—*rhodium platinum*; Cu up to 0.8%; Ni—from traces up to tenths of a per cent, sometimes in sizable quantities—*nickel platinum.*

System, cubic; symmetry, hexoctahedral $3L^44L_6^36L^29PC$. Space group $Fm3m$ (O_h^5). $a_0 = 3.9158$. **Crystal structure.** Face-centred cube (Cu-type). **Habit.** Usually irregularly shaped grains; rare small crystals are predominantly cubic in form (Fig. 72). The combination of faces, besides the dominant form {100}, include {110}, {210}, {310} and some others. Penetration twins with (100) as the twinning plane and contact twins on (111) are the most frequent forms of twinning. **Aggregates.** Individual grains of native platinum occurring in ores often form small clusters, and sometimes solid masses or nuggets (Fig. 73). The biggest nugget ever found in a primary deposit in the Urals weighed

427.5 g. Nuggets found in placers were sometimes as big as 10 × 18 cm and weighed from 8 to 9 kg.

Colour, silver-white to steel-black. **Streak**, metallic, steel-grey. **Lustre**, typically metallic.

Hardness, 4 to 4.5 and as high as 6 to 7 in iridium-rich varieties. Malleable. Hackly fracture. **Cleavage**, usually none. **Specific gravity**, 15 to 19. It has been observed that the lower specific gravity is due either to the presence of cavities filled with natural gases or to inclusions of foreign minerals. **Other properties.** Magnetic. Good conductor of electricity.

Diagnostic features. Outwardly polyxene most closely resembles native silver and native iron. It is distinguished from native silver by greater hardness and higher specific gravity, by being infusible in the blowpipe flame and insoluble in acids (except aqua regia). The latter property also distinguishes it from native iron.

Genesis and occurrence. The platinum minerals, in the majority of cases, occur in typically magmatic deposits genetically related to *ultrabasic* igneous rocks. They are among the last to crystallise in ore bodies (after silicates and oxides) at the hydrothermal stage of the magmatic process.

Palladium-poor platinum minerals (polyxene, iridioplatinum, etc.) occur in deposits in dunites—olivine non-feldspatic rocks high in magnesia and low in silica. Paragenetically, they are very closely associated with chrome-spinellids which are oxides of complex composition: $(Fe, Mg)(Cr, Al, Fe)_2O_4$.

Palladium platinum and nickel-palladium platinum are, for the most part, found in *basic* igneous rocks (norites, gabbro-diabases), generally in association with sulphides: pyrrhotite (FeS), chalcopyrite ($CuFeS_2$), and pentlandite $(Fe, Ni)_9S_8$.

Under exogenous conditions the disintegration of rocks and primary deposits gives rise to platinum placers (Fig. 56). The majority of the minerals of the subgroup are chemically inert under these conditions.

Along with gold, platinum has been known to man since ancient time. In Europe, platinum attracted attention in 1735 when Spanish mathematician Antonio de Ulloa, who had travelled in South America, brought from Colombia metallic grains resembling silver in colour, but strongly differing from the latter in other properties.

In the Urals, native platinum first attracted attention as an admixture to placer gold in 1819. Later, rich platinum placers of world importance were found in the *Middle* and *Northern Urals*, where they were confined to outcrops of ultrabasic rock masses (dunites and pyroxenites). Numerous small primary deposits occur in the dunite mass of *Nizhny Tagil* (the Urals). Native platinum (polyxene) accumulations, more often than not, are confined to chromite ore bodies composed of chrome-spinellids with an admixture of silicates (olivine and serpentine).

At the present time, a major supplier of platinum metals for industry and commerce is the ore deposit at Sudbury (Canada) from which they are extracted as a by-product of nickel, copper and cobalt.

Uses. Originally, not only was platinum rejected as useless, but was considered to be a harmful impurity of placer gold with which it was extracted. It was either discarded with the tailings of gold washing or used by hunters for shot. Sometimes, attempts were made to gild and pass it for gold. Thus, the first articles made of native platinum in the Urals, later displayed at the Leningrad Mining Museum, were crude chains and rings, barrel hoops, etc. It was only later that the outstanding properties of the platinum metals were discovered.

These valuable properties include refractoriness, electrical conductivity and chemical inertness, all of which make platinum an important material in the manufacture of laboratory equipment, the production of sulphuric acid, in electrical engineering, etc. A great deal of platinum is consumed in jewelry and dentistry.

"Crude" platinum is delivered to special refineries where it is separated into its pure constituent metals.

3. OSMIUM-RUTHENIUM (OSMIRIDIUM) GROUP

These two elements are found on the extreme left of the triads of the platinum group elements in the periodic classification (Fig. 70). In nature they characteristically isomorphously replace one another and readily form solid solutions with the elements in the middle of these triads, i.e., with rhodium and especially with iridium, but not with palladium or platinum. The presence of platinum as an element, though often indicated by chemical analysis of the minerals of the group, is probably limited to mechanical impurities, which is in some cases confirmed by the microscopic examination of polished sections. Thus, the principal metals of the group are osmium and iridium and, to a lesser degree, ruthenium and rhodium.

Although found together with the minerals of the iron-platinum group, the minerals of this group sharply differ from them in many properties such as: (1) characteristically tabular crystal habit; (2) pronounced optical anisotropy; (3) definitely higher hardness due to which the osmiridium platelets stand out in polished sections against the background of native platinum (Fig. 74); (4) a relatively high specific gravity; and (5) an unusual chemical inertness (insoluble even in boiling aqua regia).

The principal species are generally distinguished by their osmium-to-iridium ratio and content.

NEVYANSKITE—(Ir, Os). Named after its place of discovery in the Nevyansk district north of Sverdlovsk (the Urals). The most widespread mineral variety of this group in nature.

Chemical composition. The minerals described under the general name of nevyanskite vary in the content of individual metals as follows (per cent): Ir 46.8 to 77.2, Os 21.0 to 49.3, Ru 0 to 0.5, Rh 0.5 to 7.7, Pt 0.1 to 5.5, Cu 0 to 0.9, Fe 0 to 1.4.

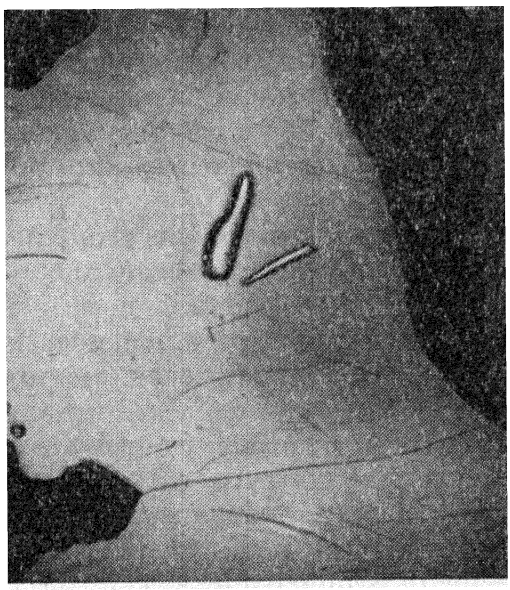


Fig. 74. Two plates of osmiridium of different hardness (difference in relief) showing against the polished surface of a polyxene grain (white). Dark-grey surrounding grains are chrome-spinellids. × 75.

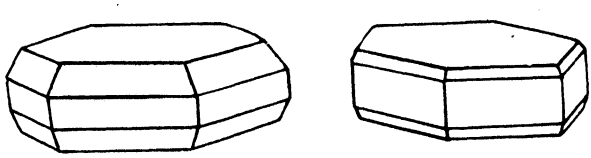


Fig. 75. Osmiridium crystals.

The Ir : Os ratio varies from 4 : 1 to 1 : 1. Sometimes there is a large proportion of rhodium isomorphously admixed with iridium.

System hexagonal; symmetry dihexagonal-dipyramidal $L^6 6 L^2 7 PC$. Space group $C6/mmc(D^4_{6h})$. $a_0 = 2.62$; $c_0 = 4.60$.

Crystal structure hexagonal, closest packing. **Habit.** In contrast to the minerals of the iron-platinum group, the varieties of this group are very well individualised crystallographically. Due to the predominant {0001} pinacoidal development, the crystals are usually small hexagonal plates or tabular grains (Fig. 75) bounded at the sides by $\{10\bar{1}0\}$ prism and $\{10\bar{1}1\}$ hexagonally-dipyramidal faces. Hexagons with unequal sides, approximately triangular in shape, have been observed. Intergrowths of platy individuals fairly frequent.

Colour, tin-white to light-grey. **Lustre**, metallic. Optically anisotropic.

Hardness, 6 to 7. Brittle. **Cleavage**, {0001} perfect, but the folia are not easily separated. Folia friable. **Specific gravity**, 17.0 to 21.0. Low specific gravity is caused by the presence of small gas-filled vesicles, sometimes very numerous (up to 17% by volume).

Diagnostic features. Easily recognisable by platy habit, lighter colour (as compared with syssertskite) and higher hardness.

Infusible in the blowpipe flame. When fused with nitre, gives off fumes of osmic anhydride (OsO_4) with a pungent odour. When the fused mass is dissolved in water, a black iridium powder is precipitated. Highly resistant to acids.

Genesis and occurrence. Minerals of this group are for the most part genetically associated with igneous ultrabasic rock masses (dunites and peridotites) in which they are found in close association with the platinum-group minerals, chrome-spinellids, occasionally with copper sulphides. They may also occur in the rocks, i.e., are not accompanied by other ore materials.

Occurrences have been recorded from hydrothermal auriferous quartz veins. Nevyanskite intergrowths with gold have also been found.

Due to its chemical inertness nevyanskite, together with gold and native platinum minerals, passes into placers deriving from the weathering and erosion of primary deposits.

Osmiridium occurs in placers confined to the outcrops of ultrabasic igneous rock masses. It is found as insignificant admixture in many gold placers in the Urals, Siberia, and also in California and Oregon (U.S.A.). On the island of *Tasmania* placers are known in which the osmiridium minerals prevail over the platinum metals. Osmiridium is also extracted as a by-product at the *Witwatersrand* gold fields (Transvaal, South Africa).

Uses. The larger crystals (at least 1 mm in diameter) of osmiridium are used in the natural state (without chemical treatment) in the manufacture of instruments for special purposes (grain no less than 0.5 mm in size, preferably oval, not platy, are required for this purpose). Smaller grains are used for fountain-pen nibs, the cutting parts of surgical instruments, etc.

SYSSERTSKITE, (Os, Ir). Named after the place of discovery—the Syssert district (near Sverdlovsk) in the Urals.

Chemical composition. In syssertskite osmium prevails over iridium. Ru is often present in considerable quantities, replacing osmium.

System, hexagonal; symmetry, dihexagonal dipyramidal. Syssertskite has been observed in hexagonal platy crystals, rounded plates and fragments (in platiniferous placers). No special study of its crystals has been made.

Colour, steel-grey to dark-grey. **Lustre**, dull metallic.

Hardness, about 6. Brittle. **Cleavage**, {001} distinct. **Specific gravity** varies from 17.8 to 22.5. Magnetic properties unstudied.

Diagnostic features. Distinguished from nevyanskite only by darker colour. Other distinguishing features can be established only by chemical analysis.

Infusible in the blowpipe flame. On thorough ignition in an oxidising flame, becomes black, giving off vapours of osmic anhydride (OsO_4) of pungent unpleasant odour. Fused with nitre, forms a green mass which on boiling gives a black precipitate of iridium. Highly resistant to acids.

Genesis. See "Nevyanskite". Often occurs together with nevyanskite both in placers and in primary platinum deposits.

4. GROUP OF SEMIMETALS

Besides arsenic, this group includes antimony and bismuth, i.e., the elements of the long periods of Group V of the periodic table. All of them are found native, though rarely. They crystallise in the same system and form crystal structures of the same type. However, they do not occur together nor do they form solid solutions or compounds of definite composition, with the exception of arsenic and antimony which at high temperatures form solid solutions in all proportions, while at low temperatures only AsSb (allemontite), a stable intermetallic compound, is formed.

The structural peculiarity of the semimetals under consideration is that each atom is bonded by covalent bonds to three out of the six atoms surrounding it, thus forming sheets of closely packed structural units. Between the layers, the bonding is by van der Waals forces, i.e., is very weak, which results in perfect cleavage along (0001), high optical anisotropy and low hardness.

ARSENIC, As. Found comparatively rarely and usually in small quantities*.

Chemical composition. Arsenic content 84 to 98%. Impurities: Sb 1.7 to 9.2%, less often Ag, Fe and Ni, occasionally Bi and V. It is possible that the content of Ag, Ni, Fe and Bi is due to mechanical inclusions of foreign minerals (native bismuth, and nickel and iron arsenides with which native arsenic is sometimes closely intergrown).

System, trigonal; symmetry, ditrigonal scalenohedral $L_6^3 3L^2 3PC$. Space group $R3m(D_{3d}^5)$. $a_{rh} = 4.142$; $\alpha = 54°07'$. **Habit.** Extremely rare crystals, rhombohedral or pseudocubic. **Aggregates.** Usually occurs in crusts with a reniform surface; stalactitic, conchoidal formations (Fig.76) which show a crystalline granular structure on fracture.

Colour, tin-white on freshly broken surface. On exposure to air it soon turns yellow-brown and then black. **Streek**, grey, tin-white. **Lustre**, metallic, strong on fresh fracture, soon grows dull, and with time blackens due to surface oxidation.

Hardness 3.5. Brittle. **Cleavage** {0001} perfect and $(01\bar{1}2)$ less perfect. Fracture granular. **Specific gravity** 5.63 to 5.78.

* Of the several arsenic modifications, rhombohedral arsenic is the most stable.

Diagnostic features. Native arsenic is rather easily identified by its form, black-tarnished surface, high specific gravity, strong metallic lustre on fresh fracture and perfect cleavage.

Volatilises in the blowpipe flame (at about 360°) without fusion, giving off a peculiar garlic odour, and leaves a white coating on charcoal. Liquefies only under high external pressure. In the closed tube gives an arsenic mirror. Smells of garlic when struck with a hammer.

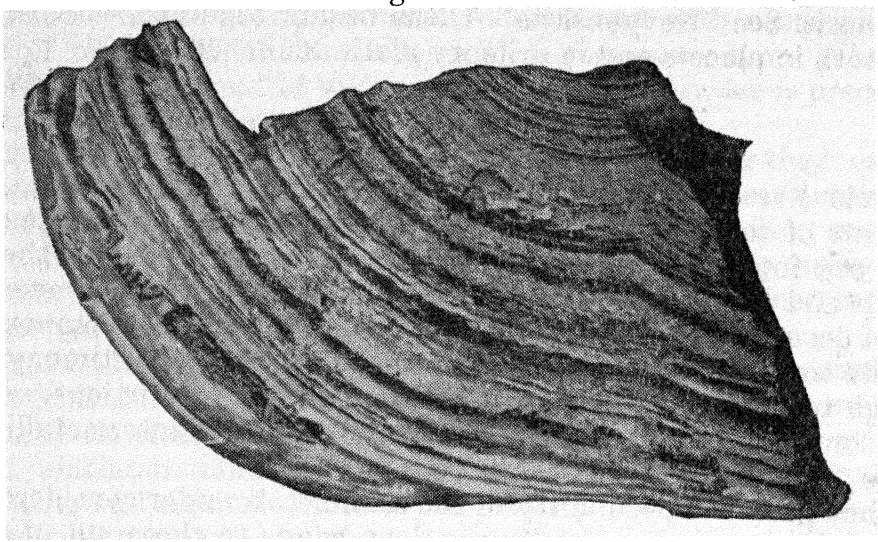


Fig. 76. Fragment of a large nodule of native arsenic (¾ natural size).
Concentrically-banded structure well visible on weathered surface.

Genesis and occurrence. Arsenic is found in *hydrothermal* deposits in cavities as metacolloidal formations, and is evidently formed at the very last stages of hydrothermal activity. May occur in association with diverse arsenides, antimonides, less often sulphides of nickel, cobalt, silver, lead, etc., as well as nonmetallic minerals.

Secondary formation of arsenic in the weathering zones of arseniferous ore deposits mentioned in literature seems highly unlikely because under the circumstances it is very unstable and rapidly oxidises with complete decomposition. The black crusts formed constitute a mixture of arsenic and arsenolite (As_2O_3) which, in the end, turn into pure arsenolite.

In the U.S.S.R., native arsenic has been found in a few deposits. As reniform masses on crystalline calcite together with galena and sphalerite it has been repeatedly recorded from the *Sadon* hydrothermal lead-zinc deposit. Large reniform masses of native arsenic of a concentric-conchoidal structure were found on the left bank of the *Chikoy* river (Trans-Baikal Region). The only mineral observed in paragenesis with arsenic was calcite occurring as fluccans on the walls of thin veins cutting across ancient crystalline schists. Arsenic fragments (Fig. 76) have also been found in the area of *Dzhalinda* Station of the Amur railway, and elsewhere.

In a number of deposits of Saxony (Freiberg, Schneeberg, Annaberg, etc.) native arsenic was found in association with arsenious compounds of cobalt, nickel, silver, native bismuth, etc.

These and other finds of native arsenic are of no practical value.

BISMUTH, Bi. Although native bismuth occurs much more frequently than arsenic and antimony, it is a rare mineral nevertheless and usually is not found in large accumulations.

Chemical composition. Generally bismuth is almost pure. However, there may be insignificant impurities or rather traces of Fe, As, S, and Sb.

System trigonal; symmetry ditrigonal-scalenohedral $L_6^3 3L^2 3PC$. Space group $R3m(D^5_{3d})$. $a_{rh}=4.736$; $\alpha=57°16'$. Extremely rare crystals are poorly developed. More frequently occurs as impregnated grains, sometimes as large, lamellar or granular aggregates, and also as plumose dendrites.

Colour on fresh fracture, silver-white with a yellow tinge; with time a peculiar reddish tarnish appears. **Streak**, grey. **Lustre**, metallic, strong.

Hardness, 2.5. Slightly malleable. **Cleavage**, {0001} highly perfect and $\{10\bar{1}1\}$ distinct. **Specific gravity**, 9.70 to 9.83 (when liquid 10.03). **Other properties.** Melting point about 270°. Boiling point about 1450°. Diamagnetic.

Diagnostic features. Easily recognisable by slight yellow-reddish tarnish, strong metallic lustre, perfect cleavage, relatively low hardness and relatively high specific gravity.

Readily fusible in the blowpipe flame. On prolonged blowpiping vaporises giving white coatings on charcoal which change to orange-yellow and become lemon-yellow on cooling. Fused with KI and S, gives a characteristic coating on charcoal with a bright-red fringe of BiI_3. Readily soluble in nitric acid, giving a white precipitate upon dilution.

Genesis and occurrence. Bismuth is almost invariably found in formations of *hydrothermal* origin.

In some instances it is genetically associated with high-temperature formations, occasionally with pegmatites but more often with tin-tungsten deposits—in association with such minerals as arsenopyrite (FeAsS), bismuthite (Bi_2S_3), wolframite ($FeWO_4$), molybdenite (MoS_2), cassiterite (SnO_2), topaz, beryl, tourmaline, etc.

In other instances, native bismuth is closely associated with the arsenious compounds of nickel and cobalt, uranium minerals, sulphur compounds of silver, lead and zinc, etc. Examples are the associations in the numerous veins of the Erzgebirge mountains (at the border between Saxony and Bohemia) in the vicinity of *Schneeberg*, *Annaberg* and *Jachymov*. Native bismuth occurs in larger quantities together with bismuthite (Bi_2S_3) in the quartz-barite veins of the *Tasna* and *Oruro* in Bolivia, and elsewhere.

5. SULPHUR GROUP

This group comprises native elements of Group VI of the periodic table: sulphur, selenium, and tellurium. Of these sulphur is a typical metalloid, whereas selenium and especially tellurium possess certain properties of semimetals.

Also three natural polymorphous modifications of sulphur are known, of which only the orthorhombic α-sulphur is stable in natural conditions. At atmospheric pressure and temperatures over 96.5°, it changes to β-sulphur in the monoclinic system and on cooling resumes its former crystallinity; γ-sulphur, although monoclinic, is not stable at atmospheric pressure and low temperatures, and at room temperature it turns into α-sulphur. Three other polymorphous modifications of sulphur obtained artificially never occur in nature.

SULPHUR, S. α-sulphur, the most stable form at room temperature, is generally referred to as orthorhombic sulphur of simply sulphur.

Chemical composition. Occasionally native sulphur is chemically pure, but usually it is contaminated with mechanical impurities such as clayey or organic matter, oil drops, gases, etc. Also known are rare varieties with an isomorphous admixture of Se, usually up to 1 per cent, less often up to 5.2 per cent in the form of *selenosulphur*, and also with Te, As, and, in exceptional cases, with Tl.

System, orthorhombic; symmetry, rhombic-dipyramidal $3L^23PC$. Space group $Fddd$ (D_{2h}^{24}). $a_0=10.48$; $b_0=12.92$ and $c_0=24.55$. **Crystal structure.** Orthorhombic sulphur, according to X-ray data, has a *molecular* and very complex lattice which is uncommon in inorganic substances. In the crystal structure each atom on two sides has spheres which intersect with the spheres of the adjacent atoms, chains composed of 8 atoms forming closed zigzag-shaped or "puckered" rings (Fig.77). Hence it is evident that the sulphur molecule is S_8. The distance between the S—S atoms is 2.12 Å. The unit cell is composed of 16 such electrically neutral molecules (rings) very loosely held together by van der Waals forces. **Habit.** Commonly pyramidal (Fig. 78) or truncated pyramidal (Fig. 79), less commonly rhombotetrahedral (Fig. 80). Characteristic forms: {001}, {011}, {111}, {113}, etc. Twins are rare with (111), sometimes (011) and (110) as the composition plane. **Aggregates.** Often massive or earthy. Occasionally in sinter reniform forms and coatings (in areas of active volcanoes).

Colour. α-sulphur may have various shades of yellow: straw yellow, honey yellow, yellowish grey, brownish, and black (due to carbonaceous impurities). **Streak**, almost white, though powder is pale yellow. **Lustre**, adamantine on faces, greasy on fracture. Crystals translucent.

Hardness, 1 to 2. Brittle. **Cleavage** {001}, {110} and {111} imperfect. **Specific gravity**, 2.05 to 2.08. **Other properties.** Very poor conductor of electricity and heat (good insulator). Becomes negatively electrified on rubbing. May decrepitate from the warmth of the hand.

Diagnostic features. Recognisable by colour, low hardness, brittleness, greasy lustre on fracture and low melting point.

Easily melts before the blowpipe and even in the flame of a match (at 112.8°); burns with a blue flame and with the characteristic SO_2 odour (which distinguishes it from similar auripigment, As_2S_3). Readily soluble in carbon disulphide, turpentine and kerosene, but does not decompose in hydrochloric and sulphuric acids. Strong nitric acid and aqua regia oxidise sulphur to H_2SO_4.

Being the only mineral in this section which possesses a *molecular* structure, native sulphur is altogether unique in its properties. The presence of electrically neutral S_8 molecules as structural units explains such properties as poor electrical and heat conductivity, loose intermolecular bonds with the consequent low melting and sublimation points, low mechanical strength, low hardness and indistinct cleavage, due to which it gives very uneven fracture and shows a greasy lustre. The circular shape of the structural units (S_8 molecules) which is strikingly different from the spherical shape also determines the pronounced optical anisotropy of the crystalline matter, the anisotropy of heat expansion, etc.

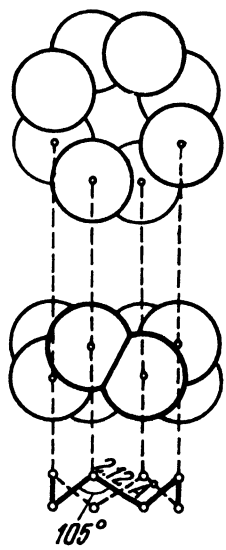


Fig. 77. Top and side views of eight-atom sulphur ring (molecule).
Distribution of atoms shown below.

Such properties as low specific gravity and melting point are taken advantage of in the recovery of native sulphur from deep-seated sulphur-bearing strata. Superheated steam is injected into boreholes, through pipes, and the molten sulphur which incidently drops its impurities rises with the upward stream to the surface where it is collected by most simple methods.

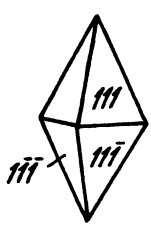


Fig. 78. Sulphur crystal of pyramidal habit.

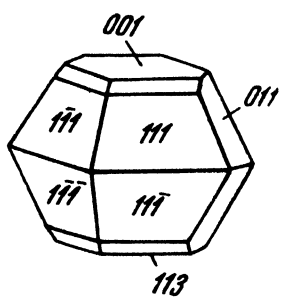


Fig. 79. Sulphur crystal of truncated-pyramidal habit.

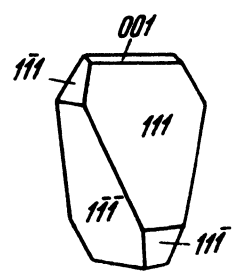


Fig. 80. Rhombotetrahedral sulphur crystal.

Genesis and occurrence. Native sulphur occurs exclusively in the uppermost parts of the earth's crust or right on its surface. It is formed in various ways.

1. During volcanic eruptions, as sublimates on the walls of craters and in rock fissures. Sometimes molten sulphur is carried out with hot waters of solfataric springs and solidifies upon cooling in gullies and valleys in regions of modern active volcanoes (the Kurile Islands, Japan). It is often associated with other sublimates as well as with sulphates formed by the action of SO_2 on enclosing rocks. It is also formed through incomplete oxidation of hydrogen sulphide in solfataras or as a product of the reaction of H_2S with sulphur dioxide:

$$2H_2S+2O=2H_2O+2S;\ H_2S+SO_2=H_2O+O+2S$$

2. Through the decomposition of metal sulphides, chiefly pyrite, in the lower part of the zone of oxidation of ore deposits. It is usually strongly contaminated with various mechanical impurities.

3. Through the decomposition of gypsiferous sedimentary strata. Often occurs in paragenesis with gypsum on the decomposed parts of which it forms crystalline or powdery masses. The mechanism of this process is still not very clear.

4. By sedimentation (biochemically) in normal sedimentary rocks (Fig. 57) usually in beds containing gypsum, solid and liquid bitumens (asphalt, petroleum), etc. Deposits of this type are widespread all over the globe and are of great commercial importance. The bulk of native sulphur apparently has formed syngenetically, i.e., simultaneously with other sediments. However, not infrequently there are found epigenetic sulphur formations in host rocks, due apparently to later migration caused by tectonic processes, transportation by oils, solutions, etc.

The biochemical genesis of sulphur is also linked with the life activity of anaerobic bacteria which results in the evolution of hydrogen sulphide, the incomplete oxidation of which results in precipitation of sulphur.

In the Soviet Union, numerous sulphur deposits are found in Central Asia.

Outside the U.S.S.R., best known are the huge deposits in *Sicily* and those associated with salt domes in *Texas* and *Louisiana* (U.S.A.).

Uses. The most important use of sulphur is in the manufacture of sulphuric acid which is vital to many industries; it is also used in agriculture (pest control), in the rubber industry (vulcanisation), in making matches, fireworks, dyes, etc.

6. CARBON GROUP

This group of minerals also holds a special position among the native elements. It comprises two polymorphous modifications of carbon sharply differing in physical properties: diamond and graphite.

The crystal structure of *diamond* (Fig. 81), which on the whole is similar to that of a face-centred cube, differs from the latter in that the

atoms of carbon are located both on the faces of the cube and also in the centres of half of the small cubes which alternate with small empty cubes. This structure is more clearly shown in Fig. 81*b* as a combination of tetrahedra in which, in addition to the four atoms at the apexes, there is a fifth atom in the centre (Fig. 82*c*). Each apex of each tetrahedron is shared with four adjacent tetrahedra.

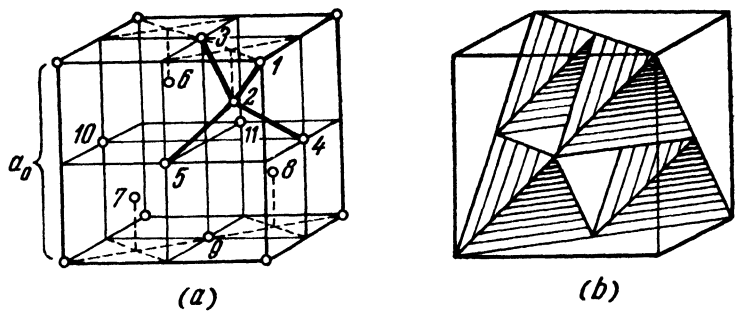


Fig. 81. Crystal structure of diamond.

a – centres of atoms; *b* – the same structure presented as tetrahedra whose apexes and centres are centres of carbon atoms.

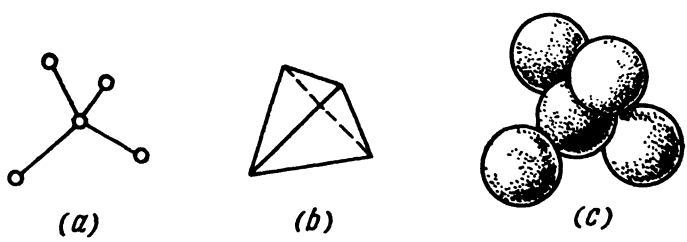


Fig. 82. Different representations of tetrahedral distribution of atoms.

Distances between atom centres in all three figures are equal.

The general conception is that the carbon atoms in the crystal structure of diamond are linked to each other exclusively by covalent bonds along directions connecting the centre of a tetrahedron with its apexes. However, N.V. Belov has suggested a more natural conception of diamond structure as one of the ZnS type with two kinds of ions, C^{4+} and C^{4-} (the C^{4+} cation radius is about 0.15Å and the C^{4-} anion radius is about 1.5Å) which accounts for the closest packing of the anions in the structure. This concept agrees well with the crystal forms of diamond and its properties such as absence of colour, low electrical conductivity, exceptionally high hardness*, high stability within a wide range of temperatures and pressures (in particular it does not show any change when

* From the viewpoint of quantum mechanics, the unusual mechanical strength of diamond is explained by the continuous oscillation occurring in the given structure: the ions being negative at one moment turn into positive ions at the next moment, and vice versa.

heated up to 2500° C in the absence of oxygen), high resistance to acids and alkalis, etc.

The structure of *graphite* differs strikingly from that of diamond. The ions of carbon in graphite lie in sheets which are presented by planar hexagonal nets (Fig. 83). According to N.V. Belov, the crystal structure of graphite consists of most closely packed large C^{4-} anions with half of the triangles in each sheet occupied by smaller C^{4+} cations.* Each ion in the planar net is surrounded by three neighbouring ions at a distance of 1.42 Å (1.54 Å for diamond), while the distance between the planar nets is more than twice as large (3.40 Å). Hence the specific properties of graphite: its much lower specific gravity, as compared with diamond, great ability to split into thin scales, pronounced optical anisotropy, and hardness anisotropy which is revealed only by very accurate and delicate investigation techniques (perpendicular to the cleavage plane hardness is 5.5, but at the same time graphite is so soft owing to the loose cohesion of the sheets so that it soils the fingers and marks paper). The same structural peculiarities explain the non-uniform light absorption of graphite and its consequent black colour.

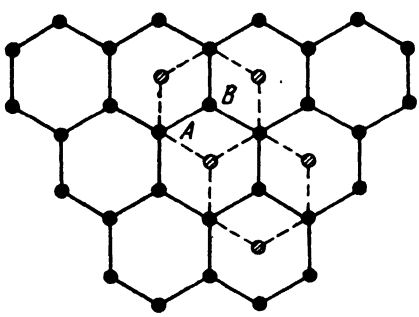


Fig. 83. Distribution of atom centres in structural sheets of graphite.

Each adjacent sheet is, as it were, displaced by half the diameter of hexagonal rings.

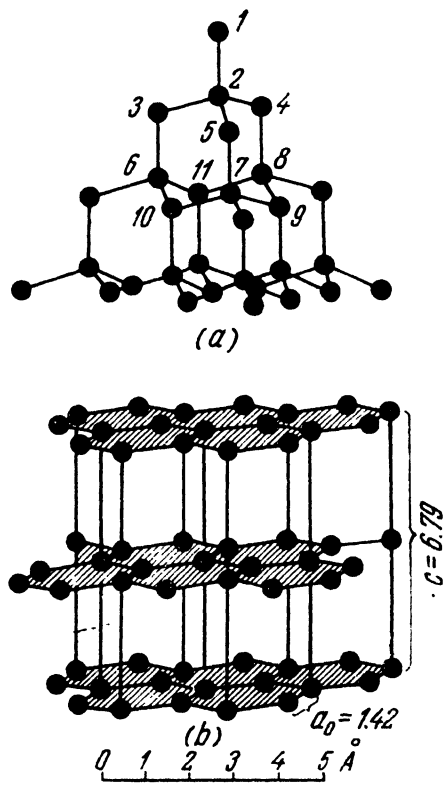


Fig. 84. Distribution of atom centres in diamond (*a*), with planar networks spaced horizontally, parallel to (111); in graphite (*b*).

* "As in the case of diamond, continuous oscillation takes place: the ions that are cations at one moment of time become anions at the next. The resonance of the two geometrically identical structures leads to even shorter distances between the centres of the C atoms as compared with diamond (1.42 Å instead of 1.54 Å). If the difference between the cations and anions is disregarded, the centres of gravity of the C atoms give a network of regular hexagons." (N.V. Belov.)

It is assumed that, in contrast to diamond, the type of bonding in graphite is somewhat metallic, i.e., "metallic" electrons also take part in the bonding. This agrees well with such properties as submetallic lustre, good electrical conductivity, etc. In chemical and thermal stability, however, graphite is quite close to diamond.

If we represent the structure of diamond as in Fig. 84*a*, i.e., along the trigonal axis (cf. the numbers of the atoms in Fig. 81*a*), we shall also observe hexagonal rings in the horizontal planar nets (atoms 6, 11, 8, 9, 7, and 10) with the difference that the nets are not quite planar: three of the atoms are somewhat above the other three. That is why diamond crystals have medium cleavage parallel to {111}, while in graphite crystals cleavage is perfect parallel to {0001}.

DIAMOND, C. The name is derived from the Greek "adamas" meaning invincible (owing to its supreme hardness and resistance to the action of chemical and physical agents).

Varieties: (1) *bort*, irregular intergrowths and spherical radiate aggregates; (2) *carbonado*, close-grained porous aggregates coloured brownish black by amorphous graphite and other impurities.

Chemical composition. Colourless diamonds are pure carbon. Coloured and opaque varieties yield on combustion a residue, as high as a few per cent, containing SiO_2, MgO, CaO, FeO, Fe_2O_3, Al_2O_3, TiO_2, etc. Graphite and other minerals are often present as inclusions.

System, cubic; symmetry, hexoctahedral $3L_4^24L^36P$. Space group $Fd3m(O_h^7)$. $a_0=3.559$.

Habit, octahedral (Fig. 85), less common dodecahedral; seldom cubic, and occasionally tetrahedral. Characteristic forms: {111}, {100}, and {110}. Curved faces are quite frequent (Fig. 86) as well as so-called "dodecahedroids" and "octahedroids" described in detail by Soviet scientists I.I. Shafranovsky and A.A. Kukharenko. Penetration twins occur along (111), less often along (100). Crystals range in size from very fine to very large specimens weighing hundreds or even thousands of carats (a metric carat is 0.2 g). The largest stones ever found: "The Cullinan", 3,025 carats; "The Excelsior", 969.5 carats; "The Victoria", 457 carats; "The Orloff", 199.6 carats; etc.

Colour. Colourless water-transparent or light blue, yellow, brown, and black. **Lustre** strong, adamantine. Refractive index $n=2.40$ to 2.48.

Hardness, 10. Absolute hardness is 1,000 times greater than that of quartz and 150 times greater than that of corundum. Brittle. **Cleavage**, (111) distinct. **Specific gravity**, 3.47 to 3.56. Poor conductor of electricity.

Diagnostic features. Diamond is unique among minerals in its hardness. Other characteristics are its strong adamantine lustre and frequent curved crystal faces. Fine grains in heavy concentrates are easily recognised by their fluorescence in ultraviolet light. The fluorescence colours are usually blue, sometimes green.

Genesis and occurrence. Primary deposits are genetically associated with ultrabasic plutonic igneous rocks: peridotites, kimberlites, etc. In these rocks, diamond probably crystallises at great depths at high temperatures and pressures. Judging by its form and mode of occurrence, diamond was among the first (minerals) to crystallise from the magmas. It is not clear whether diamond crystallised from the carbon contained in the magma itself or from that assimilated from the

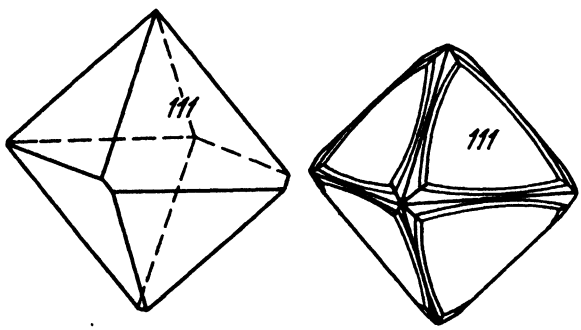


Fig. 85. Octahedral diamond crystals.

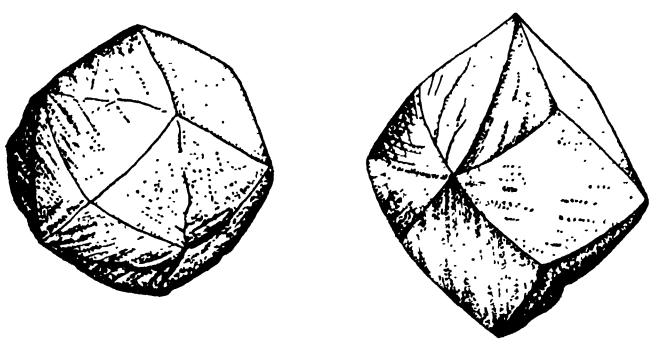


Fig. 86. Diamond crystals with curved faces.

invaded rock. Common associates: graphite; olivine, $(Mg, Fe)_2SiO_4$; chromespinellids, $(Fe, Mg)(Cr, Al, Fe)_2O_4$; ilmenite, $(FeTiO_3)$; pyrope (red garnet); magnetite, $(FeFe_2O_4)$; and hematite, (Fe_2O_3), etc.

The world's largest diamond deposits are located in a number of areas in South Africa: along the Vaal River, in South Western Transvaal, and on the south-western coast of Africa. In these localities the diamond-bearing rocks are semi-decomposed kimberlites which, together with clastic rocks, fill gigantic vertical volcanic pipes which are several kilometres deep. The pipes which are of elliptical or irregular cross section have probably resulted from the tremendous explosive processes which once took place at great depths. In some deposits diamonds are recovered from depths exceeding 1 km (Kimberley). The extracted ore ("blue ground") is crushed and washed at concentration plants. The mean diamond content in the ore is 0.000052 per cent by weight. It was in South Africa that the world's largest diamonds were

found ("The Cullinan", "The Excelsior", etc.). In addition to mines, there are many rich alluvial placers in South-West Africa, in the basins of the Vaal and Orange rivers. The Congo is another major producer of diamond.

Recently relatively many diamond-bearing pipes have been discovered in Northern Yakutia. These are filled, however, with somewhat more recent kimberlites. Some of the pipes were given such names as "The Peace Pipe", "Summer Lightning", etc. The output of diamonds in Siberia is increasing year by year.

Placer diamond deposits are formed through the weathering and erosion of diamond-bearing rocks. They are found in South Africa, Brazil (Minas Gerais), and India where diamond mining dates to ancient times, and where large diamonds like "The Orloff" and "The Koh-inoor" were found. Diamond is also found in some other localities.

Uses. Perfectly transparent diamond is the most valued gemstone. Very small diamonds, and also bort and carbonado are used in metal-working, stonecutting industries, in the production of abrasives, etc.

GRAPHITE, C. The name derives from the Greek "grapho" meaning *I write*. Varieties: *graphitite*—cryptocrystalline variety, *schungite*—amorphous variety, probably derived from the natural coking of coals.

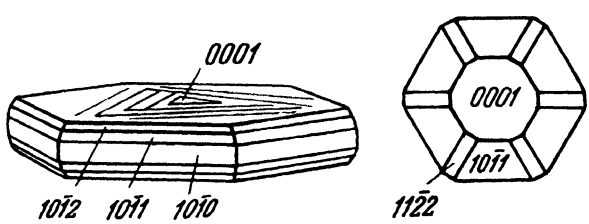


Fig. 87. Graphite crystals.

Chemical composition. Rarely found pure. May contain as much as 10 to 20 per cent of ash comprised of various constituents (SiO_2, Al_2O_3, FeO, MgO, CaO, P_2O_5, CuO, etc.), sometimes also water, bitumens, and gases (up to 2%).

System, hexagonal; symmetry, dihexagonal-dipyramidal $L^6 6L^2 7PC$. Space group $C6/mmc$ (D^4_{6h}). $a_0 = 2.47$; $c_0 = 6.79$. **Habit.** Well-developed crystals extremely rare and are in the form of hexagonal plates or tablets (Fig. 87), sometimes with trigonal striations on the (0001) face. Characteristic forms: {0001}, sometimes $\{10\bar{1}1\}$ and $\{11\bar{2}2\}$, etc. **Aggregates**, often scaly. Less often in rod-like or fibrous masses.

Colour, iron black to steel grey. **Streak**, shiny black. **Lustre**, submetallic; cryptocrystalline aggregates dull. Optically negative. Refractive index $n_y = 1.93\text{-}2.07$. Transmits grey light in thin folia.

Hardness, 1. Thin folia flexible. Greasy touch. Marks paper and soils the fingers. **Cleavage** {0001} perfect. **Specific gravity**, 2.09 to 2.23 (depending on the degree of dispersion and the presence of very fine

pores), 1.84 to 1.98 in the case of shungite. **Other properties.** Good conductor of electricity due to very close packing of atoms in the sheets.

Diagnostic features. Easily recognisable by colour, low hardness, and greasy touch. Distinguished from molybdenite (MoS_2) by darker iron-black colour, weaker lustre, lower specific gravity (floats in bromoform) and higher electrical conductivity (molybdenite is a poor conductor of electricity). When touched with a zinc bar through a drop of $CuSO_4$, a thin film of copper will be deposited on graphite.

Infusible in the blowpipe flame. When heated in oxygen burns with greater difficulty than diamond. Volatilises without fusing in the electric arc. Insoluble in acids. In powdered form burns with a flash when mixed with KNO_3 and heated.

Genesis and occurrence. In nature graphite is formed in the course of reduction processes at high temperatures.

Sometimes occurs in *magmatic* rocks of diverse composition. In many instances, the source of carbon are carboniferous enclosing rocks.

Graphite is also found occasionally in *pegmatites*. In the provinces of Ontario and Quebec in Canada graphite deposits are found in limestones near the contact with igneous rocks. Vein deposits of coarsely laminated graphite occur in Ceylon.

Very widespread are deposits of graphite formed *metamorphically* from coal or bitumen in the conditions of regional metamorphism or under the action of magmatic intrusions.

In the U.S.S.R., vast deposits of graphite are found at *Aliber* in the Tunkin mountains. The graphite is found in the form of stocks in igneous rocks (syenites) and constitutes a mixture of high-grade scaly or finely crystalline graphite with magmatic minerals (microcline, nepheline, etc.). In places these ore bodies are fringed by coarse-grained limestone. The magmatic rocks themselves also contain graphite. Very interesting graphite formations of the secretion type are found within graphite masses. These are irregular small bodies with outer crust of tangentially oriented scales and an internal radial structure. Graphite is believed to be genetically associated with the reduction of the carbon oxide evolved when limestones were engulfed by magma.

Along the north-western shore of the *Sea of Azov* there are worked deposits of impregnated coarse-scaly graphite occurring in the form of superficially weathered beds in ancient metamorphic rocks (gneisses). An interesting point is that marginal portions of intersecting pegmatite and aplite veins contain coarse-crystalline hexagonal graphite individuals, whereas in the middle of the veins finely-crystalline segregations are present.

Uses. Graphite has a wide variety of applications such as in the manufacture of graphite crucibles, in foundry facings, the manufacture of pencils, electrodes, lubricants, and pigments.

SULPHIDES, SULPHOSALTS, AND SIMILAR COMPOUNDS

General. This section deals with sulphur, selenium, tellurium, arsenic and antimony compounds of metals. Many of them are minerals of great economic importance and are an essential part of numerous deposits of metallic ores.

The vast majority of these minerals are sulphur compounds (sulphides and sulphosalts*). All of them, with the exception of hydrogen sulphide, occur in nature as solids.

In all, 40 chemical elements in some form or another combine with sulphur. The most important of them are H, V, Mn, Fe, Ni, Co, Cu, Zn, (Ga), Ge, As, Mo, Ru, (Rh), (Pd), Ag, Cd, (In), Sn, Sb, (Re), (Os), (Ir), Pt, Hg, Tl, Pb, and Bi. The elements given in parentheses do not combine with sulphur and occur only as isomorphous admixtures.

Sulphur compounds, according to V. I. Vernadsky, account for no more than approximately 0.15 per cent of the earth's crust by weight, Fe being the predominant metal constituent in these compounds. The sulphur compounds of all other elements, excluding hydrogen sulphide, constitute a negligible percentage of the weight of the earth's crust (about 0.001%). The elements which form the most common sulphur compounds are Zn, Pb, Cu, Ag, Sb, Bi, Ni, Co, Mo, and Hg.

Selenium compounds (selenides) are known for the following elements: H, Cu, Ag, Hg, Pb, and Bi. Moreover, selenium is often present in sulphur compounds as an isomorphous admixture.

Tellurium compounds (tellurides) are more common in nature than selenides, although the elements which combine with tellurium are fewer in number, namely, Cu, Ag, Au, Hg, Pb, Bi, Ni, and Pt. All these elements form separate minerals.

Simple *arsenic* compounds (arsenides) are known for only a few elements, namely, Fe, Ni, Co, and Pt. Complex compounds in the form of sulphosalts are more widespread as sulphoarsenites, chiefly of Cu, Ag, and Pb.

Simple compounds of *antimony* (antimonides) are known only for Ni, whereas complex compounds such as sulphoantimonites of Cu, Ag, and Pb, are rather common.

* Sulphosalts are the salts of hypothetic sulphoacids the sulphoanhydrides of which would be As_2S_3, Sb_2S_3, Bi_2S_3, etc.

Simple *bismuth* compounds are not known in nature, but sulphobismuthites of Cu, Ag, and Pb have been found.

Selenium, tellurium, arsenic, antimony and bismuth compounds are incomparably fewer than sulphur compounds.

Chemical features of compounds. The periodic table (Fig. 88) shows that sulphur compounds are typical of the elements almost exclusively located on the right-hand side of the table, especially of the metals of

	H 1																
He 2	Li 3	Be 4	B 5	C 6	N 7	O 8	F 9										
Ne 10	**Na** 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17										
Ar 18	K 19	**Ca** 20	Sc 21	Ti 22	**V** 23	**Cr** 24	**Mn** 25	**Fe** 26	**Co** 27	**Ni** 28	**Cu** 29	**Zn** 30	**Ga** 31	**Ge** 32	**As** 33	Se 34	Br 35
Kr 36	Rb 37	**Sr** 38	Y 39	Zr 40	Nb 41	**Mo** 42	Tc 43	**Ru** 44	**Rh** 45	Pd 46	**Ag** 47	**Cd** 48	**In** 49	**Sn** 50	**Sb** 51	Te 52	I 53
Xe 54	Cs 55	**Ba** 56	TR 57-71	Hf 72	Ta 73	**W** 74	Re 75	**Os** 76	Ir 77	Pt 78	Au 79	**Hg** 80	**Tl** 81	**Pb** 82	**Bi** 83	Po 84	At 85
Rn 86	Fr 87	Ra 88	Ac 89	Th 90	Pa 91	U 92											

Fig. 88. Elements characteristically forming sulphides and similar compounds (bold and medium type).

the so-called subperiods. The same is true of selenium, tellurium, arsenic, and similar compounds.

A place apart among the elements on the left-hand side of the table is held by hydrogen whose sulphide, H_2S, is analogue of water and plays a tremendous role in the formation of sulphides.

The pronounced affinity of sulphur with heavy metals is shown by the fact that it reacts with them to form compounds which are almost insoluble in water. In contrast to these, the corresponding compounds of the light metals (Na, K, Mg, Ca, etc.) are found only in aqueous solutions.

Chemically, sulphides and sulphosalts under consideration are similar to simple oxides and oxygen salts and, indeed, the formulas of these two types of compounds have much in common (e.g., Cu_2O and Cu_2S, HgO and HgS, Sb_2O_3 and Sb_2S_3, Cu_3AsS_4 and $Cu_3[AsO_4]_2$, etc.).

The majority of simple sulphur, selenium and tellurium compounds, from the chemical viewpoint, derive from H_2S, H_2Se, and H_2Te (e.g., Cu_2S, ZnS, HgSe, PbS, PbTe, Sb_2S_3, etc.).

In complex sulphur compounds, these simple sulphides either form *binary compounds* or such which chemically are regarded as a separate class of *sulphosalts*.

Furthermore, there are simple compounds of the AX_2 type or *disulphides* which, according to V.I. Vernadsky, are derived from H_2S_2. Comparing them with oxides, Vernadsky considered them to be ana-

logues of peroxides. Indeed, on heating, disulphides yield some of their sulphur content in the same way that peroxides lose some of their oxygen.

Arsenides and *antimonides* (simple compounds of metals with arsenic and antimony) materially differ in chemical nature from sulphides. Contrary to the older conception, neither arsenic nor antimony are capable of isomorphous replacement of sulphur. Examples of arsenides and antimonides are NiAs, NiSb, $FeAs_2$, $CoAs_2$, etc. Close to disulphides and diarsenides, both chemically and physically, are *sulphoarsenides* (FeAsS, etc.) and *sulphoantimonides* (NiSbS, etc.).

Many compounds of this class form solid solutions with each other, either as continuous series or with limited miscibility in the solid state. Such are, for instance, the HgS—HgSe and $CoAs_2$—$NiAs_2$—$FeAs_2$ series. Finally, there are numerous polymorphous modifications.

Crystal structure and physical properties. According to X-ray data, sulphides and similar compounds should be classed with ionic compounds, although in their majority in a whole number of characteristic properties, they differ sharply from typical ionic oxygen compounds and are closer to native elements than to oxides or oxygen salts. These differences are due to the inherent properties of the atoms or ions entering into the composition of sulphides, selenides, tellurides, arsenides, and antimonides.

As compared with oxygen, the ions of S, Se, Te, As, and Sb have much greater radii, are more easily polarised and form weak homopolar bonds. On the other hand, the metallic ions which form compounds with them and which are situated on the right-hand side of the periodic table (in the iron family and in the subgroups of the long periods) have an 18-electron outer shell and are strongly polarising. Complex ions, though present in complex sulphur compounds, such as sulphosalts, have bonds which are not as strong as those of silicates and other oxygen salts.

Polarisation phenomena in the crystal structures result in pronounced merging of many electrons of oppositely charged neighbouring ions, which may be inferred from the pronounced *metallic lustre* characteristic of sulphides and similar compounds, and generally typical of metals. This agrees well with the fact that most sulphur, arsenic and other similar compounds are *good conductors of electricity* and also explains why there are fewer metal atoms as compared with the number of metalloid atoms (for instance, in pyrrhotite, $Fe_{1-x}S$), and the frequent absence of strict Dalton ratios in minerals.

In S, Se and Te compounds, metallic properties become more pronounced as the sulphur is replaced by selenium and tellurium. In the iron group these properties increase from Mn to Ni. The same is true in the As, Sb, and Bi series where metallic properties increase towards the bismuth end. In fact, bismuthite (Bi_2S_3) has a stronger metallic lustre than antimonite (Sb_2S_3), whereas orpiment (As_2S_3) is translucent and has an adamantine or submetallic lustre.

Mode of occurrence. The overwhelming majority of accumulations of sulphides and similar compounds occur in ore deposits of hydrothermal origin. This warrants the assumption that heavy metals are carried out of the magmatic hearth as volatile or mobile compounds and precipitate at lower temperatures and pressures mainly in the form of sulphur compounds. On the basis of experiments it is considered possible that these compounds could have been transported by hydrothermal solutions as true solutions of the heavy metals in combination with Cl, F, and B, from which sulphur compounds were precipitated as poorly soluble products of exchange decomposition (A.G. Betekhtin) at lower temperatures, due to increased dissociation of dissolved H_2S into H^+ and S^{2-} ions. The solutions may have also contained complex salts with sulphur alkalis or sulphohydrates (NaHS, KHS, etc.) which readily dissolve even gold. Their decomposition at lower temperatures may have yielded native gold along with common metal sulphides (gold sulphides do not occur in nature, whereas gold tellurides do).

In sedimentary argillaceous rocks and bitumen- and coal-bearing seams, sulphides are formed in a different way. The most common sulphides in these rocks are pyrite and marcasite (FeS_2). These are formed in reducing conditions, in the presence of H_2S which is a decomposition product of protein substances in organic remains, either in the complete absence of oxygen or when it is deficient. It is also probable that not infrequently bacteria take part in this process.

In the course of weathering, i.e., in the presence of water and oxygen, practically all these minerals readily oxidise and decompose, yielding first mostly sulphates which are easily soluble in water, and then hydroxides, oxides, carbonates, and other oxygen compounds usually found in the so-called zone of oxidation of ore deposits. The only exceptions are certain minerals, such as cinnabar (HgS), sperrylite ($PtAs_2$) and laurite (RuS_2), which are chemically stable under these conditions.

Classification of sulphides and similar compounds. On the basis of the chemical characteristics of individual types of compounds, they fall into two primary classes.

Class 1. Simple and binary sulphides, selenides, tellurides, arsenides, and antimonides.

Class 2. Sulphosalts, i.e., minerals which are very similar in chemical constitution to salt-like compounds.

CLASS 1.

SIMPLE SULPHIDES AND SIMILAR COMPOUNDS

With the exception of hydrogen sulphide, all sulphides and similar compounds occur in the earth's crust as solid crystalline substances. Depending on the type of chemical compounds, they are further divided into different principal groups of minerals (sulphides, arsenides, and antimonides).

1. CHALCOCITE GROUP

This group comprises copper and silver minerals of the type A_2S, A_2Se, and A_2Te. Many of them exist in nature in two modifications: a higher-temperature cubic modification and a lower-temperature orthorhombic or monoclinic modification.

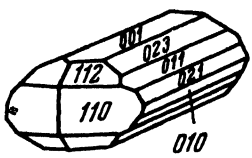


Fig. 89. Prismatic chalcocite crystal.

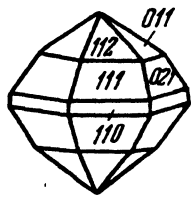


Fig. 90. Hexagonal chalcocite crystal.

CHALCOCITE, Cu_2S. The name is derived from the Greek "chalcos" meaning copper. Synonym: copper glance.

Cu_2S occurs in three modifications: a low-temperature orthorhombic modification stable below 91° (chalcocite proper or β-chalcocite); two high-temperature modifications (over 91°) which are respectively hexagonal and cubic (α-chalcocite). The hexagonal modification, the composition of which strictly conforms to the formula Cu_2S, is unstable and on decomposition alters to the cubic modification, α-chalcocite (digenite), which has an antifluorite structure and a composition, expressed by the formula $Cu_{2-x}S$, where $x = 0.03$ to 0.11 ($a_0 = 5.55$). The prerequisite for the stability of α-chalcocite is a statistic blank of about 10% of Cu positions, with the replacement of another 10% of univalent copper by divalent copper.

The high-temperature hexagonal modification of Cu_2S has a structure of closest hexagonal packing. The copper ions are located at the centres of all the triangles comprised of sulphur anions of each layer of packing, $a_0 = 3.89$, $c_0 = 6.68$.

Natural chalcocite is often a mixture of low-temperature orthorhombic (β-chalcocite) and α-chalcocite.

Chemical composition. Cu 79.9%, S 20.1%. Usually contains as impurities Ag, sometimes Fe, Co, Ni, As and Au. Some of them, at least the latter, are mechanical impurities.

System, orthorhombic; symmetry class, rhombic-dipyramidal $3L^23PC$. Space group $Ab2m$ (C_{2v}^{15}). $a_0 = 11.9$; $b_0 = 27.2$; $c_0 = 13.41$. Occasionally pseudocubic. The following faces are characteristic of chalcocite which crystallises at temperatures under 91°: prismatic {110}, {021}, {011}, and {023}; pinacoidal {001}; dipyramidal {111}, {112}, {113}, etc. The **crystal structure** of orthorhombic chalcocite is highly complex and has not yet been studied in detail. **Habit.** Crystals are rare. Most often they occur as thick tablets parallel to {001} and short columns parallel to the *a* axis (Fig. 89). They are often hexagonal (Fig. 90), owing to formation of trillings with {110} as the composition

planes. Penetration twins are also sometimes observed with (032) as the twinning plane, less often (112). **Aggregates.** Usually occurs as fine-grained massive or as impregnations in pseudomorphs after bornite and chalcopyrite, sometimes after sphalerite, galena, covellite, pyrite, etc.

Colour, lead grey. **Streak**, dark grey. **Lustre**, metallic.

Hardness, 2 to 3. Poorly malleable. **Cleavage**, {110} indistinct. **Specific gravity**, 5.5 to 5.8. Good conductor of electricity.

Diagnostic features. Lead-grey colour, low hardness, low malleability (the point of a knife leaves a shiny scratch, which distinguishes it from otherwise similar tetrahedrite). Green colour of solution in HNO_3. Typical associates with copper minerals, most often with bornite.

Fusible in the blowpipe flame, colouring the flame blue. After roasting on charcoal with soda gives a globule of copper. Dissolves in HNO_3 more readily than in other acids with the separation of sulphur.

Genesis and occurrence. Natural orthorhombic chalcocite is formed both endogenously and exogenously, but only at temperatures below 91°.

As an endogenous mineral, it is occasionally found in certain *hydrothermal* copper-rich and sulphur-poor sulphide deposits. In this case, its most frequent paragenetic associate is endogenous bornite. Examples of such deposits are Jezkazgan (Kazakhstan) and Redruth in Cornwall (Britain).

However, the bulk of chalcocite is formed *exogenously* in the so-called zones of secondary sulphide enrichment in all copper-sulphide deposits (Fig. 55). Similarly to other secondary copper sulphides, chalcocite is formed by reactions between primary sulphides and copper sulphate solutions which percolate from the zone of oxidation of copper deposits. Often it develops metasomatically in place of secondary bornite. Sometimes it directly replaces primary chalcopyrite, and occasionally galena, sphalerite, and other sulphides of primary ores.

Cases are known of chalcocite being formed from cupriferous solutions in *sedimentary* rocks containing organic remains in the form of pseudomorphs which retain all the structural details of the remains, principally wood.

In the zone of oxygen weathering chalcocite is unstable and upon decomposition alters to cuprite (Cu_2O), malachite, azurite, and other oxygen compounds. Incomplete oxidation of chalcocite often results in the formation of native copper after the reaction:

$$Cu_2S + 2O_2 = CuSO_4 + Cu$$

Large deposits of chalcocite ores are comparatively rare. In considerable quantities the ores are formed in the lower parts of oxidation zones of copper-rich sulphide deposits, the upper parts of which had been thoroughly reworked by surface agents. Chalcocite, which in this case is the principal copper mineral, forms zones of secondary sulphide enrichment.

In the U.S.S.R., massive chalcocite ores had been mined at *Turya* in the Northern Urals, from which well-formed crystals have also been recorded. They were studied in detail by Academician P.V. Yeremeyev. Huge deposits of poor disseminated chalcocite ores are found in the Soviet Union at *Kounrad*, Kazakhstan (north of Lake Balkhash), at *Almalyk* (south of Tashkent), and elsewhere.

Well known deposits occur in the *Butte*, Montana (U.S.A.), where chalcocite in paragenesis with bornite, enargite, pyrite and other minerals is found in primary ores well below the ground-water table, i.e., as an endogenous mineral.

Uses. Chalcocite is the most copper-rich sulphide which makes chalcocite copper ore the most important sulphide ore of industry. A very large part of the world's production of copper is obtained from chalcocite ores. Such, in particular, are the huge deposits of disseminated ores of the Kounrad deposit, the mining of which is economically worthwhile, despite the relatively low copper content.

ARGENTITE, Ag_2S. The name comes from the Latin "argentum" meaning silver. Synonym: silver glance. "Silver black" is a pulverulent variety of silver sulphide and occurs in association with compact argentite.

Ag_2S occurs in two modifications: (1) high-temperature cubic which is stable at temperatures above 179° and is known as *argentite*, and (2) a low-temperature orthorhombic modification which forms at temperatures below 179° and is called *acanthite*. At temperatures below 179° the cubic modification undergoes paramorphic alteration to the orthorhombic, as shown by X-ray examination of the cubic crystals.

Although special names have been suggested for each modification of silver sulphide, the general name of "argentite" has remained in use in mineralogy and is applied also to low-temperature paramorphs of the high-temperature modification.

Chemical composition. Ag 87.1%; S 12.9%. Cu is often found among isomorphous admixtures in argentite. Usually is also contaminated with compounds of Pb, Fe, Sb, etc.

System, cubic; symmetry, hexoctahedral. Space group $m3m(O_h^9)$.

Low-temperature argentite (acanthite) is monoclinic. Space group $P2_1/c(C_{2h}^5)$; $a_0 = 9.47$; $b = 6.95$; $c = 8.28$; $\beta = 124°$ (has not been studied in sufficient detail). Occurs as imperfect crystals (paramorphs): cubes, cubic octahedra (Fig. 91), occasionally rhombododecahedra.

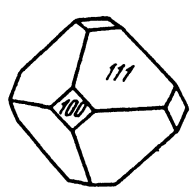


Fig. 91. Argentite crystal (common form).

Colour, lead grey. **Lustre** on fracture, metallic.

Hardness, 2 to 2.5. Malleable. **Cleavage**, {110} and {100} imperfect. **Specific gravity**, 7.2 to 7.4. **Other properties.** Conducts electricity only at high temperatures. A polished surface tarnishes within a few seconds on exposure to strong light.

Diagnostic features. Difficult to recognise with the naked eye. Often associated with "silver black", sometimes with native silver.

After roasting on charcoal in the blowpipe flame gives a malleable silver globule. Dissolves in nitric acid with the separation of sulphur; when hydrochloric acid is added, a thick curdy white precipitate of AgCl is formed, which is soluble in ammonia.

Genesis and occurrence. Argentite occurs in hydrothermal sulphide silver-ore deposits, often in paragenesis with native silver and other argentiferous minerals.

However, this mineral, or acanthite to be more precise, most frequently occurs in the lower parts of *oxidation zones* of argentiferous sulphide ore deposits, in association with cerussite ($PbCO_3$), cerargyrite (AgCl), native silver, etc. Pseudomorphs of argentite have been found after native silver and many minerals of complex composition—sulphides, arsenides, and antimonides of silver (proustite, pyrargyrite, stephanite, etc.).

Argentite is rarely found in large accumulations important in their own right. Considerable masses have been found together with native silver, at the *Kongsberg* deposit (Norway), and also at Zacatecas and Guanajuato and other deposits in *Mexico* where it occurs in association with sulphosalts of silver (polybasite, pyrargyrite, proustite, etc.).

In the U.S.S.R., it occurs as selvages, less often as small masses, at *Zmeinogorsk* (Altai), Nerchinsk (Eastern Trans-Baikal Region), and Verkhoyansk (Eastern Siberia).

Uses. As an associate of other argentiferous minerals, argentite is a source of silver, since a minimum content of 0.02% of silver makes mining worthwhile.

2. GALENA GROUP

Of the minerals of this group we shall discuss only galena, the one which is most widespread in nature.

GALENA, PbS. From Latin "galena" meaning lead ore. Synonym: lead glance. Variety: *selenium galena.* There is a physical variety called "bleischweif" which is compact dull close-grained mass.

Chemical composition. Pb 86.6%, S 13.4%. The most frequent impurities are Ag (up to tenths of a per cent), Cu, Zn, sometimes Se (selenium galena), Bi, Fe, As, Sb, Mo, rarely Mn, U, etc. In the majority of cases these elements are present as microinclusions of foreign minerals.

System, cubic; symmetry, hexoctahedral $3L^44L_6^36L^29PC$. Space group $Fm3m(O_h^5)$. $a_0 = 5.924$. The **crystal structure**, in which the sulphides of the galena group crystallise, is of the halite type (Fig. 92). The sulphur anions are spaced according to the law of cubic (treble-layer) closest packing, while the lead cations fill all the octahedral spaces between the anions. The unit cell is fundamentally a cubic face-centred structure in which the ions are located at the corners of the cube

and face centres of the cell, with the difference that two types of ions take part in the structure (Fig. 92*b*). If the unit cell is divided into smaller cubes, their corners will be alternately occupied by each of the two types of ions. The coordination number of either type of ions is 6. In Fig. 92, the sulphur ions occupy the corners of the greater cube and

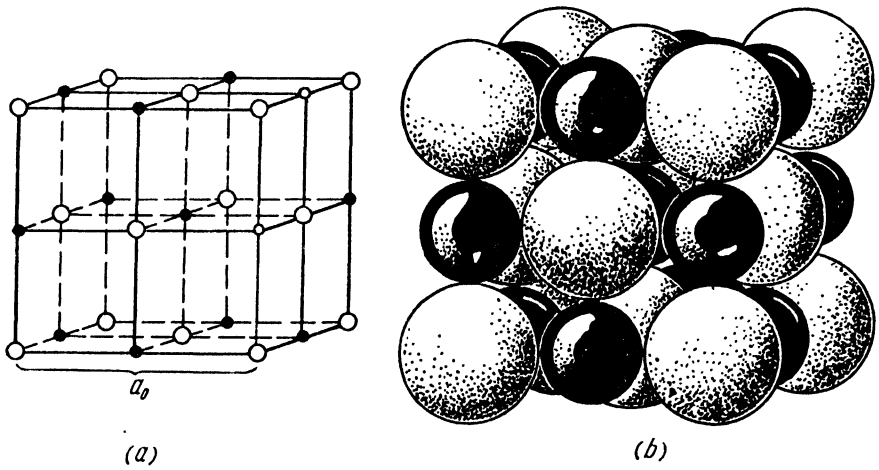


Fig. 92. Crystal structure of galena.

a – distribution of ionic centres (black circles – Pb, light-coloured circles – S;
b – crystal structure shown as spheres, drawn to the same scale.

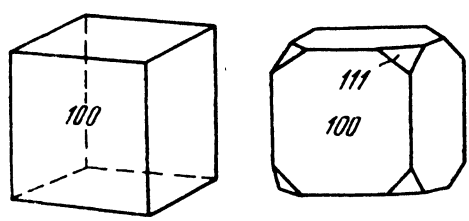


Fig. 93. Cubic galena crystals.

the face centres, while the lead ions occupy the interspaces. The pattern may be reversed without changing the nature of the structure. **Habit.** Mostly cubic, sometimes with octahedral faces (Fig. 93), less often octahedral. The most common forms are: {100}, {111}, and less often {110}. Twins on (111) as the composition plane. Galena crystals are found only in druse cavities. Usually granular massive or in the form of irregular segregations.

Colour, lead grey. **Streak**, greyish black. **Lustre**, metallic.

Hardness, 2 to 3. Brittle. **Cleavage**, very perfect, cubic. Bismuth-bearing varieties display parting parallel to {111}, which disappears on heating and the usual cubic cleavage appears. **Specific gravity**, 7.4 to 7.6. **Other properties.** Poor conductor of electricity but has good rectifying properties.

Diagnostic features. Easily recognisable by colour, lustre, characteristic cubic cleavage, low hardness and low specific gravity. In cryptocrystalline masses is distinguished from similar antimonides and arsenides by specific gravity and behaviour before the blowpipe.

Easily fusible in the blowpipe flame. Roasted with soda, gives a lead globule. Readily soluble in nitric acid, giving sulphur and white $PbSO_4$ precipitate due to partial oxidation during solution.

Genesis and occurrence. Almost exclusively confined to *hydrothermal* deposits. Often found in huge masses. Typically is associated with sphalerite (ZnS), the amount of which is usually greater than that of galenite. Hydrothermal lead-zinc deposits occur either as regular veins or as irregular metasomatic bodies in limestones or, lastly, as disseminated ores.

Other galena associates are pyrite, chalcopyrite, grey ores, the sulphosalts of silver, zinc, copper, and arsenopyrite. Apart from quartz and calcite, the nonmetallic minerals in these ores are barite ($BaSO_4$), fluorite (CaF_2) and various carbonates.

In the course of oxidation in the process of weathering, galena is covered with an anglesite ($PbSO_4$) crust which alters to cerussite ($PbSO_3$) at the surface. These poorly soluble compounds form a sort of solid coating around undecomposed galena protecting it from the oxidising agents. Therefore, it is not surprising that galena nodules protected by such a coating are found in the zone of clayey alluvium and even in placers. Unlike sphalerite, galena in the zone of oxidation gives rise not only to anglesite and cerussite, but also to other poorly soluble oxygen compounds such as phosphates, arsenates, vanadates and molybdates. Owing to this, the oxidised zones of lead-zinc deposits are, as a rule, enriched in lead.

The most important of the numerous galena ore deposits of the U.S.S.R. are the following: the *Sadon* vein deposit, Northern Caucasus; the *Turlan* (Achisay), unusually coarsely crystalline massive galena occurs in the limestones of the Kara-Tau range, north-east of the town of Turkestan; the *Altai* polymetallic ore deposits composed of very fine-grained pyrite, sphalerite, chalcopyrite, galena, and grey ores; numerous deposits in Kara-Mazar mountains, and elsewhere in *Central Asia*; the *Nerchinsk* deposits in the Trans-Baikal Region, etc.

In *Missouri* (U.S.A.) large deposits occur in the form of impregnations and pockets in limestones and shales over a vast territory; other deposits are worked in *Leadville*, Colorado, and elsewhere.

Uses. Galena is the most important ore of lead. Practically all of the world's production of lead is obtained from this ore.

Apart from being used for the smelting of lead, the applications of which are well known, a small amount of galena ores are processed into litharge (PbO) to obtain pigments (white, red, and yellow lead) and glazes. Considerable quantities of silver (and occasionally some bismuth) are obtained as by-product of lead smelting from argentiferous minerals associated with galena.

3. SPHALERITE GROUP

Dimorphous AX-type minerals which crystallise in the cubic and hexagonal systems (crystal structures of the sphalerite and wurtzite type with tetrahedral ionic coordination) are included under this heading. In this section we shall also describe mercury sulphide (cinnabar) which, though close to the sphalerite group in some properties, materially differs from it in crystal structure.

SPHALERITE, ZnS. The name comes from the Greek "sphaleros" meaning deceptive, probably because it bears no outward resemblance to common metal sulphides. Synonym: zinc blende. Varieties: *cleiophane* which is light-coloured or colourless (almost without impurities); *marmatite* which is black and ferruginous; and *pribramite* which is rich in cadmium (up to 5%).

Chemical composition. Zn 67.1%, S 32.9%. The most common impurity is Fe (up to 20%); upon microscopic examination, this variety shows minute inclusions of pyrrhotite (FeS) which is a product of the disintegration of solid solution. Sometimes microinclusions of chalcopyrite ($CuFeS_2$) and, occasionally, of stannite (Cu_2FeSnS_4) are also found, which explains the presence of copper and tin admixtures in sphalerite. Often other isomorphous admixtures are present in sphalerite. These are Cd (usually up to tenths of one per cent), In (up to hundredths of one per cent), Ca, Mn, Hg, etc.

System, cubic; symmetry, hexoctahedral $3L_4^24L^36P$. Space group $\bar{F}43m(T_d^2)$. $a_0 = 5.40$. **Crystal structure** is characterised by treble-layer (cubic) closest packing of sulphur anions. The zinc cations occupy half the tetrahedral spaces between the anions. This type of structure is similar to that of diamond, the difference being that the centres of the smaller cubes are occupied by atoms (ions) which are different from those at the corners and the face centres of the larger cube. As shown in Fig. 94, each S ion at the tetrahedral apexes is surrounded by four Zn ions. In the unit cell which is shown diagrammatically, there are four sulphur ions at centres of half the number of smaller cubes. It should be noted that all the tetrahedra are uniformly oriented, which results in tetrahedral rather than cubic symmetry. In contrast to diamond, cleavage in sphalerite crystals is parallel not to the octahedral planes but to the rhombododecahedral planes {110}, since these planar nets contain Zn and S ions simultaneously and in equal numbers.

Habit. Well-developed sphalerite crystals often occur in druse cavities. The tetrahedral habit is the most common (Fig. 95), the positive and negative forms often differing in lustre and etch figures. Sometimes {110} faces prevail and the crystals acquire a dodecahedral habit. Commonly twinned along {111}. **Aggregates.** Compact masses show pronounced granular structure, easily recognisable by the very distinct cleavage of the individual grains. Botryoidal forms are less common.

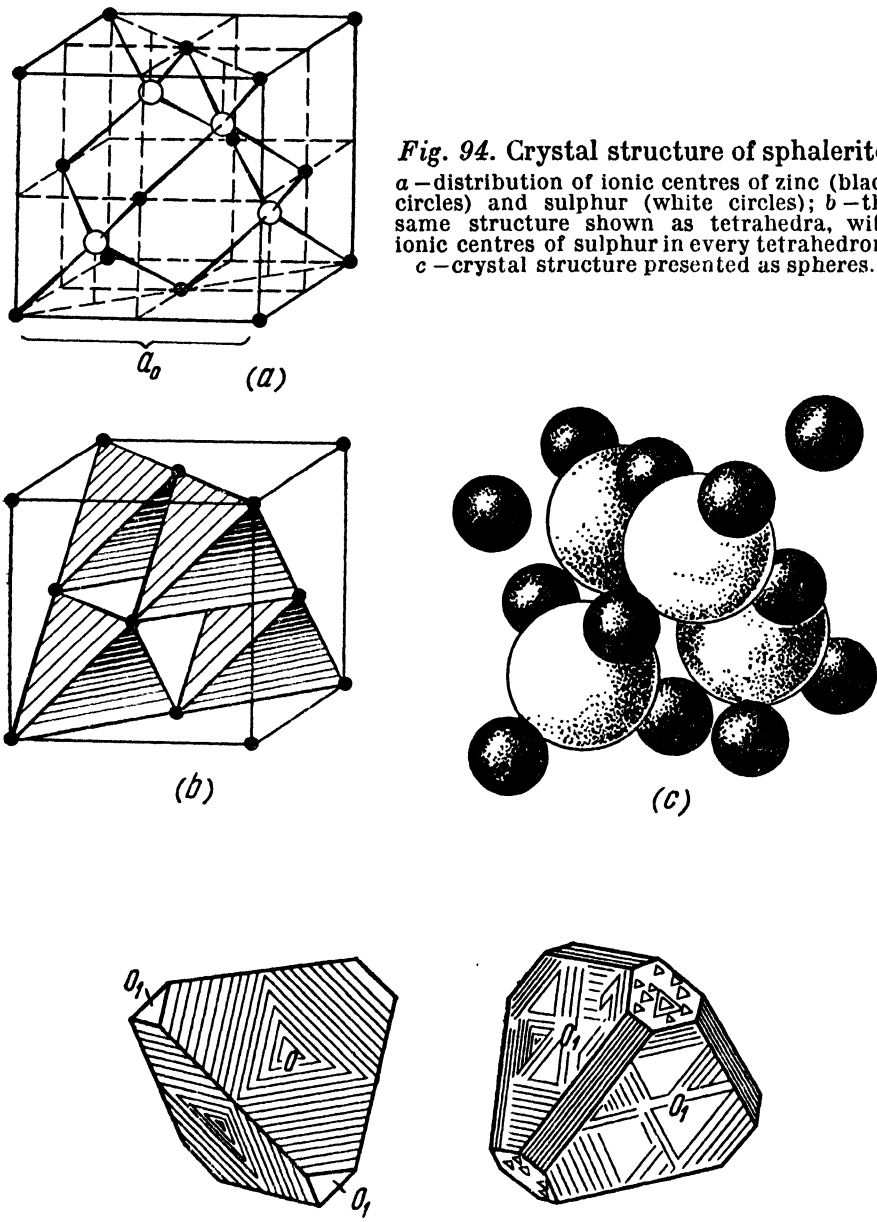


Fig. 94. Crystal structure of sphalerite.
a – distribution of ionic centres of zinc (black circles) and sulphur (white circles); *b* – the same structure shown as tetrahedra, with ionic centres of sulphur in every tetrahedron; *c* – crystal structure presented as spheres.

Fig. 95. Tetrahedral sphalerite crystals.

Colour, usually brownish to brown; often black (marmatite), less often yellow, red or greenish. Perfectly colourless varieties (cleiophane) are also known. **Streak**, white or light yellow to brown. Iron-rich varieties have a brown streak. **Lustre**, adamantine. Refractive index in Na-light $n = 2.37$.

Hardness, 3 to 4. Rather brittle. **Cleavage**, {110} excellent. **Specific gravity**, 3.9 to 4. **Other properties.** Non-conductor of electricity. Polar pyroelectric. Certain varieties phosphoresce on rubbing or splitting.

Diagnostic features. Characteristic isometric crystal grains with rhombododecahedral cleavage, i.e., in the six directions corresponding to the structural planar nets composed of Zn and S atoms. This distinguishes the ferruginous varieties of sphalerite from wolframite (Fe, Mn) WO_4 and enargite, Cu_3AsS_4, which are similar to the former in colour, hardness, lustre and other features, but have a prismatic habit of grains and unidirectional cleavage.

Decrepitates in the blowpipe flame but practically does not fuse. On charcoal in the reducing flame gives a white coating of zinc oxide. Dissolves in concentrated nitric acid with separation of sulphur.

Genesis and occurrence. Most of sphalerite deposits, as those of galena, with which sphalerite is practically always associated, are of the *hydrothermal* type (see "Galena"). In certain sulphide deposits, it is sometimes associated with chalcopyrite.

Under exogenous conditions sphalerite is formed extremely rarely. It has been found in some coal seams.

On oxidation sphalerite decomposes rather rapidly with the evolution of zinc sulphite which is readily soluble in water; that is why the oxidation zones are, as a rule, heavily depleted of zinc (cf. galena). When the enclosing rocks of a deposit are limestones, zinc carbonate (smithsonite) will accumulate in them.

In lead-zinc deposits, examples of which have already been cited (under "Galena"), sphalerite usually occurs in much greater quantities than galena.

In some deposits, there are found druses of well-developed crystals of sphalerite together with calcite, quartz, and other minerals, for example, in the deposits of the *Nagolny ridge*, the Ukraine.

Sphalerite may also occur as metacolloidal concentrically-banded botryoidal formations in cavities in limestones, in association with galena, pyrite, marcasite, chalcopyrite, calcite, or dolomite.

In close association with chalcopyrite (almost without galena) it occurs in a number of pyrite deposits in the Urals, such as the *Karpushino* and the *IIIrd International* deposits, and elsewhere.

Outside the U.S.S.R., the most interesting deposits, from the mineralogical standpoint, are *Přibram* (Czechoslovakia), *Binnenthal* (Switzerland) where excellent crystals occur in cavities in dolomite, and the *Santander* deposits (Spain) where remarkable transparent sphalerite crystals have been found.

Uses. Sphalerite is the principal ore of zinc. Apart from zinc, sphalerite ores yield, as by-products, valuable rare metals: Cd, In, and Ga.

In the course of roasting and smelting of polymetallic ores, ZnS, oxidised to ZnO, escapes in large amounts with the flue gases. For this reason, the ores are usually pretreated to separate the lead and the zinc concentrates. The latter, after preliminary roasting in special furnaces in order to oxidise the zinc, is smelted in a reducing atmosphere in sealed retorts so as to sublimate the zinc.

The metallic zinc which is obtained by sublimation is not pure and is used to galvanise iron. Crude zinc is refined electrolytically and goes into brass, bronze, and other alloys.

Small quantities of sphalerite are used directly for making zinc white, fluorescent screens, etc.

Cadmium, the bulk of which is obtained from sphalerite ores as a by-product, is used in electroplating, as an anticorrosion coating for steel and iron; in the preparation of fusible alloys which are stronger and more resistant to high temperatures and wear than babbit alloys which require a great admixture of costly tin; in storage batteries; in the manufacture of automatic fire-fighting equipment.

Gallium is a metal which has many properties in common with aluminium. It melts at 29° and forms an alloy with aluminium which is liquid at room temperature. The boiling point of gallium, unlike that of mercury, is very high (1700 to 2300°) making it in some applications a good substitute for mercury in thermometers and other precision instruments. Gallium lamps emit light closely similar to daylight.

Indium is used as an anticorrosive coating for metals and in the manufacture of reflectors for spotlights and automobile headlights. Organic compounds of indium are used in medicinal preparations for the treatment of sleeping sickness.

WURTZITE, ZnS. Variety: erythrozincite, i.e., manganiferous wurtzite, (Zn, Mn)S.

Chemical composition, identical with that of sphalerite. Usually contains more cadmium.

System, hexagonal; symmetry, dihexagonal pyramidal $L^6 6P$. Space group $C6mc$ (C_{6v}^4). $a_0 = 3.798$; $c_0 = 6.23$. **Crystal structure** is characterised by hexagonal (double-layer) closest packing of sulphur anions (Fig. 96)*. As in the sphalerite structure, the zinc cations occupy half the vacant tetrahedral spaces. This similarity in crystal structure explains the similarity in a number of physical properties (specific gravity, hardness, colour, etc.). However, wurtzite differs essentially from sphalerite by optical anisotropy and crystal form. **Habit**, pyramidal, short-columnar or tabular.

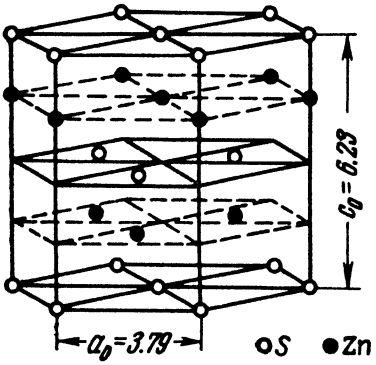


Fig. 96. Crystal structure of wurtzite.

Colour, similar to that of sphalerite, but varies with Fe content from white to brown and black. **Streak** accordingly varies from white to brown. **Lustre**, adamantine.

Hardness, 3.5 to 4. Brittle. **Cleavage**, {11$\bar{2}$0} perfect and {0001} indistinct. **Specific gravity**, 4.0 to 4.1.

* Recently rare natural modifications of wurtzite were discovered with 4-, 6-, and 15-layer closest packings.

Diagnostic features. Massive wurtzite is outwardly indistinguishable from sphalerite. Its optical anisotropy is revealed only by microscopic examination. Behaviour before the blowpipe and reactions with acids are the same as those of sphalerite.

Genesis and occurrence. Wurtzite is a comparatively rare mineral. It occurs together with sphalerite in certain hydrothermal deposits of low-temperature origin.

In the U.S.S.R., it occurs together with sphalerite in some of the Urals deposits: *Blyava*, *Yaman-Kasy*; and in Kirghizia: at *Ak-Tyuz*, *Karavash*, and elsewhere.

Most interesting mineralogically are the concentrically-banded metacolloid varieties in Přibram, Czechoslovakia, the well-formed pyramidal crystals of the *Butte* district of Montana (U.S.A.) and at *Oruro* and *Potosi* (Bolivia).

The mineral is of no economic value.

GREENOCKITE, CdS. Synonym: cadmium glance. Rare. Cadmium content 77%. Sometimes contains indium.

System, hexagonal; symmetry, dihexagonal pyramidal. Space group identical with that of wurtzite, $a_0=4.142$; $c_0=6.724$.

Recently there has been found a cubic modification of this compound which has been called *hauleite*.

Rare crystals are small and barrel-shaped or acute pyramidal in form. Usually occurs as powdery or earthy selvages.

Colour, yellow, orange-yellow or dark orange. **Streak**, orange-yellow to brick red. **Lustre**, adamantine.

Hardness, 3 to 3.5. Brittle. **Cleavage**, $\{11\bar{2}0\}$ perfect. **Specific gravity**, 4.9 to 5.0.

Diagnostic features. Differs from similar orpiment, As_2S_3, realgar AsS, and wulfenite $PbMoO_4$, by behaviour before the blowpipe (on strong ignition with soda gives a red-brownish film of CdO). When dissolves in acids gives off a strong odour of H_2S. The reaction for cadmium is performed in an alcohol solution of diphenylcarbazide on filter paper.

Genesis and occurrence. Is found in association with cadmium-bearing sphalerite or wurtzite. No large accumulations of greenockite have been observed.

Has occurred in the oxidised zones of the following deposits: *Kyzyl-Espe* (Central Kazakhstan), Gaynakh-Kan, Kan-Sai and Obisorbukh (Central Asia). Has been also found in cavities as tiny crystals on chalcopyrite and galena in a pyrite bed of the *Sibai* deposit, Southern Urals, where it is obviously in exogenous mineral.

Other localities are *Přibram*, Czechoslovakia; *Friedensville*, Pennsylvania (U.S.A.), etc.

For the uses of cadmium see "Sphalerite".

CINNABAR, HgS. The name presumably comes from India where it is applied to a red resin and to "dragon blood". A cubic modification of HgS is known as *metacinnabarite.*

Chemical composition. Hg 86.2%, S 13.8%. Foreign elements are usually mechanical admixtures.

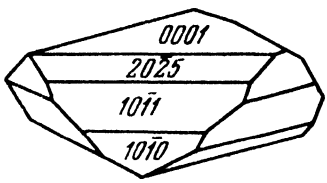


Fig. 97. Cinnabar crystal.

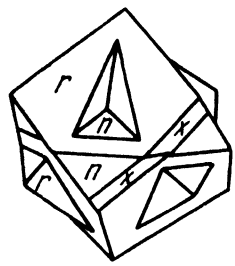


Fig. 98. Cinnabar twin *r* {10$\bar{1}$1}, *n* {20$\bar{2}$1}, *x* {42$\bar{6}$3}.

System, trigonal; symmetry, trigonal trapezohedral L^33L^2. Space group $C3_12(D_3^4)$ or $C3_2(D_3^6)$. $a_0=4.16$; $c_0=9.54$. **Crystal structure**, hexagonal. On the whole, it may be regarded as a distorted structure of NaCl with a coordination number of 6 (both for Hg and for S). A peculiar feature of the crystal structure are continuous spiral chains of S—Hg—S with covalent bonding between the ions, the chains being parallel to the *c* axis (along the right- or left-hand helical axis). This explains the pronounced ease of rotation of the plane of polarisation. The weaker bonding between the chains accounts for the distinct prismatic cleavage parallel to {10$\bar{1}$0}.

Habit. Cinnabar occurs in small thick tabular (0001) or rhombohedral crystals with faces {10$\bar{1}$1}, {20$\bar{2}$5}, etc., (Fig. 97) and sometimes with trapezohedral faces. Characteristic twinning along (0001) (Fig. 98). **Aggregates.** Most often observed as impregnated irregular grains, sometimes massive, and also as powdery selvages and coatings. The so-called "hepatic" ore is a cryptocrystalline mass with abundant earthy and organic impurities.

Colour, red, sometimes with a lead-grey tarnish. **Streak**, red. **Lustre**, strong, submetallic. Translucent.

Hardness, 2 to 2.5. Brittle. **Cleavage**, {10$\bar{1}$0} rather perfect. **Specific gravity**, 8.09. **Other properties.** Unlike metacinnabarite, cinnabar does not conduct electricity.

Diagnostic features. Easily identified by red colour, low hardness, high specific gravity, and behaviour before the blowpipe.

Volatilises completely in the blowpipe flame on charcoal. Sublimation begins at 200° C. When heated in the closed tube, gives a black sublimate of HgS, metallic mercury, and a sulphur coating. When heated in the open tube, i.e., in the presence of oxygen, tiny globules of metallic mercury are formed on the cool walls of the tube according to the equation: $HgS+O_2=Hg+SO_2$. This is essentially the method employed in industry to obtain mercury.

Cinnabar is soluble in aqua regia and is decomposed by chlorine. It also dissolves in caustic alkali solutions of sulphides, but is insoluble in nitric and sulphuric acids.

Genesis and occurrence. Cinnabar deposits, without exception, belong to the low-temperature *hydrothermal* type. Instances are known of cinnabar deposited from hot alkaline springs at the daylight surface (Steamboat Springs in Nevada, and Sulphur Bank Springs in California, U.S.A.). The ore minerals associated with cinnabar are: antimonite (Sb_2S_3), pyrite, less often arsenopyrite (FeAsS), realgar (AsS), occasionally sphalerite, chalcopyrite, etc. The usual nonmetallic associates are quartz, calcite, often fluorite and barite, sometimes gypsum, etc.

In the oxidation zones of mercury deposits, black films of metacinnabarite, native mercury, and occasionally mercury chlorides occur sometimes as secondary minerals. In general, cinnabar is rather stable in oxidising conditions, in contrast to many other sulphides. This is why it is often found in placers where due to its high specific gravity it shows in the heavy concentrates.

The Soviet Union's largest deposit is at *Nikitovka* (3 km from the Nikitovka Station, Northern-Donets railway) where cinnabar occurs both as an impregnation and in veinlets, in association with quartz, antimonite, arsenopyrite, and occasionally with pyrite, mostly in sandstones.

A number of small deposits are situated in the Caucasus. Of these the *Khideshlep* deposit is interesting mineralogically, since there cinnabar is associated with bright-red realgar (AsS).

Larger deposits are found at *Khaidarkan* and *Chauvai* in Central Asia, chiefly along the northern foothills of the Altai and Turkestan ranges. There cinnabar in the form of small grains in brecciated ores is associated with quartz, antimonite, fluorite, calcite, barite, and other minerals.

World famous are the deposits at *Almaden* (Spain), and *Idria* (Italy).

Uses. Cinnabar is practically the only source of metallic mercury since native mercury is rather rare. The principal use of mercury is for the amalgamation of gold in extracting the latter from primary ores. It is also used for the manufacture of chemicals, fulminate of mercury Hg(CNO) for detonating high explosives, and in scientific instruments.

4. PYRRHOTITE GROUP

This group includes the compounds of metals of Group VIII of the periodic table (in particular Fe, Ni, and Co) with S, As, and Sb. These compounds have the general formula AX (or a very similar formula).

We shall consider here the minerals: pyrrhotite, niccolite, millerite, and pentlandite.

PYRRHOTITE, $Fe_{1-x}S$ (most often $x=0.1$ to 0.2). Usually its formula is presented as FeS. The name comes from the Greek "pyrrhos" meaning the colour of fire. Synonym: magnetic pyrite.

Chemical composition. Usually the sulphur content is higher than the one indicated by the formula FeS: instead of 36.4% it may be as high as 39 to 40%. Sometimes minor impurities of Cu, Ni, Co, and occasionally of Mn and Zn are found (the first three metals are usually present in the form of the chalcopyrite and pentlandite inclusions).

System, hexagonal; symmetry, dihexagonal dipyramidal $L^6 6L^2 7PC$. This modification is stable at temperatures below 138°. Space group $C6/mmc$ (D^4_{6h}). $a_0=6.872$; $c_0=11.444$ (x increases with c)*. The **crystal structure** is characterised by the hexagonal structure of niccolite (see below). According to X-ray data, the excess sulphur (against the formula FeS) cannot be accounted for by additional large S^{2-} ions fitting somewhere into the empty spaces of the pyrrhotite crystal structure since these spaces are too small. It may be assumed that either S^{2-} ions partly replace Fe ions or, if the number of S^{2-} ions in the lattice is constant, some of the sites for Fe cations remain vacant. The problem was solved by comparing the calculated specific gravities for either case. The upper curve (Fig. 99) represents the calculated specific gravities on the assumption that the S ions partly replace the Fe ions; the lower curve represents the other case in which the assumption is that some of the sites for the Fe ions remain vacant; the circles indicate the specific gravities of pyrrhotite varieties actually existing in nature. It is evident from the graphs that the second assumption is correct. Therefore, it should be assumed that in order to neutralise the total negative charge of the S^{2-} anions, some of the Fe ions must have a trivalent positive charge, not a divalent charge. This has been confirmed by very accurate chemical analyses.

Habit. Crystals are generally rare. Usually they are tabular, less often columnar or pyramidal (Fig. 100 and 101), mostly with the following faces: pinacoidal {0001}, prismatic $\{10\bar{1}0\}$, dipyramidal $\{10\bar{1}1\}$, $\{20\bar{2}1\}$, etc. Twins are rare, with $\{10\bar{1}1\}$ as the twinning plane. Commonly massive or in the form of irregular disseminated grains.

Colour, dark bronze-yellow with a dark-brown tarnish. **Streak**, grey-black. **Lustre**, metallic.

Hardness, 4. Rather brittle. **Cleavage**, {1010} imperfect. Apart from this, there is a parting parallel to {0001}. **Specific gravity**, 4.58 to 4.70. **Other properties.** Occasionally magnetic. Sulphur-rich varieties ferromagnetic. Good conductor of electricity.

Diagnostic features. Identifiable by characteristic colour and, often, by magnetic properties.

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* In the deposits at Ixoen (Sweden), a monoclinic modification of pyrrhotite (β-pyrrhotite) has been found: $a_0 = 5.936$; $b_0 = 3.427$; $c_0 = 5.689$; $\beta = 89°38'$. It occurs together with common pyrrhotite.

Fuses in the blowpipe flame into a black magnetic bead. Dissolves with difficulty in nitric and hydrochloric acids, which sharply distinguishes it from troilite (FeS).

Genesis and occurrence. Pyrrhotite only in rare instances is a high-temperature mineral. Its formation, which is the same as that of pyrite (FeS_2), depends not so much on temperature as on the concentration of sulphur in solutions: at high S^{2-} concentration, the iron precipitates as a sulphide (FeS_2), while at low concentration a monosulphide (FeS) is formed.

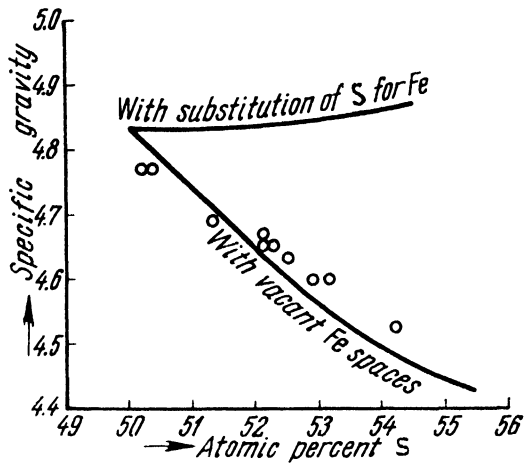


Fig. 99. Curves show calculated specific gravities; circles show actual, specific gravities of pyrrhotite.

Pyrrhotite is almost exclusively confined to endogenous deposits of diverse genesis.

1. It is quite widespread in basic igneous rocks, chiefly in norites, and sometimes in gabbro-diabases, where pyrrhotite is the principal mineral in sulphide accumulations occurring in close association with pentlandite and chalcopyrite (deposits of copper-nickel sulphide ores).

2. Sometimes forms large masses in contact-metasomatic deposits, mainly at the boundary with limestones. Chalcopyrite, pyrite, magnetite, blackjack, arsenopyrite, sometimes cassiterite (SnO_2) scheelite ($CaWO_4$), calcite and quartz occur in paragenesis with pyrrhotite. All of them are formed in the later stages of skarn formation. In the U.S.S.R., the best known contact-metasomatic deposits are the *Bashmakovskoye* and *Bogoslovskoye* in the Turya group of mines (Northern Urals).

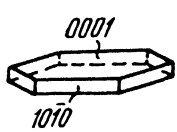


Fig. 100. Tabular pyrrhotite crystal.

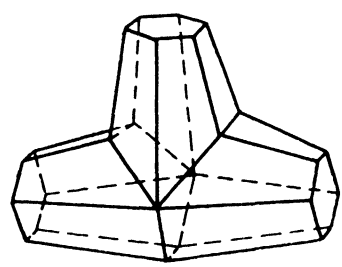


Fig. 101. Pyrrhotite twin.

3. In a number of typical hydrothermal deposits pyrrhotite occurs associated with sphalerite, galena, chalcopyrite, cassiterite, arsenopyrite, ferruginous chlorites, carbonates, etc., being the latest to be formed of all these minerals. Well-formed crystals are usually found

in druse cavities as a later growth on such earlier minerals as sphalerite, quartz, calcite, etc.

4. Rare finds of unusual pyrrhotite concretions in association with siderite were recorded from sedimentary rocks at the Kerch iron deposit, and also in phosphorite nodules.

In conditions of weathering in the zone of oxidation, it is the most easily decomposed sulphide. At first, ferrous sulphate is formed and this changes in the presence of oxygen to ferric sulphate. The latter hydrolyses to form insoluble ferrous hydroxides (limonite) and free sulphuric acid which passes into solution.

Uses. Deposits of massive pyrrhotite ores which do not contain other metallic minerals are of limited economic value. As stock material for the production of sulphuric acid they are greatly inferior to pyrite ores. Their sulphur content usually does not exceed 30 to 32%, while in pyrite ores it may be as high as 45 to 50%.

NICCOLITE, NiAs. Synonym: copper nickel.

Chemical composition. Ni 43.9%; As 56.1%. Impurities Fe (up to 2.7%), S (up to 5%), sometimes Sb and Co. The commonly observed broad variations in the composition of niccolite are often due to inclusions of foreign minerals which can be seen under the microscope.

System, hexagonal; symmetry, dihexagonal-dipyramidal $L^6 6L^2 7PC$. Space group $C6/mmc(D^4_{6h})$. $a_0 = 3.616$; $c_0 = 5.020$. **Crystal structure**, hexagonal with closest packing of arsenic atoms and with nickel atoms occupying all the octahedral spaces. Each arsenic atom is surrounded by six nickel atoms forming a trigonal prism, whereas each nickel atom is surrounded by six arsenic atoms forming an octahedron (Fig. 102). In addition, each arsenic atom is close to two nickel atoms (vertically) which are also its closest neighbours. This explains the partly ionic and partly metallic bonding of atoms in this type of crystalline structures. It also explains not only the higher reflectivity and electrical conductivity, but also the certain variability of the composition of compounds which form crystal structures of this type.

Habit. Crystals are extremely rare and are poorly developed, with predominant $\{10\bar{1}0\}$ faces. Usually massive, sometimes in botryoidal and other forms.

Colour, pale copper-red. **Streak**, dark brownish black. **Lustre**, metallic.

Hardness, 5. Brittle. **Cleavage**, $\{10\bar{1}0\}$ imperfect. **Specific gravity**, 7.6 to 7.8. Good conductor of electricity.

Diagnostic features. Readily identifiable by pale copper-red colour and metallic lustre.

Fuses on charcoal before the blowpipe into a brilliant brittle globule and gives off a strong garlic odour.

If intensely heated in the closed tube, forms an arsenic mirror on the cool walls. Solution in nitric acid is apple green which turns blue on

addition of ammonia. With dimethylglyoxime yields a thick pink precipitate.

Genesis and occurrence. Occurs mostly in *hydrothermal* vein deposits, sometimes in large amounts, as impregnations or block masses. Common paragenetic associates: diarsenides of nickel, such as chloanthite, rammelsbergite, sometimes native bismuth and silver, etc.

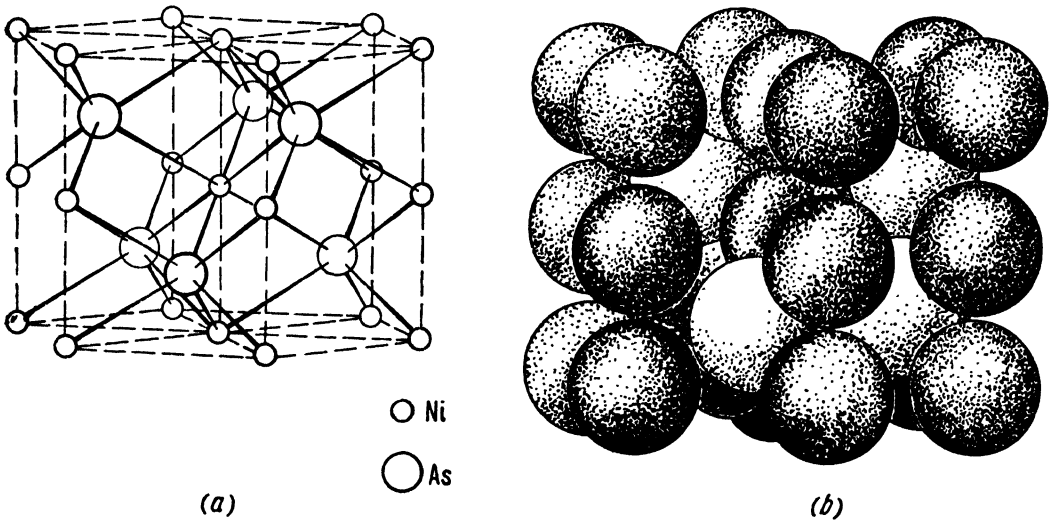


Fig. 102. Crystal structure of niccolite.
a – distribution of atomic centres of nickel and arsenic; *b* – crystal structure shown as spheres.

The weathering of niccolite gives rise to bright-green annabergite, $Ni_3[AsO_4]_2 \cdot 8H_2O$.

In the U.S.S.R., most interesting finds of niccolite were made at the *Berikul* primary gold deposit, Western Siberia. Together with other nickel arsenides (rammelsbergite, gersdorffite, etc.), it was found as continuous irregularly shaped pocket-like masses in carbonate veinlets.

Other notable occurrences are the hydrothermal vein deposits of the *Erzgebirge mountains* (Saxony) of the so-called cobalt-nickel-silver formation with native bismuth (Schneeberg type), and the *Cobalt deposit* in Ontario, Canada, where it occurs in association with sulphides and arsenides of nickel and cobalt, as well as with native silver and other minerals.

Uses. Niccolite ores when found in quantities are of great economic importance.

MILLERITE, NiS. Synonym: capillary pyrite.

Chemical composition. Ni 64.7%, S 35.3%. Impurities: Fe (up to 1-2%), Co (up to 0.5%), Cu (up to 1%).

System trigonal; symmetry, ditrigonal-scalenohedral $L_6^3 3L^2 3PC$. Space group $R\bar{3}m(D_{3d}^5)$ or $R3m(C_{3v}^5) \cdot a_0 = 9.60$; $c_0 = 3.15$. **Crystal structure** differs from the structures of pyrrhotite and the artificial modifica-

tion of NiS (niccolite type with coordination number 6). The structure of this modification with coordination number 5 (intermediate between the high-temperature NiS modification and pentlandite) is very complex and will not be described here.

Habit. Crystals usually acicular with coarse lengthwise striation. **Aggregates.** Often in radiating hair-like groups, hence the name of capillary pyrites.

Colour, brass yellow, sometimes with an iridescent tarnish. **Streak,** greenish black. **Lustre,** strong metallic.

Hardness, 3 to 4. Brittle. Capillary crystals somewhat elastic. **Cleavage,** $\{10\bar{1}1\}$ and $\{01\bar{1}2\}$ perfect. **Specific gravity,** 5.2 to 5.6. **Other properties.** Good conductor of electricity.

Diagnostic features. Identifiable by very characteristic frequent needle-like forms and radially fibrous brass-yellow aggregates. When found in irregularly shaped grains or masses, requires for identification chemical tests for nickel and sulphur.

Fuses in the blowpipe flame on charcoal to give a brilliant boiling bead. In the reducing flame it finally gives a compact, slightly magnetic nickel globule. Dissolves in nitric acid and aqua regia colouring the solution green (due to the presence of nickel) with the separation of sulphur. With dimethyl glyoxime gives the characteristic nickel reaction.

Genesis and occurrence. A relatively rare mineral, it is nearly always a typical product of *hydrothermal* processes.

Sometimes occurs in deposits of copper-nickel sulphide ores as a later hydrothermal mineral formed at the expense of pentlandite.

In typical hydrothermal vein deposits is found in association with other nickel and cobalt minerals, mostly sulphides and arsenides. In these cases it is observed in radial groups in paragenesis with linneite, gersdorffite, galena, fluorite, calcite, quartz, etc.

In the U.S.S.R., mineralogically important finds of millerite have been recorded from the area of the *Beryozovskoye* gold fields as radiated and sheaf-like aggregates in thin carbonate veinlets in listvenites (hydrothermally altered ultrabasic rocks).

In other countries the best known are the deposits in the *Erzgebirge mountains* (Saxony), namely *Freiberg*, *Schneeberg*, etc., where millerite associates with other sulphides of nickel and cobalt, and also with galena, calcite, fluorite, etc. Fine-radial aggregates of millerite have been found in the coal mines of Kladno, Czechoslovakia.

Uses. As a nickel-rich mineral, millerite is important economically even when found as a sparse dissemination in rocks or ores, especially if associated with other nickel or cobalt minerals.

PENTLANDITE, $(Fe, Ni)_9S_8$. Synonym: iron-nickel pyrite.

Chemical composition, variable. Fe-Ni ratio is usually 1:1. Cobalt is always present in some quantity (0.4 to 2.5% or more) as an isomorphous admixture to nickel.

System, cubic; symmetry, hexoctahedral $3L^44L_6^36L^29PC$. Space group $Fm3m(O_h^5)$. $a_0=10.02$. Has never been found in well-formed crystals. Occurs in pyrrhotite ores of magmatic deposits of the Sudbury type as irregular grains and inclusions. **Crystal structure.** The sulphur anions are arranged in cubic closest packing. The iron and nickel cations in the main occupy half the tetrahedral interstices (the number of which equals that of the sulphur anions), and some of them (according to the chemical formula) occupy one eighth of the octahedral interstices.

Colour, bronze-yellow, somewhat lighter than that of pyrrhotite. **Streak**, greenish black. **Lustre**, metallic.

Hardness, 3 to 4. Brittle. **Cleavage**, octahedral {111}, perfect. **Specific gravity**, 4.5 to 5. **Other properties.** Not magnetic. Good conductor of electricity.

Diagnostic features. Identifiable with difficulty without the aid of the microscope, since it usually occurs as minutest segregations in a pyrrhotite groundmass. Only large grains can be distinguished by their somewhat lighter colour as compared with pyrrhotite and clearly defined cleavage.

Before the blowpipe it fuses into a black magnetic globule. Dissolves in HNO_3 imparting a green colour to the solution. A dark-brown precipitate of ferrous hydroxide is formed on addition of ammonia. Gives the characteristic nickel reaction with dimethyl glyoxime.

Genesis and occurrence. Almost always occurs in paragenesis with pyrrhotite and chalcopyrite, but only in those sulphide ores which are associated genetically with basic and ultrabasic igneous rocks (gabbro-norites, peridotites, etc.). The paragenesis of the three minerals in such rocks is so characteristic that it is enough to establish in them the presence of the more easily identifiable pyrrhotite and chalcopyrite to be sure that microscopic examination will reveal the presence of pentlandite, which is of great economic importance. Magnetite and platinum minerals such as sperrylite—$PtAs_2$, palladium platinum, cooperite—PtS and braggite—(Pt, Pd, Ni) S are also found in small quantities.

In the zone of oxidation, nickel sulphides alter to nickel sulphate which is readily soluble in water, and is often observed in cavities and on the walls of mine workings as pale-green stalactites and crystalline encrustations of the following composition: $NiSO_4 \cdot 7H_2O$ (morenosite) or $NiSO_4 \cdot 6H_2O$ (roetgersite).

The largest deposit of such ore is at *Sudbury* in Ontario, Canada. The ore bodies in the form of large beds and veins lie in the lower parts of magmatic masses composed of basic rocks (norites, gabbro, etc.), and also in the rocks underlying the metamorphic complex. The ore contains: Ni 1 to 5 per cent, Cu and platinum metals 2 to 3%.

Uses. Pentlandite ores are the chief source of nickel. About 90% of the world's nickel production comes from copper-nickel sulphide ores (mostly from Sudbury). In addition to nickel, extracted from these ores are cobalt, copper, platinum metals, and in small quantities, selenium and tellurium.

Nickel is used in the manufacture of special tools, utensils, in the production of many important alloys (white copper, nickel steel, and copper-zinc alloy for rheostats, coinage, etc.) in nickel-plating compounds, etc.

5. CHALCOPYRITE GROUP

Under this group we shall describe the complex sulphides of Cu, Fe, and Sn—chalcopyrite and stannite—which crystallise in the tetragonal system. Although very similar to sphalerite in crystal structure, they differ sharply from it in physical properties. These sulphides sometimes occur in sphalerite as minute inclusions resulting from the disintegration of a limited solid solution, which may be explained by the close similarity of the crystal structures, especially at high temperatures. In turn, sphalerite may be present in stannite as a product of disintegration of a solid solution.

Bornite and cubanite also belong to this group, the former being a complex copper-iron sulphide very similar to chalcopyrite with which it can form a wide variety of isomorphous mixtures, although these break up upon cooling.

CHALCOPYRITE, $CuFeS_2$. "Chalcos" is the Greek for copper, "pyros" fire. Synonym: copper pyrite.

Chemical composition. Cu 34.57%, Fe 30.54%, S 34.9%. The data of chemical analyses usually closely agree with these figures. Negligible admixtures of Ag, Au, etc., are sometimes present.

System, tetragonal; symmetry, tetragonal-scalenohedral $L_4^2 2L^2 2P$. Space group $I\bar{4}2d(D_{2d}^{12})$. $a_0 = 5.24$; $c_0 = 10.30$. $a : c = 1 : 1.9705$.

Crystal structure is a relatively simple, nearly cubic, tetragonal lattice (Fig. 103). The unit cell of chalcopyrite may be described as that of the sphalerite type doubled vertically (cf. Fig. 94). As in sphalerite, each sulphur ion is surrounded by four metallic ions which are located at the corners of a tetrahedron, i.e., ions of copper and iron are spaced in each sheet after a definite pattern. In the first and fifth cationic sheets, i.e., on the upper and lower faces of the tetragonal prism (Fig. 103*a*) Fe ions occupy the corners of the square, while Cu ions occupy the centre. In the third sheet (in the middle of the prism) the arrangement is reversed: Cu ions occupy the corners of the square, while Fe ions are at the centre. In the second and fourth sheets, two Cu ions intersect with two Fe ions, the Fe cations being beneath the Cu cations of the second sheet and vice versa. All the tetrahedral groupings have the same orientation which accounts for the crystals being hemihedral. In distinction from sphalerite, chalcopyrite is opaque, has a clearly metallic lustre, and does not possess perfect cleavage.

Habit. Crystals are rare and occur only in druse cavities. Mostly octahedral with combinations $\{112\}$ and $\{1\bar{1}2\}$, or tetrahedral (Fig. 104); less often scalenohedral, etc. The faces of the basic tetrahedron are either dull or striated, while the negative faces are smooth. Often

twinned, with twinning plane (112), less often (102). **Aggregates.** Usually massive or in irregular disseminated grains. Also occurs in colloform kidney-shaped and grape-like forms.

Colour, brass yellow often with dark-yellow or iridescent tarnish. **Streak**, black with a greenish tint. Opaque. **Lustre**, strong metallic.

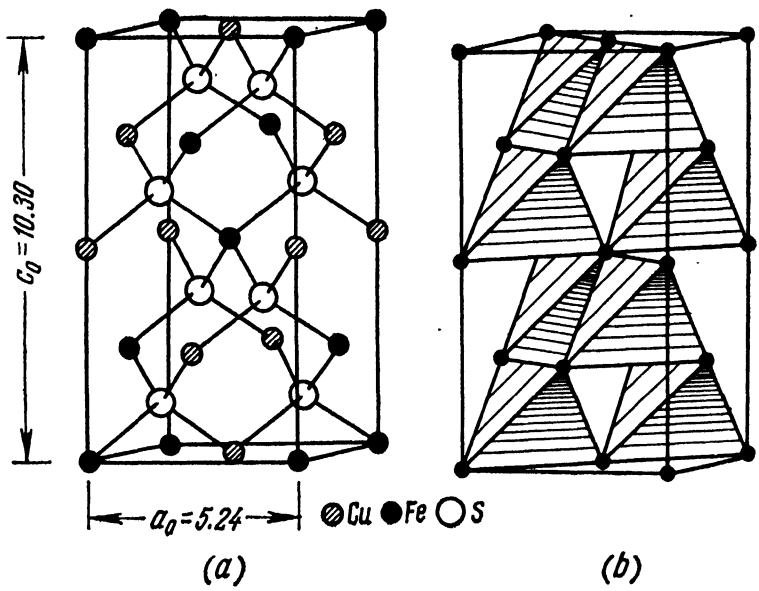


Fig. 103. Crystal structure of chalcopyrite.
a – distribution of atomic centres of copper, iron, and sulphur;
b – the same structure shown as tetrahedra.

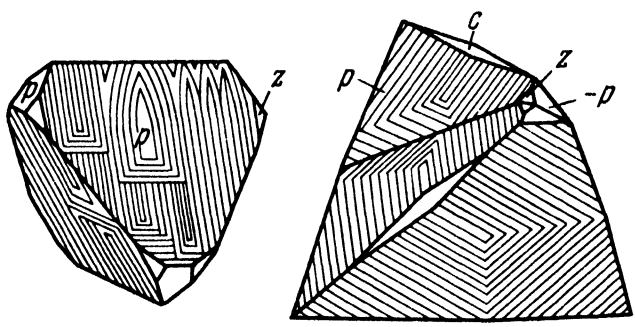


Fig. 104. Tetrahedral crystal and twin of chalcopyrite:
p {112}, *z* {011}, *c* {001}.

Hardness, 3 to 4. Rather brittle. **Cleavage**, {101} imperfect. **Specific gravity**, 4.1 to 4.3.

Diagnostic features. Readily identifiable by colour; hardness very different from that of pyrite which on fracture often shows an iridescent tarnish, somewhat similar to the colour of chalcopyrite. Irregularly-shaped grains of millerite look like chalcopyrite but have a stronger lustre and a higher nickel content.

In the blowpipe flame decrepitates and fuses to a magnetic globule. Roasted with soda on charcoal, gives a copper globule. In the closed tube, it gives a sulphur sublimate. In nitric acid gradually decomposes with separation of sulphur.

Genesis and occurrence. In nature, chalcopyrite forms under a variety of conditions.

As an accessory of pyrrhotite, it often occurs in deposits of copper-nickel sulphide ores of *magmatogene* origin in basic igneous rocks in association with pentlandite, magnetite, sometimes cubanite, etc.

It most commonly occurs in typical *hydrothermal* vein and metasomatic (including contact-metasomatic) deposits.

Is often associated with pyrite, pyrrhotite, sphalerite, galena, grey ores and many other minerals. The nonmetallic minerals in these deposits are quartz, calcite, barite, silicates of diverse composition, etc.

Chalcopyrite is very rarely the product of *exogenous* processes in sedimentary rocks forming in the conditions of hydrogen-sulphide fermentation in the course of decomposition of organic remains and an influx of cupriferous solutions. Along with chalcocite and marcasite it sometimes replaces wood fibres and other organic remains.

As a result of chemical weathering chalcopyrite yields copper and iron sulphates. Interacting with CO_2, or with carbonates in the presence of oxygen and water, soluble copper sulphate forms malachite and azurite; reacting with SiO_2 hydrosols, it gives chrysocolla; whereas reactions with different acids formed in the zone of weathering give rise to various salts: arsenates, phosphates, vanadates and, sometimes, chlorides. However, in a very dry climate various copper sulphates survive in the oxidised zone despite their ready solubility in percolating surface waters.

Pseudomorphs after chalcopyrite, i.e., its replacement by secondary copper sulphides, such as bornite, chalcocite and covellite, are common in the zones of secondary sulphide enrichment of copper deposits.

Chalcopyrite, as an associate, occurs in varying amounts in practically all the hydrothermal deposits of most diverse sulphide ores. It forms a substantial part of the ores of many deposits and is therefore of economic value. The U.S.S.R. has deposits of all genetic types in which chalcopyrite is the principal copper mineral.

Other important localities for chalcopyrite are *Bingham*, Utah (U.S.A.); *Chuquicamata*, Chile; the cupriferous sandstones of *Katanga*, Congo, and Northern Rhodesia, south of Katanga.

Uses. Chalcopyrite ores are a major source of copper. The average copper content usually ranges between 2 to 2.5%.

The copper smelted from the ores is used either pure or in the form of alloys (brass, bronze, tombac, etc.). The chief use of copper is in electrical engineering. Other major uses are in the machine-building and ship-building industries, in the manufacture of chemical equipment, plumbing, etc.

STANNITE, Cu_2FeSnS_4. Synonym: tin pyrite.

Chemical composition. Cu 29.5%, Fe 13.1%, Sn 27.5%, S 29.9%. Content according to analyses: Sn 22.0 to 27.7%, Cu 22.9 to 31.5%, Fe 4.7 to 23.3%. Impurities: Zn 0.75 to 10.1%, Sb up to 3%, Cd up to 1.5%, Pb up to 2%, Ag up to 1%.

System, tetragonal; symmetry, tetragonal-scalenohedral $L_4^2L^22P$. Space group $I\bar{4}2d(D_{2d}^{12})$. $a_0=5.46$; $c_0=10.725$; $a:c=1:1.966$. Rare small crystals have cubic or tetrahedral habit. Externally very similar to chalcopyrite crystals. Usually occurs as irregular grains or massive. **Crystal structure**, perfectly identical with that of chalcopyrite (Fig. 103). The cations are arranged as follows: in the first and fifth sheets, Sn ions are at the corners of the square, while Fe ions are at the centre; in the middle sheet, the reverse is observed—Fe ions are at the corners, while Sn ions are at the centre; the even sheets (second and fourth) are composed of Cu ions. Thus, the crystal structures of stannite and chalcopyrite are very similar in ionic arrangement to that of sphalerite.

Colour, steel grey with a characteristic olive-green tint on fresh fracture. When numerous microscopic chalcopyrite inclusions are present, stannite becomes definitely yellowish. **Streak**, black. Opaque. **Lustre**, metallic upon fresh fracture but quickly turns dull.

Hardness, 3 to 4. Brittle. **Cleavage**, {110} and {001} imperfect, rarely observed. **Specific gravity**, 4.3 to 4.5.

Diagnostic features. Has a characteristic colour with an olive-green tinge and is readily distinguished by the naked eye from grey ores which are similar to stannite in a number of properties (hardness, brittleness, etc.).

Fuses before the blowpipe on charcoal, turning white at the surface, and giving a white coating of SnO_2 around the assay. The presence of copper, iron, and sulphur is determined by chemical reactions. Decomposes in nitric acid with separation of sulphur and stannous oxide, imparting a deep blue colour to the solution.

Genesis and occurrence. Stannite is a comparatively rare mineral and occurs in *hydrothermal* tin ore deposits.

In tungsten-tin deposits, it is observed in association with cassiterite (SnO_2) chalcopyrite, arsenopyrite, wolframite, and other minerals.

Stannite is much more common in stanniferous sphalerite-galena and sphalerite-pyrrhotite ores. In these it is closely associated paragenetically with sphalerite, chalcopyrite, and sometimes pyrrhotite, galena, etc. Instances are known when it is replaced by cassiterite (SnO_2) and vice versa.

In the oxidation zone it readily decomposes to give finally limonite and cassiterite. In this process, however, most of the tin apparently passes into colloidal solution which finally coagulates to form earthy, spongy or colloform cassiterite concretions. In the U.S.S.R., stannite occurs in numerous stanniferous ore deposits, most often in association

with chalcopyrite in grains of up to 1 cm in diameter in paragenesis with cassiterite and sphalerite.

Outside the U.S.S.R., it has been found at *Zinnwald* (Erzgebirge mountains, Czechoslovakia) and in considerable quantities in Southern China, in *Tsihan* (Tasmania), and especially in *Bolivia* (Ahota, Potosi, etc.).

Uses. Stannite very rarely is found in considerable quantities and, therefore, it is of lesser importance to industry than cassiterite.

BORNITE, Cu_5FeS_4. Synonym: variegated copper ore. In nature, it forms limited solid solutions with chalcopyrite, which disintegrate upon cooling. The process of disintegration has been studied experimentally.

Chemical composition is variable. Theoretically, according to the chemical formula Cu_5FeS_4 the composition should be: Cu 63.3%, Fe 11.2%, S 25.5%. However, the composition of bornite varies widely because the mineral may contain chalcopyrite and chalcocite in the form of solid solutions. Another frequently observed chemical impurity is Ag.

System, cubic; symmetry, hexoctahedral $3L^44L_6^36L^29PC$. Space group $Fd3m(O_h^7)$. $a_0=10.93$. Crystals are extremely rare. Usually massive or in the form of impregnations. **Crystal structure.** Complicated cubic. According to X-ray data, two kinds of copper ions occupy different positions and its chemical formula is probably: $2Cu_2S \cdot CuFeS_4 = (Cu_4CuFeS_4)$, i.e., four of the copper ions are univalent, while the fifth copper ion and the iron ion are divalent.

Colour, dark copper-red on fresh fracture; usually shows a bright variegated (mostly blue) tarnish. **Streak**, greyish black. Opaque. **Lustre**, submetallic.

Hardness, 3. Rather brittle. **Cleavage**, practically none. **Specific gravity**, 4.9 to 5.0. **Other properties.** Conductor of electricity.

Diagnostic features. Easily recognised by colour and variegated, predominantly blue, tarnish, and low hardness. May be mistaken for covellite because of bright blue tarnish (but when scratched with a knife, shows its real colour).

Before the blowpipe bornite fuses into a magnetic bead: roasted with soda on charcoal, gives a copper globule. Being acted upon by HNO_3 it decomposes with separation of floating sulphur.

Genesis and occurrence. Bornite may be of both endogenous and exogenous origin.

Bornite of *endogenous* origin occurs in certain *hydrothermal* deposits. It sometimes contains microscopic, usually platy, chalcopyrite inclusions, which are a product of solid solution disintegration. Apart from chalcopyrite, paragenetic associates of bornite include occasionally endogenous chalcocite, galena, sphalerite, pyrite, etc.

Exogenous bornite is widespread in *the zones of secondary sulphide enrichment.* As the earliest secondary sulphide, it is formed metasomat-

ically mostly after chalcopyrite as irregular veinlets, selvages or in massive forms. Although present in numerous copper sulphide deposits, bornite seldom occurs in quantity. Bornite is less stable than other secondary copper sulphides and is replaced by chalcocite and covellite which are richer in copper. Decomposition of bornite in the oxidation zone gives rise to oxygen compounds: malachite, azurite, less often cuprite, etc.

In the U.S.S.R., considerable quantities of endogenous bornite in association with chalcopyrite have been found in the *Uspenskoye* deposit.

Exogenous bornite occurs in large amounts in the zones of secondary sulphide enrichment in almost all copper sulphide deposits, especially under the conditions of weathering in a temperate climate.

Uses. Since bornite contains much more copper than chalcopyrite, even its impregnation ores, if found in sufficient quantities, are definitely worth mining.

CUBANITE, $CuFe_2S_3$. System, orthorhombic. Chemical composition: Cu 22 to 24%, Fe 40 to 42%, S 34 to 35%. Colour, bronze yellow similar to that of pyrrhotite. Lustre, metallic. Hardness, 3.5. Cleavage, none. Specific gravity, 4.03 to 4.18. Highly magnetic.

Paragenetically, cubanite is closely associated with chalcopyrite. Is often observed in the latter as platy inclusions visible under the microscope, formed as a result of the disintegration of solid solutions. First discovered in the gold-quartz veins of *Morro-Velho*, Minas Geraes, Brazil.

6. COVELLITE GROUP

This group includes compounds which have a simple empirical formula, but a complex crystal structure in which each element is represented by two sorts of ions (this applies equally to the cations and the anions). Therefore, the chemical formula appears more complex. We shall consider only one mineral of this group—covellite.

COVELLITE, CuS, or $Cu_2^{\cdot}S{\cdot}Cu^{\cdot\cdot}S_2$. Named for the Italian mineralogist Covelli. Synonym: copper indigo.

Chemical composition. Cu 66.5%, S 33.5%. Chemical analyses reveal impurities of Fe, and, less often, of Se, Ag, and Pb.

System, hexagonal; symmetry, dihexagonal dipyramidal L^66L^27PC. Space group $C6/mmc$ (D_{6h}^4). $a_0=3.80$; $c_0=16.32$.

Extremely rare crystals are small, thin and tabular. **Crystal structure.** Covellite has a peculiar layered hexagonal lattice (Fig. 105). X-ray studies have shown the structure to be much more complex than the original CuS formula suggests. The sulphur ions proved to be of two kinds: S^{2-} single ions and $[S_2]^{2-}$ coupled ions, i.e., compact pairs of ions which are similar to those found in the crystal structure of pyrite and having the same S—S distance, namely, 2.05 Å (Fig. 115). The cop-

per ions are also of two kinds: Cu^{1+} ions and smaller Cu^{2+} ions. Each divalent copper ion is surrounded by three single S^{2-} ions, forming an equilateral triangle. The triads are connected to each other through the corners to form sheets (shown black in Fig. 105) in the crystal structure of covellite, which are oriented perpendicular to the sixfold axis. Between these sheets there are two layers of tetrahedra with univalent ions Cu^{1+} at the centre. The bases of the tetrahedra facing one another are connected by vertically oriented $[S_2]^{2-}$ ion pairs (in the middle, upper, and lower layers, and which are shown in Fig. 105 as hollow shortened triangular prisms); the tetrahedral apexes opposite to these are occupied by single S^{2-} ions which are shared by the triangular sheet and the apexes of the next tetrahedral layer. Thus, the structure of covellite is a combination of the structural elements of both modifications of carbon (diamond and graphite). If the ionic composition of the crystal structure is calculated, it will be seen that the formula of covellite is to be more correctly represented as $Cu_2^{\cdot}S{\cdot}Cu^{\cdot\cdot}S_2$. These structural features agree well with the shape, cleavage and unusual optical properties of the mineral and its ability to yield a part of its sulphur as sublimate on heating, etc.

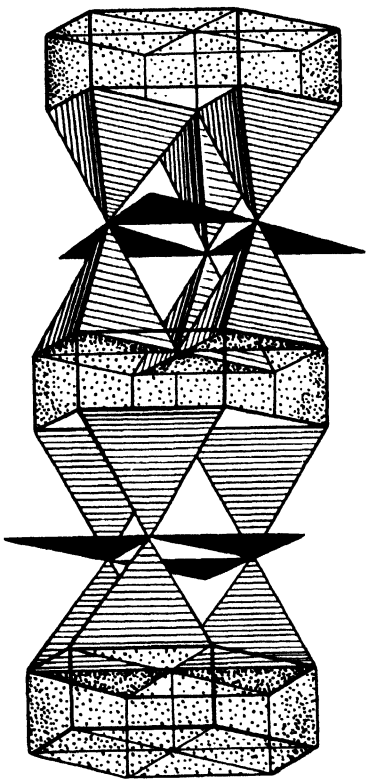


Fig. 105. Crystal structure of covellite.

Aggregates. Covellite usually occurs as thin bright deep blue coatings or crusts or as deep blue-black powdery or sooty masses.

Colour, indigo-blue. **Streak**, grey to black. Opaque. Translucent and green in extremely thin plates. **Lustre**, metallic.

Hardness, 1.5 to 2. Brittle. Thin plates somewhat flexible. **Cleavage**, {0001} perfect. **Specific gravity**, 4.59 to 4.67.

Diagnostic features. Easily recognisable by deep blue colour, low hardness, and copper sulphide associations.

Before the blowpipe covellite fuses readily and burns with a blue flame, evolving SO_2. Unlike chalcocite, it gives a sulphur sublimate in the closed tube. Dissolves in hot HNO_3 with the separation of sulphur.

Genesis and occurrence. Usually found in small quantities, covellite is a most typical exogenous mineral of the zone of secondary sulphide enrichment in copper deposits. As a rule, it is formed metasomatically after primary and secondary copper sulphides, such as chalcopyrite, bornite, chalcocite, etc. May also be deposited along fissures as colloform or earthy masses.

Covellite of *hydrothermal* origin in paragenesis with pyrite is extremely rare and occurs in small amounts in Butte, Montana (U.S.A.), and elsewhere.

As a sublimation product from fumaroles, it is found in the lavas of Vesuvius, where it was first described.

It never forms deposits in its own right, but is found in negligible quantities in virtually all copper sulphide deposits (in the zones of secondary sulphide enrichment). Large masses occur on *Kawau Island* (New Zealand).

Covellite-chalcocite ores are twice as rich in copper as equally disseminated primary chalcopyrite ores.

7. ORPIMENT GROUP

In this group we shall review a sulphide of trivalent arsenic known as orpiment (auripigment), and also realgar with which it has much in common.

ORPIMENT, As_2S_3. The name (orpiment or auripigment) comes from the Latin "aurum", gold, and "pigmentum", paint. It was formerly believed that this mineral contained gold.

Chemical composition. As 61%, S 39%. Usually contains only mechanical impurities: Sb_2S_3, FeS_2 (marcasite), SiO_2, clayey matter, etc. Only Se, Sb, V (up to 0.02%) and Ge (up to $4 \cdot 10^{-5}$%) may be regarded as isomorphous admixtures.

System, monoclinic; symmetry, rhombic prismatic L_2PC. Space group $P2_1/n(C_{2h}^5)$. $a_0 = 11.46$; $b_0 = 9.59$; $c_0 = 4.24$; $\beta = 90°27'$.

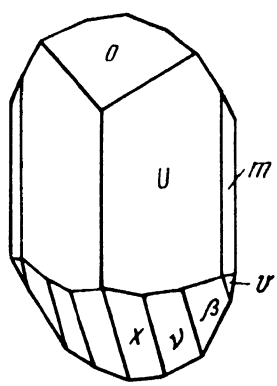


Fig. 106. Crystal of auripigment: *o* {301}, *U* {210}, *m* {110}, *x* {$\bar{3}11$}, *ν* {$\bar{3}21$}, *β* {$\bar{1}2.9.4$}, *v* {$\bar{3}31$}.

X-ray data (obtained by V.I. Mikheyev) indicate that certain specimens of orpiment contain considerable amounts of native sulphur as a mechanical impurity. **Crystal structure** is layered. The layers composed of As_2S_3 are loosely linked by van der Waals forces, which results in excellent cleavage parallel to (010), low hardness, high optical anisotropy, and other properties. **Habit.** Crystals usually prismatic (Fig. 106), often with curved faces. Most common forms are pinacoids {100} and {010}, and prisms {110}, {301}, {210}, etc. **Aggregates** are often rod-like, or cockscombed, also in botryoidal, reniform, and globular masses with a radial structure (Fig. 107).

Colour, lemon yellow to brownish yellow: cryptocrystalline masses, containing admixtures of finely dispersed FeS_2, are dirty yellow with a greenish tint. **Streak** has the same colour but is somewhat brighter. Translucent; cleavage flakes transparent. **Lustre**, adamantine to submetallic, depending on direction, which fully agrees with the refractive indices: $n_x = 3.0$, $n_y = 2.8$, and $n_z = 2.4$.

Hardness, 1 to 2. Lamellae, flexible but not elastic. **Cleavage**, {010} highly perfect, and {100} imperfect. **Specific gravity**, 3.4 to 3.5. **Other properties.** Non-conductor of electricity. Becomes electrified when separated along cleavage planes.

Diagnostic features. Easily recognisable by bright lemon-yellow colour, low hardness, excellent cleavage, and strongly adamantine or submetallic lustre on fracture. In powdery masses, may be mistaken for

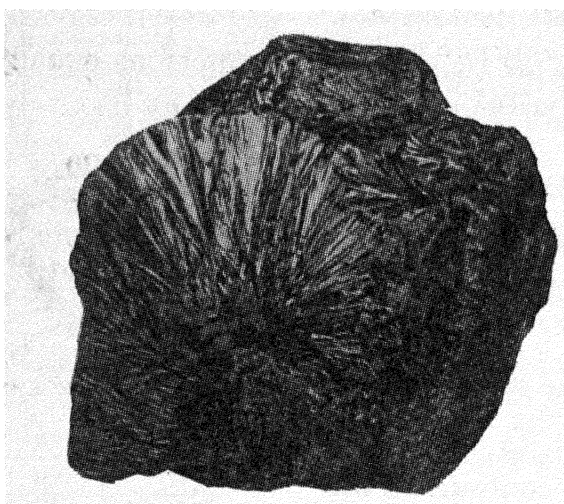


Fig. 107. Radially-fibrous aggregates of auripigment. Reduced 2.5 times.

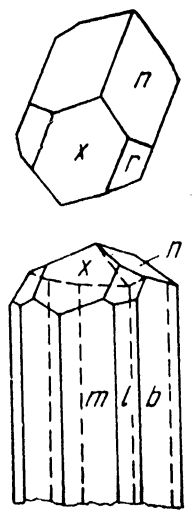


Fig. 108. Realgar crystal. Lukhum deposit. *m* {110}, *l* {120}, *b* {010}, *n* {011}, *x* {$\bar{1}$01}, *r* {$\bar{1}$11}.

pulverulent native sulphur, and also for certain uranophosphates, or uranovanadates, such as autunite and tyuyamunite, from which it can be distinguished by characteristic behaviour before the blowpipe, optical properties, and non-radioactivity.

Easily fuses and volatilises, leaving on charcoal a white coating of As_2O_3 with a sharp arsenical (garlic) odour. Dissolves in nitric acid and aqua regia with separation of floating sulphur, and is readily soluble in KOH, leaving no residue.

Genesis and occurrence. Occurs in *hydrothermal* deposits in association with minerals which are formed at comparatively low temperatures, such as realgar, antimonite, marcasite, pyrite, and also with quartz, calcite gypsum, etc. Is deposited from the well-known mineral hot springs in Steamboat, Nevada (U.S.A.) together with realgar, opal, aragonite, etc.

In very small amounts it has been found on the walls of craters, in the cavities in porous lavas as a sublimate together with native sulphur, chlorides, and other minerals.

Exogenous orpiment is very rarely found in negligible quantities, as coatings and earthy accumulations in coal and brown iron ore deposits, being probably the product of the action of hydrogen sulphide of organic origin on arsenious solutions.

In the U.S.S.R., orpiment is found in substantial quantities as an arsenic ore in association with realgar. The ores of the *Lukhum* deposit are remarkable for the colouring of hand specimens, which are composed of crystalline masses of bright-yellow auripigment, red realgar, milk-white quartz and calcite. In cavities there often occur druses of well-formed crystals from 0.5 to 5 cm long. Orpiment or auripigment has also been found as large continuous reniform masses, which on fracture show a radial structure (Fig. 107).

The auripigment ores of the relatively young *Julfa* deposit (north of the town of Julfa, Nakhichevan Autonomous Soviet Socialist Republic) are quite different in appearance. These occur in Tertiary folded marls and argillaceous rocks. Auripigment here was observed in the form of cryptocrystalline (metacolloidal) masses with a waxy lustre on fracture and greenish-yellow colour (due to admixtures of finely-dispersed iron disulphides). During mining operations, abundant evolution of gases, such as CO_2, H_3As, and H_2S, took place. In the vicinity of the deposits, mineral springs containing $Ca(HCO_3)_2$, Na_2SO_4, $CaHAsO_4$, Br, Li, etc., are still flowing.

Other notable auripigment deposits are at *Allachar*, Macedonia, from which large crystals have been recorded, and at *Mercure*, Utah (U.S.A.), and elsewhere.

Uses. When found in quantity is used for obtaining arsenic trioxide, also in dyeing and for other purposes.

REALGAR, AsS. **Chemical composition.** As 70.1%; S 29.9%. Chemical analysis data almost wholly agrees with the theoretical. Isomorphic admixtures of other elements have not been found.

System, monoclinic; symmetry, rhombic prismatic L^2PC. Space group $P2_1/n(C_{2h}^5)$. $a_0 = 9.27$; $b_0 = 13.50$; $c_0 = 6.56$; $\beta = 106°33'$. **Crystal structure** is rather complex, being composed of separate As_4S_4 molecules. The sulphur ions form a square, whereas the arsenic ions form a tetrahedron. The centres of the square and the tetrahedron coincide. **Habit.** Crystals usually prismatic (Fig. 108) and shortened or elongated along the vertical axis with thin striations parallel to it on the faces. The most common forms are pinacoids {001}, {010} and orthorhombic prisms {110}, {120}, {011}. **Aggregates.** Also occurs in massive granular aggregates, sometimes as coatings, crusts or earthy friable masses.

Colour, orange-red, less often dark red. Semitransparent. **Streak**, light orange. **Lustre**, adamantine on crystal faces, resinous to greasy on fracture. Refractive indices in Li-light: $n_x = 2.61$, $n_y = 2.59$, and $n_z = 2.46$.

Hardness, 1.5 to 2. **Cleavage**, {010} and {120} quite perfect. **Specific gravity**, 3.4 to 3.6. **Other properties.** On exposure to light it gradually turns into a light-orange powder. On exposure to electric light the crystals decrepitate and form the same light-orange powder. According to X-ray data, this is accompanied by a breakdown of the crystal structure. Non-conductor of electricity.

Diagnostic features. Characteristic orange-red colour, low hardness, and striation of faces parallel to the crystal elongation axis. Another characteristic feature is its paragenetic association with orpiment, which is easily recognisable by its external features. It differs from similar crocoite ($PbCrO_4$) by lower hardness, different habit, and behaviour before the blowpipe (roasted on charcoal with soda, crocoite gives a lead globule). Cinnabar is distinguished from realgar by its bright-red streak, high specific gravity and different behaviour before the blowpipe.

Fuses readily in the blowpipe flame, and volatilises giving off the characteristic garlic odour. Dissolves in aqua regia with separation of sulphur. Unlike cinnabar, dissolves in hot KOH and gives a lemon-yellow flocculent precipitate on addition of hydrochloric acid.

Genesis and occurrence. Realgar occurs in nature under conditions absolutely similar to those of orpiment with which it is constantly associated (cf. orpiment). It never occurs at the earth's surface, since on exposure to daylight it decomposes and partly alters to orpiment.

In the U.S.S.R., extremely large (1 to 2 cm) realgar crystals (Fig. 108) and beautiful druses have been recorded from *Lukhum* deposit (Rachinsky ridge on the southern slope of the Caucasus in Western Georgia) in association with orpiment, and occasionally with antimonite, pyrite, marcasite, melnikovite, quartz, calcite, etc.

As an associate, realgar occurs practically in all orpiment deposits.

Uses. Realgar is a rather rare mineral. In a few cases it forms purely arsenic deposits together with orpiment, one example being the deposit at Lukhum. When thus found, it is a raw material for obtaining As_2O_3 (by roasting). Arsenic sulphide (AsS), both artificial and natural, is used in dyeing, fireworks, in glass making, and in other applications.

8. ANTIMONITE GROUP

The sulphides of trivalent antimony and bismuth—antimonite and bismuthinite—which belong to this group fundamentally differ from orpiment in crystal structure and physical properties (opacity, metallic lustre, etc). This is obviously linked with the higher polarising ability of the Sb^{3+} and Bi^{3+} cations.

ANTIMONITE, Sb_2S_3. From the Latin "antimonium". Synonyms: stibnite, antimony glance.

Chemical composition. Sb 71.4%, S 28.6%. Impurities: As, Ag, and Au. Compounds of the last two elements are probably present as mechanical inclusions. Native gold has been repeatedly observed in the antimonite groundmass in polished sections under the microscope.

System, orthorhombic; symmetry, rhombic-dipyramidal $3L^23PC$. Space group *Pbnm* (D_{2h}^{16}). $a_0 = 11.20$; $b_0 = 11.28$; $c_0 = 3.83$. **Crystal structure** consists of bands of closely bonded Sb and S ions which are parallel to the *c* axis and which are made up of zigzag chains —Sb—S— —Sb—S—. The bonds between the bands are weaker than those

between the ions within the bands. This, naturally, is reflected not only on the shape of the crystals, but also in such properties as cleavage, hardness, brittleness, etc.

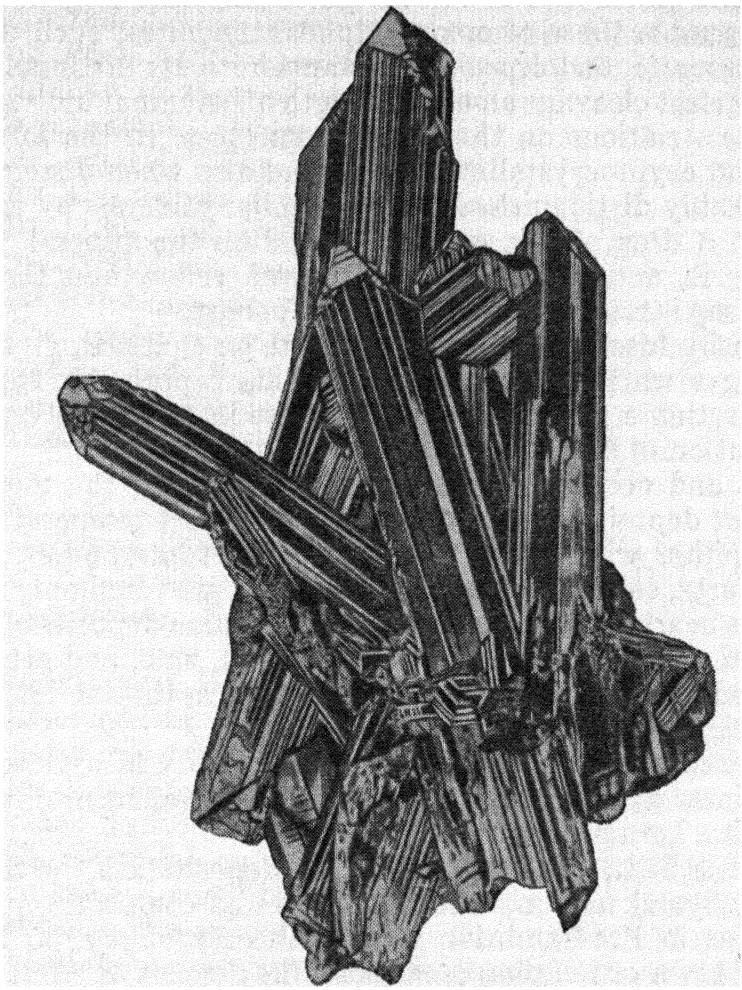


Fig. 109. Druse of prismatic antimonite crystals.

Habit. Usually prismatic (Fig. 109), columnar, acicular, vertically striated. Often, especially in the case of large crystals; curved or even twisted individuals are found. The following combinations are the most characteristic of the many known faces: prism {110}, pinacoid {010}, and pyramids {111}, {113}, {121}, etc. (Fig. 110). **Aggregates.** Occurs as massive granular aggregates, often radial, or, less often, with a felted texture, also as granular impregnations in a quartz groundmass.

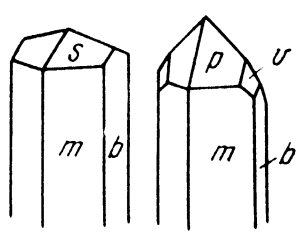


Fig. 110. Antimonite crystals: *m* {110}, *b* {010}, *s*{111}, *p*{331}, *v*{121}.

Colour and streak, lead grey. Crystals often show a dark bluish tarnish. Opaque. **Lustre,** metallic, and strong on cleavage surfaces.

Hardness, 2 to 2.5. Brittle. **Cleavage**, {010} perfect, and {110} imperfect. **Specific gravity**, 4.6. **Other properties.** Non-conductor of electricity.

Diagnostic features. The colour and mechanical properties of aggregates resemble those of many sulphoantimonites, such as boulangerite, jamesonite, and especially bismuthinite. Its distinguishing features are perfect cleavage along the length of columnar individuals, and a cross-wise striations on the shearing surfaces. In the form of fine-granular and cryptocrystalline masses and also when disseminated, it is unmistakably distinguished from all similar minerals by its reaction with KOH. A drop of this reagent placed on the mineral vigorously decomposes it, and the mineral first turns yellow and then orange; when the drop is removed, a red spot will persist.

Very easily fuses in the blowpipe flame on charcoal, giving off SO_2 and leaving a white coating of Sb_2O_3 which vaporises in the reducing flame, imparting a green colouration to the latter. Dissolves in HNO_3 with separation of Sb_2O_5.

Genesis and occurrence. Antimonite occurs for the most part in *hydrothermal* deposits, being formed at the lowest temperatures, composing, together with quartz, veins and sheet-like bodies. Cinnabar, fluorite, quartz, calcite, kaolinite, barite, etc., are commonly associated with it. It is nearly always an accessory mineral in deposits of cinnabar, realgar, and orpiment, rarely in those of lead, zinc, and other metals.

Has been observed in negligible quantities in the sublimates of volcanic eruptions.

In oxidised zones it decomposes quite readily into various yellow and sometimes dark-brown antimony oxides (valentinite, servantite, senarmontite, kermesite, etc.).

In the U.S.S.R., the most important deposits are the *Razdolninskoye*, Krasnoyarsk region, where it occurs as composite quartz-antimonite veins in Pre-Cambrian schists; the *Kadamjay*, 35 km southwest of the town of Ferghana—a sheet-like deposit in "flinty breccia" where antimonite is associated not only with quartz and calcite but also with minor amounts of pyrite, marcasite, fluorite, and barite.

On the Island of Shikoku (Japan) unusually large (up to 0.5 m long and 5 cm thick) (Fig. 109) antimonite crystals have been found. Great deposits are known in Yunnan and other provinces in China where antimonite occurs in quartz veins and stock-like bodies in limestones. These deposits are the world's principal sources of antimony ores.

Uses. Antimonite ores are the chief source of antimony—an element which finds most diverse applications. It is used mainly in antifriction alloys for bearings, such as babbits. Its lead and zinc alloys go to make type, shot, pump and valve parts, etc. Antimony compounds are used in the production of rubber (vulcanisation), textile industry (impregnation of fabrics), glass manufacture, medicine, etc.

BISMUTHINITE, Bi_2S_3. Synonyms: bismuthine, bismuth glance.

Chemical composition. Bi 81.3%, S 18.7%. Minor quantities of Pb, Cu, Fe, As, Sb, Te, etc., are common admixtures; of these Pb, Sb, and Fe may isomorphously replace bismuth.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group *Pbnm* (D_{2h}^{16}). $a_0 = 11.13$; $b_0 = 11.27$; $c_0 = 3.97$. **Crystal structure,** similar to that of antimonite. **Habit.** Like antimonite, occurs in elongated columnar crystals (Fig. 111) mostly bounded by the prism faces, such as {110}, {120}, {130}, and pinacoids, such as {100}, {010}, {001}. Faces most often show thin vertical striations. **Aggregates.** Massive, granular, occasionally radial.

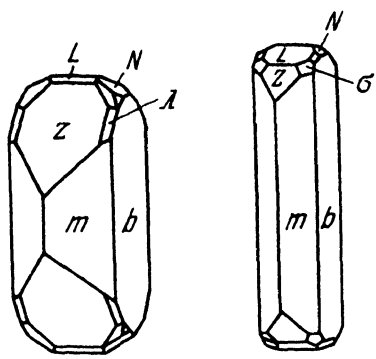


Fig. 111. Crystals of bismuthinite: {110}, *b*{010}, *z*{301}, {101}, *n* {201}, *δ* {211}, etc.

Colour, white with a lead-grey tinge. Often with a yellow or iridescent tarnish. Opaque. **Streak,** grey. **Lustre,** strongly metallic.

Hardness, 2 to 2.5. **Cleavage,** {010} perfect and {100} and {001} imperfect. **Specific gravity,** 6.4 to 6.8, sometimes up to 7.1. **Other properties.** Non-conductor of electricity.

Diagnostic features. Bismuthinite differs from antimonite by stronger lustre, higher specific gravity, and reaction with KOH (cf. antimonite). Aggregates resemble numerous sulphoantimonites and sulphobismuthinites of complex composition, from which it is not always easily distinguished without appropriate chemical tests.

Before the blowpipe on charcoal bismuthinite fuses readily, boils, and spits. In the reducing flame it gives a bismuth globule, leaving a lemon-yellow bismuth-oxide coating on the charcoal. The most characteristic reaction to bismuth is the bright-red bismuth-iodide fringe around the assay when it is fused with potassium iodide (assay button). Dissolves readily in HNO_3 with separation of floating sulphur.

Genesis and occurrence. Bismuthinite is found exclusively in *hydrothermal* (vein and contact metasomatic) deposits, though in conditions somewhat different from those of antimonite. As an accessory it is found in deposits of tin, tungsten, arsenic, often associated with native bismuth, arsenopyrite, chalcopyrite, sometimes with native gold, topaz, beryl, pyrite, galena, and many other sulphides. It rarely forms deposits of its own.

In the oxidised zone it is easily destroyed, altering to basic carbonates in the form of pseudomorphs after bismuthinite.

In the U.S.S.R., the most important deposits are in Central Asia, e.g., *Brich-Mulla* where bismuthinite, together with native bismuth, occurs in a number of quartz veins in limestones, associated with pyrite arsenopyrite, chalcopyrite, etc. In a number of deposits in the Trans-

Baikal region bismuthinite accompanies such minerals as cassiterite, chalcopyrite, arsenopyrite, etc., and sometimes occurs in granular masses.

The world's largest bismuth deposits are in Bolivia (*Tasna, Chorolque*, etc.) and in Peru (*Cerro de Pasco*). Genetically these deposits are associated with young extrusives.

Uses. Bismuthinite ores are the main source of bismuth used in the production of fusible alloys, glass with a high birefringence, chemicals, medical preparations, etc.

We shall also describe tetradymite here, though it belongs to a different group.

TETRADYMITE, Bi_2Te_2S. "Tetradymos" means fourfold in Greek (it often forms crystal fourlings). Synonym: bismuth telluride.

Chemical composition. Bi 59.3%, Te 36.2%, S 4.5%. Se, Au, Cu, Pb may be admixed in negligible amounts. Selenium content may be as high as 1%. Gold, often paragenetically associated with tetradymite, may be present as inclusions.

System, trigonal; symmetry, ditrigonal scalenohedral $L_6^3 3L_2 3PC$. Space group $R\bar{3}m(D_{3d}^5)$. Lamellar or tabular aggregates are common. Tabular or rhombohedral crystals usually occur as fourlings with $\{01\bar{1}8\}$ and $\{01\bar{1}5\}$ as the composition plane. **Crystal structure,** typically lamellar.

Colour, steel grey. **Lustre,** strongly metallic.

Hardness, 1.5 to 2.0. Thin lamellae are flexible. **Cleavage,** {0001} excellent. **Specific gravity,** 7.24 to 7.54. **Other properties.** Poor conductor of electricity. Thermoelectrical.

Diagnostic features. In many external features resembles molybdenite; differs from it by stronger lustre, higher specific gravity, behaviour before the blowpipe and reactions with acids.

Unlike molybdenite, it is readily fusible on charcoal; with S and KI gives a bright orange coating (the presence of bismuth). Dissolves in concentrated H_2SO_4, and upon heating imparts to the solution the purple colouration characteristic of Te. Readily soluble in HNO_3.

Genesis. Being the most common mineral among tellurides, tetradymite is found most often as an accessory in hydrothermal gold deposits. Paragenetically, it associates with various sulphides: pyrrhotite, chalcopyrite, pyrite, tetrahedrite, bismuthinite, and also gold, etc.

In the oxidised zone of ore deposits it readily decomposes, giving rise to so-called bismuth ochres.

In the U.S.S.R., it has been found in the *Frolovsky* mine of the Turya group (Northern Urals); the *Shilovo-Iset* gold deposit (66 km east of Sverdlovsk); the Kumak deposit (Southern Urals) and in a number of localities of Western and Eastern Siberia.

Elsewhere in the world it has occurred in a number of gold deposits of the U.S.A., Mexico, British Columbia, etc.

Uses. Tetradymite forms no deposits in its own right. Being an accessory in bismuth and gold deposits it may be a source of bismuth and tellurium obtained as by-products.

9. MOLYBDENITE GROUP

This group includes sulphur compounds of tetravalent Mo and W ions. Tungsten sulphide is an exceptionally rare mineral.

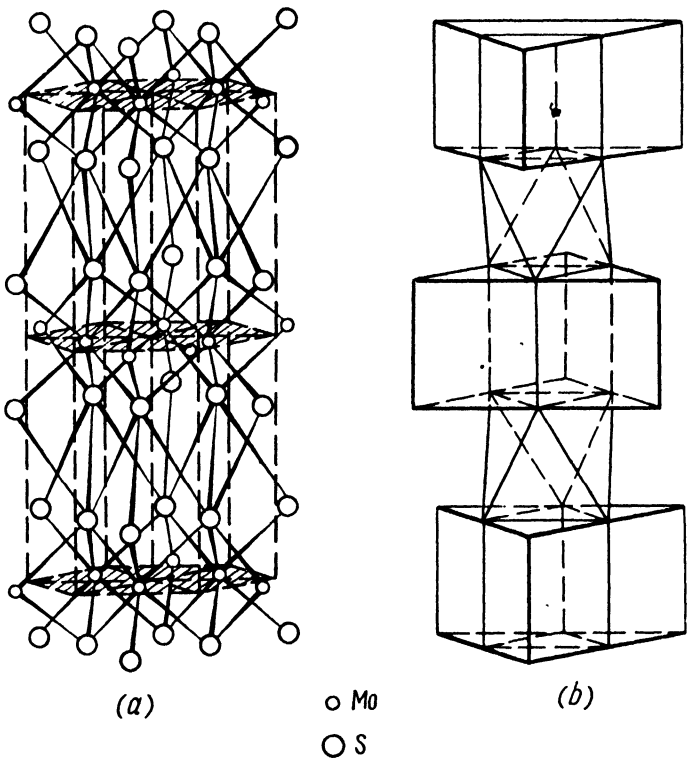


Fig. 112. Crystal structure of molybdenite.
a – distribution of ionic centres (sheets containing molybdenite ions are shaded); *b* – the same structure as shown by N.V. Belov.

MOLYBDENITE, MoS_2. The name comes from the Greek "molybdos", lead.

Chemical composition. Mo 60%, S 40%. According to chemical analyses, Mo content varies from 57.1 to 60.05%, and S content, from 39.7 to 42.0%. Often chemically pure, i.e., without isomorphous impurities, except rhenium. According to spectral analysis data, rhenium content in molybdenite is higher than in any other sulphide ($5 \cdot 10^{-7}$ to $2 \cdot 10^{-4}$%).

System, hexagonal; symmetry, apparently dihexagonal dipyramidal $L^6 6L^2 7PC$. Space group $P6_3/mmc(D^4_{6h})$. $a_0 = 3.156$; $c_0 = 12.275$.

Crystal structure, typically layered, with certain peculiar features.

Sheets of Mo ions are located between two S ions (Fig. 112), parallel to (0001). The ions in the sheets are strongly bonded, while the bonding between the "treble" sheets is much weaker; hence the perfect cleavage of molybdenite crystals. The coordination number of molybdenite is 6, but because of the peculiar Mo electron shell, the structural arrangement has the form of a trigonal prism rather than that of an octahedron. In this case the structure, according to N.V. Belov, may be visualised better as trigonal layers of prisms with Mo ions in the centres alternating with empty layers of octahedra (Fig. 112*b*). **Habit.** Crystals are mostly imperfect. The common forms are {0001}, {10$\bar{1}$0}, {10$\bar{1}$1}. The (0001) faces are striated (Fig. 113). Crystals occur mostly as hexagonal plates, more seldom as prisms. Aggregates, usually lamellar or scaly. Greyish-black spherulitic formations and earthy varieties also occur occasionally.

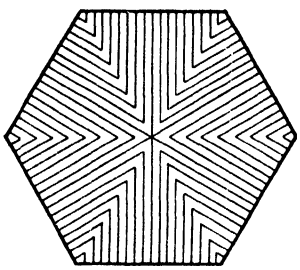


Fig. 113. Three systems of striations on basal face of a molybdenite crystal.

Colour, lead grey. **Streak**, grey, often with a greenish tinge. **Lustre**, metallic.

Hardness, 1. Thin laminae flexible. Greasy feel. Marks paper like graphite. **Cleavage**, {0001} very perfect. **Specific gravity**, 4.7 to 5.0. **Other properties.** Poor conductor of electricity at room temperature, conductivity increasing with temperature.

Diagnostic features. Lead-grey colour, typically metallic lustre, very low hardness, basal cleavage. May easily be mistaken for coarse-scaly varieties of graphite, from which it differs by lighter streak, stronger lustre, higher specific gravity, and low electric conductivity. Differs from similar tetradymite by weaker lustre and behaviour before the blowpipe.

Infusible in the blowpipe flame, but imparts to the latter a yellowish-greenish colour. Decomposes with great difficulty in nitric acid with evolution of SO_2 and a white or greyish MoO_3 precipitate. Concentrated H_2SO_4 decomposes it only at the boiling point.

Genesis and occurrence. Deposits of molybdenite are genetically associated with acid intrusives, chiefly granites and granodiorites, in which the mineral is sometimes sparsely disseminated. Occurs in pegmatite dikes but in economically unimportant quantities.

Economically important molybdenite deposits are associated with *hydrothermal* formations. Occurrences in quartz veins or silicified rocks are especially widespread. In general, in the overwhelming majority of cases molybdenite occurs in paragenesis with quartz. Sometimes, molybdenite segregations are confined to very thin quartz veinlets barely visible to the naked eye. In other instances it is finely dispersed in quartz, giving the latter greyish or bluish tint. These segregations are visible only in polished sections under the microscope.

Quartz-molybdenite veins often contain no other sulphides except rare pyrite grains. Deposits of other types may contain such associ-

ates as fine-scaly micas, fluorite, wolframite, more seldom beryl, tourmaline, or sulphides of copper (mostly chalcopyrite), of iron (pyrite, pyrrhotite), zinc (sphalerite), etc. Only in rare instances do molybdenite segregations occur in the sulphide-rich zones of deposits. Large irregularly disseminated crystalline segregations are sometimes observed in quartz veins in the form of rosettes or hexagonal tablets.

In the oxidised zone, the most common pseudomorph after molybdenite is powellite ($CaMoO_4$); sometimes typical solution cavities, which retain the shape of molybdenite crystals, are observed.

A notable molybdenite deposit is in *Colorado* (U.S.A.); it is an enormous stock-like body of secondary quartzite reaching down to a great depth.

Large deposits occur also in scheelite-bearing skarn zones at the contacts of limestones and granites. Molybdenite in such deposits is mostly confined to numerous thin quartz veinlets intersecting the skarn rocks.

Uses. It is the only industrial source of molybdenum—a metal of great economic value.

About 90 per cent of the world's production of molybdenum goes into high-grade steels. The remainder is used in electrical engineering, manufacture of dyes and paints, radio equipment, chemical industry, etc.

10. PYRITE GROUP

We shall review here an extensive group of AX_2-type compounds where A = Fe, Co, Ni as well as Mn, Pt, and Ru, and $X_2 = S_2$, Se_2, As_2, AsS and SbS. These are the so-called disulphides, diarsenides, sulphoarsenides, and sulphoantimonides. All of them have many properties in common.

This large group may be divided, according to specific mineralogical features, into four subgroups:

(1) *pyrite subgroup* (in the narrow sense), where FeS compound is dimorphous (pyrite and marcasite);

(2) *cobaltite subgroup*, which comprises sulphoarsenides and sulphoantimonides of Ni and Co (Fe in minor amounts); the members crystallise in the cubic system; although these minerals are similar to pyrite in crystal structure, their symmetry is of a lower order;

(3) *löllingite subgroup* comprising diarsenides of Fe, Ni and Co which crystallise in the orthorhombic system;

(4) *arsenopyrite subgroup* which includes sulphoarsenides and sulphoantimonides, chiefly those of Fe, crystallising in the monoclinic and orthorhombic systems.

Colloidal and metacolloidal iron bisulphide occurring as finely-dispersed black masses has the special name of *melnikovite*, but it is not

regarded as a separate mineral since X-ray examination gives a debyegraph of either pyrite or marcasite.

The main characteristics of the structure of pyrite as well as of marcasite are given below.

The crystal structure of the pyrite type is diagrammatically represented in Figs. 114 and 115. Fundamental to this structure is the cubic face-centred lattice of NaCl type (cf. Fig. 92) in which the S ions, arranged in close pairs, form a $[S_2]^{2-}$ anionic group. The S—S distance in these groups is 2.05 Å (instead of 3.5 Å, the double ionic radius). The axes of the $[S_2]^{2-}$ groups are oriented parallel to the diagonals of the smaller cubes so that they do not intersect. In Fig. 115, the distance between the sulphur atoms in the pairs is somewhat reduced to show the similarity of this structure to that of the NaCl type. The actual proportions for $[S_2]^{2-}$ are shown on the right.

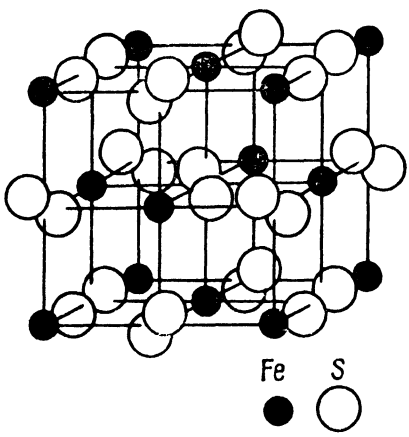


Fig. 114. Crystal structure of pyrite.

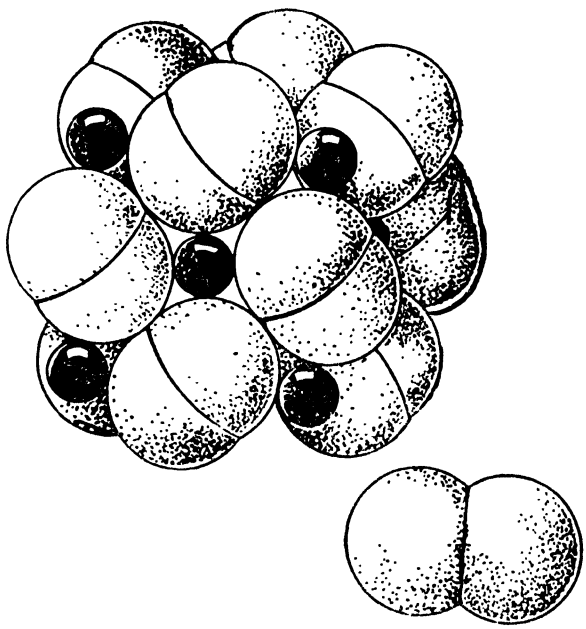


Fig. 115. Crystal structure of pyrite. Black spheres – Fe^{2+} ions; light-coloured spheres – $[S_2]^{2-}$ groups.

In the structure of the orthorhombic FeS_2 modification of marcasite we find the same $[S_2]^{2-}$ groups, as in pyrite. The Fe ions occupy the corners and the centre of the rhombic unit cell (Fig. 116*a*); they are surrounded by the $[S_2]^{2-}$ ionic groups. Below (Fig. 116*b*) the $[S_2]^{2-}$ pairs are shown to incline to the *c* axis to abut at both ends on the centres of the Fe ionic triads, i.e., the pattern is the same as for pyrite.

From these examples of the pyrite and marcasite structures it is obvious that the same type of coordination may give rise to crystal structures of entirely different symmetry.

To mention but a few of the physical properties distinguishing pyrite group minerals, we shall note that they are the *hardest* of all sulphides and similar compounds, their hardness ranging from 5 to 6

(sperrylite) and even as high as 7 to 8 (laurite). Another noteworthy feature is the absence of perfect cleavage. All minerals of the pyrite group are poor conductors of electricity.

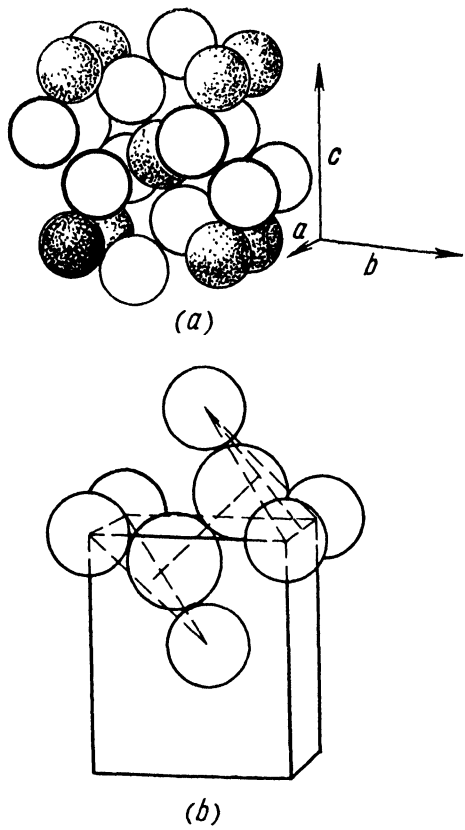


Fig. 116. Crystal structure of marcasite.

a – general view of structure; Fe^{2+} ions are dotted; *b* – orientation of the $[S_2]^{2-}$ anionic radical (in the middle) between two triads of Fe ions (at edges).

PYRITE, FeS_2. "Pyros" is the Greek for fire. The name is probably associated with the property of pyrite to give off sparks on being struck, or with its strong lustre. Synonyms: fool's gold, iron pyrite.

Chemical composition. Fe 46.6%, S 53.4%. Often contains minor amounts of impurities: Co (cobalt pyrite), Ni, As, Sb, sometimes Cu, Au, Ag, etc. The content of the latter elements is due to minute mechanical inclusions of foreign minerals, sometimes in a finely-dispersed state. In such instances we are in effect dealing with solid pseudosolutions or crystallosols.

System, cubic; symmetry, didodecahedral $3L^24L_6^33PC$. Space group $Pa3(T_h^6)$. $a_0 = 5.40667$. **Crystal structure** has been described above. **Habit.** Well-developed crystals are very common. Of the numerous forms known for that mineral, the most widespread are {100}, {210}, more seldom {111}, {321}, {110}, etc. (Fig. 117). Depending on the predominance of different faces, the habit of crystals may be cubic, pentagonal dodecahedral, less often octahedral. The crystals may be as large as several centimetres across. The faces show characteristic striations parallel to the (100):(210) edges, i.e., *a* : *e* (cf. Fig. 117*b* and *c* and Fig. 117*a*). This striation conforms to the crystals structure of pyrite and is always oriented perpendicular to each adjacent face, i.e., the external elements of symmetry fully agree with the peculiar structure of pyrite. Twins are parallel to (110), rarely to (320).

Aggregates. Pyrite occurs in many rocks and ores as impregnated crystals or rounded grains. It is often found as massive aggregates. In sedimentary rocks it often occurs as globular concretions, sometimes of radial-fibrous structure, and also as secretions in the cavities of shells (Fig. 118). Grape-like or botryoidal formations associated with other sulphides are common.

Colour, pale brass-yellow, often with yellowish-brown and irides-

cent tarnish; finely-dispersed sooty varieties are black. **Streak**, brownish to greenish black. **Lustre**, strong metallic.

Hardness, 6 to 6.5. Rather brittle. **Cleavage**, {100} and {111}, sometimes {110} poor. Fracture uneven, sometimes conchoidal. **Specific gravity**, 4.9 to 5.2. **Other properties.** Poor conductor of electricity Thermoelectrical. Some varieties have rectifying properties.

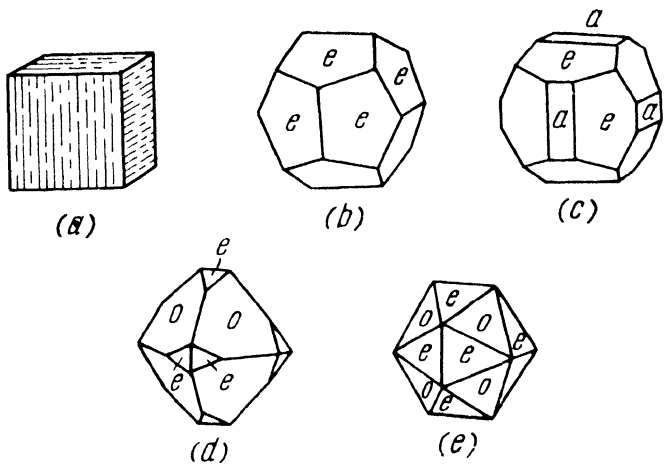


Fig. 117. Pyrite crystal forms.
a – cube; *b* – pentagondodecahedron *e* {210}; *c* – the same form combined with cube *a* {100}; *d* – octahedron *o* {111} truncated by pentagondodecahedral faces; *e* – combination of octahedron (*o*) and pentagondodecahedron (*e*): so-called mineral icosahedron (combination of octahedron with pentagondodecahedron).

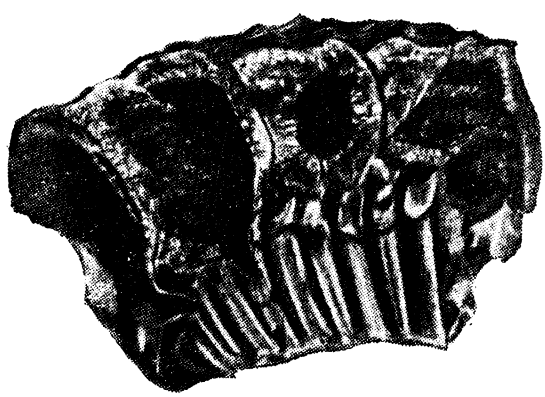


Fig. 118. Pyrite as crystalline crusts on inner walls of cavities in ammonite.

Diagnostic features. Readily identifiable by colour, crystal forms, striation, high hardness (the only widespread sulphide to scratch glass). These properties easily distinguish it from marcasite, chalcopyrite, pyrrhotite, and millerite which are somewhat similar to it in colour.

Before the blowpipe decrepitates and fuses into a magnetic globule. Gives up readily part of its sulphur which burns with a blue flame. In

the closed tube, part of the sulphur sublimates leaving FeS monosulphide as the residue. Decomposes with difficulty in nitric acid (easily when powdered) with separation of sulphur. Does not dissolve in dilute hydrochloric acid.

Genesis and occurrence. Pyrite is the most widespread sulphide in the earth's crust, and forms under most diverse geological conditions.

1. As tiny impregnations it is observed in many *magmatic* rocks. It is mostly epigenetic in relation to silicates, and is associated with superimposed hydrothermal phenomena.

2. In *contact-metasomatic* deposits it is an almost constant accessory of sulphides in the skarns and magnetite deposits. May contain cobalt. Its formation, as well as that of other sulphides, is connected with the hydrothermal stage of contact-metamorphic processes.

3. As an accessory, it is widely distributed in *hydrothermal* ore deposits of most different composition and occurs in paragenesis with most diverse minerals. It is found not only in ore bodies but also in the enclosing rocks as impregnations of well-formed crystals of metasomatic origin (metacrystals).

4. It is no less widespread in *sedimentary* rocks and ores. Pyrite and marcasite concretions in sandy-argillaceous sediments, in beds of coal, iron, manganese, bauxites, etc., are well known. Its formation in these rocks and ores is believed to be associated with the decomposition of organic remains in the absence of free oxygen in the deeper parts of water reservoirs. Its most common paragenetic associates are marcasite, melnikovite (black powdery variety of iron disulphide), siderite ($FeCO_3$), etc.

In the oxidised zone pyrite is unstable, like most sulphides, and prone to oxidise to ferrous iron sulphate, which, in the presence of free oxygen, readily passes into ferric iron sulphate. The latter undergoes hydrolysis, i.e., decomposes into insoluble iron hydroxide (limonite) and free sulphuric acid which passes into solution. Such is the process of the formation of widespread limonite *pseudomorphs* after pyrite.

Pyrite itself often forms pseudomorphs after wood and other organic remains; endogenous formations may contain pyrite pseudomorphs after pyrrhotite, magnetite (Fe_3O_4), hematite (Fe_2O_3), and other iron minerals. These pseudomorphs are due probably to the action of H_2S on the minerals.

Pyrite deposits are countless belonging to most diverse genetic types, although the most common are endogenous deposits.

The U.S.S.R. has many huge pyrite deposits.

Uses. Pyrite ores are an essential material for sulphuric acid production. The average sulphur content of ores mined for this purpose ranges from 40 to 50 per cent. The ores are roasted in special kilns. The resulting sulphurous gas (SO_2) is oxidised to H_2SO_4 by nitrogen oxides in the presence of water vapour.

An undesirable impurity in ores used in the production of sulphuric acid is arsenic.

Copper, zinc, sometimes gold, selenium, etc., commonly present in pyrite ores may be extracted as by-products. The pyrite cinders which remain after roasting, depending on their purity, find uses in the production of pigments or as a source of iron.

Ores containing cobalt pyrite may be a source of cobalt in spite of its low content (0.5 to 1 per cent in the mineral).

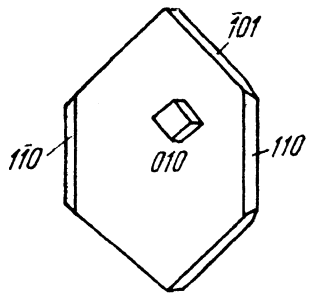


Fig. 119. Tabular crystal of marcasite with implanted pyrite cube.

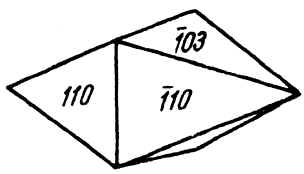


Fig. 120. Marcasite crystal.

MARCASITE, FeS_2. The name comes from the ancient Arabic term for pyrite and marcasite.

Chemical composition. Fe 46.6%, S 53.4%. Impurities: minor amounts of As, Sb, Tl, etc.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Pnmm(D_{2h}^{12})$. $a_0 = 4.4369$; $b_0 = 5.4149$; $c_0 = 3.381$. **Crystal structure** has been described on earlier pages. **Habit**, tabular (Fig. 119),

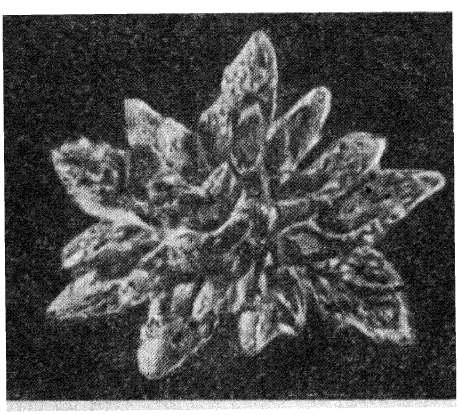


Fig. 121. Radial druse of lance-shaped marcasite crystals.

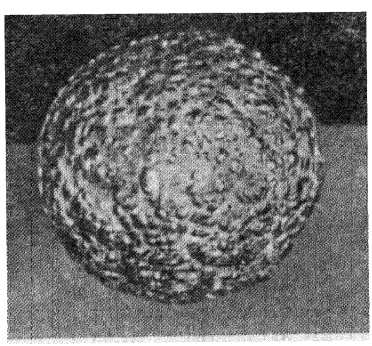


Fig. 122. Globular marcasite concretion. Natural size.

more seldom short columnar or lance-shaped (Figs. 120 and 121). Often twinned resembling cockscombs. Occurs as concretions (Fig. 122) and also as sinters, botryoidal, reniform, crusts, and other irregular forms. Common as pseudomorphs after organic remains.

Colour, brass yellow with a greyish or greenish tinge. **Streak**, dark, greenish grey. **Lustre**, metallic.

Hardness, 5 to 6. Brittle. **Cleavage,** {101} imperfect. **Specific gravity,** 4.6 to 4.9 (lower than that of pyrite). **Other properties.** Poor conductor of electricity.

Diagnostic features. Crystals of marcasite are distinguished from those of pyrite by their lance-shaped and tabular forms. Hard to distinguish from pyrite in concretions or compact masses. Fresh fracture, in contrast to pyrite, shows a greenish hue. Under the microscope in polished sections it is readily distinguished from pyrite by optical anisotropy. Debyegraphs also differ sharply from those of pyrite.

Before the blowpipe and in acids behaves exactly as pyrite.

Genesis and occurrence. Much less abundant than pyrite. Occurs both in endogenous and exogenous deposits.

Endogenous marcasite occurs in *hydrothermal*, mostly vein, deposits. It is formed, as a rule, in the latest stages of mineralisation. Most commonly found in drusy cavities as small crystals on cavity walls, sometimes as powdery coatings on crystals of quartz, calcite, galena, sphalerite, grey ores, and other minerals, less often as crusts and sinters.

In sedimentary, chiefly carboniferous sandy-argillaceous rocks, marcasite occurs as concretions, irregular grains, pseudomorphs after organic remains, and also as a finely-dispersed black sooty substance (melnikovite). Marcasite is frequently confused with pyrite.

In the oxidised zone, marcasite decomposes more readily than pyrite into iron sulphates and free sulphuric acid; oxygen deficiency results in the evolution of native sulphur. The final product of marcasite oxidation is iron hydroxide (limonite).

It has been shown experimentally that, as different from pyrite, marcasite forms relatively easily from acid solutions. Unlike pyrite, marcasite does not occur in large massive ore deposits.

A notable hydrothermal sulphide deposit containing marcasite, along with pyrite, in appreciable amounts is the *Blyavinskoye* deposit in the Orenburg Region, Southern Urals, where marcasite occurs as fine crystalline sporadically distributed aggregates. Marcasite associates not only with pyrite but also with sphalerite, wurtzite, chalcopyrite, quartz, etc.

Marcasite-bearing sedimentary rocks are widespread in the Soviet Union. Among them are the carboniferous sediments of sandy-argillaceous at *Borovichi*, Novgorod Region, in which marcasite concretions of various shapes are found. Polished sections of the concretions point to epigenetic formation of marcasite which only replaced the cementing material between the sand grains, the latter preserving their lamellar arrangement in the mass of marcasite. Besides marcasite, some sections of the concretions may contain pyrite, sometimes concentrically arranged. Some concretions have a coating of galena on their surface, deposited in exactly the same way, i.e., by replacing the cementing material in the sand masses. Generally speaking, however, the association of iron sulphides with galena in concretions is a rare phenomenon.

The argillaceous sedimentary deposits on the eastern slope of the Middle Urals, east of Sverdlovsk at *Kurya-Kamensk* and *Troitsk-Bainovo*, are well known for the wide variety of marcasite concretion forms found in them. Besides spheric nodules, there are many reniform and radial concretions terminating in well-bounded lance-shaped crystals (Fig. 121).

Hydrothermal deposits from which well-formed marcasite crystals have been recorded are known in Germany.

Uses. Like pyrite, when found in huge massive deposits, marcasite may be a material for sulphuric acid production.

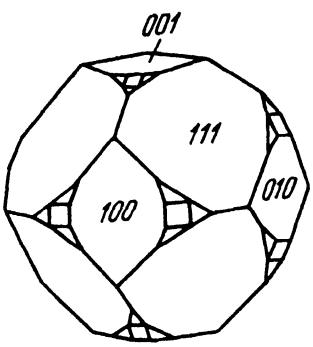


Fig. 123. Sperrylite crystal.

SPERRYLITE, $PtAs_2$. Named after the chemist who discovered the mineral in Sudbury ores.

Chemical composition. Pt 56.5%, As 43.5%. Impurities (per cent): Rh (up to 1.6), Fe (up to 0.4), Cu (up to 0.7), Sb (up to 0.6), sometimes Sn (up to 3.6).

System, cubic; symmetry, didodecahedral $3L^24L_6^33PC$. Space group $Pa3(T_h^6)$. $a_0 = 5.950$. **Crystal structure**, analogous to that of pyrite. Occurs almost exclusively in crystals, mostly small ones. **Habit**, cubic, octahedral, more rarely pentagonal dodecahedral. Often in these combinations of forms: {100}, {111}, {110}, {201}, etc. (Fig. 123). Twins are rare.

Colour, tin white. **Streak**, dark grey. **Lustre**, strong, metallic.

Hardness, 6 to 7 (in the class of sulphides and arsenides it is second to laurite in hardness). **Cleavage**, cubic. **Specific gravity**, 10.5 to 10.7 (highest for this class of minerals). **Other properties.** Poor conductor of electricity.

Diagnostic features. The most important diagnostic features are colour, high hardness, high specific gravity, occurrence in crystals, high acid-resistance, and platinum and arsenic reactions.

Before the blowpipe on charcoal fuses readily into a white metallic globule with a spongy surface, and gives off white vapour of arsenic oxide. On a red-hot platinum tablet, fine grains fuse instantaneously with separation of As_2O_3; the sponge platinum is welded to the tablet. Insoluble in acids, even in aqua regia.

Genesis and occurrence. Occurs in deposits of copper-nickel sulphide ores of the Sudbury type, in genetic association with basic igneous rocks (gabbro-norites and gabbro-diabases). Paragenetic associates are pyrrhotite, chalcopyrite, pentlandite. The most common associate among the platinum-group minerals is palladium platinum.

It has been found in the same paragenetic associations in the pegmatite formations of basic magmas in the Bushveld complex, South Africa, where largest (up to 1.85 cm across) crystals have been found.

In the same locality, it was observed in peculiar metasomatic deposits in limestones at the contact with basic rocks of the Bushveld complex, in association with skarn minerals.

Owing to its chemical inertness, sperrylite does not decompose in the oxidised zone, and upon the weathering of the deposits passes into placers, often retaining its crystal faces. In the U.S.S.R., sperrylite occurs in river placers of the *Zeya* and *Timpton* districts of the Eastern Siberia, Chita Region, commonly in well-formed small crystals (Fig.123).

Uses. Has definite economic value as a platinum-rich mineral. Even if its content in an ore is negligible, it may be extracted as a by-product. An example is Sudbury where sperrylite is extracted along with other platinum minerals from the slimes of copper-nickel ore concentration.

COBALTITE, CoAsS. Synonym: cobalt glance. An iron-rich variety is *ferrocobaltite.*

Chemical composition. Co 35.4%, As 45.3%, S 19.3%. According to analyses, Co content ranges from 26 to 34%, As from 42 to 48% and S from 18 to 21%. Ni (2 to 3%) and Fe (up to 8% and sometimes, as in the case of ferrocobaltite, up to 16%) may also be present.

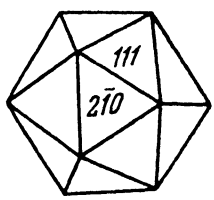


Fig. 124. Cobaltite crystal. Combination of pentagondodecahedron with octahedron.

System, cubic; symmetry, pentagonal tritetrahedral $3L^24L^3$. Space group $P2_13(T^4)$. $a_0 = 5.575$.

Crystal structure, very much like that of pyrite. Crystals quite often. **Habit,** octahedral, cubic, and pentagonal-dodecahedral (cf. Fig. 117). Hence the most common forms are the combinations characteristic of pyrite, especially {111} and {210} shown in Fig. 124. Twins along (110) and (111) are rare. Cobaltite is also found as irregular grains and massive.

Colour, white to steel grey with a reddish tinge. Iron-rich varieties are dark grey or greyish black. **Streak,** grey black. **Lustre,** metallic.

Hardness, 5 to 6. Brittle. **Cleavage,** distinct, cubic. **Specific gravity,** 6.0 to 6.5. Poor conductor of electricity.

Diagnostic features. On close examination is readily identifiable by the reddish tinge, high hardness, and often by typical combinations of forms {100}, {111}, and {210}. Is distinguished from linneite, which is of similar colour, by higher hardness. Weathered specimens are characteristically associated with intensely pink erythrite ($Co_3[AsO_4]_2 \cdot 8H_2O$).

Before the blowpipe fuses into a slightly magnetic globule, giving a coating of As_2O_3 on charcoal. Imparts deep blue colour (cobalt reaction) to the borax bead. Decomposes in nitric acid with separation of S and As_2O_3 (pink solution).

Genesis and occurrence. Occurs chiefly as a typical mineral of hydrothermal processes in contact-metasomatic and vein deposits. Commonly associated with the arsenic-sulphur minerals of cobalt and iron, and also with chalcopyrite, sphalerite, quartz, skarn minerals, ferru-

ginous chlorite, tourmaline, apatite, etc. On weathering, cobaltite, as other arsenious cobalt compounds, alters readily to earthy or crystalline erythrite whose pink colour is very conspicuous in the oxidised zones of sulphide-arsenic deposits of cobalt.

In the U.S.S.R., cobaltite occurs in the *Dashkesan* iron ore deposit of contact-metasomatic origin (Kirovabad district, Azerbaijan) in hydrothermally altered skarns in the hanging wall of a magnetite ore body. Its paragenetic associates include chalcopyrite, pyrite, sphalerite, molybdenite, magnetite, garnet, calcite, quartz, apatite, etc.

Large deposits of cobaltite occur at *Cobalt*, Ontario, Canada, associated with safflorite, skutterudite, smaltine, chloanthite, niccolite, gersdorffite, native silver, argentite, dolomite, calcite, and other minerals. Other notable deposits are at *Skutterud*, Norway, and at *Tunaberg*, Sweden.

Uses. Cobaltite is one of the principal sources of cobalt in commercial ores. In view of the high prices fetched by cobalt, sulphide-arsenic ores may be worth mining, even when their cobalt content is as low as 0.1 to 0.2%.

Cobalt has a number of valuable properties which determine its uses: (1) its various compounds make stable deep-blue and green pigments used in glass staining and tinting of ceramics; this was already known deep in antiquity; (2) when used as an alloying component in steels it imparts to them great hardness and heat resistance, and also outstanding magnetic properties; (3) gives a number of important alloys with Cr, Mo, and W, etc.

GERSDORFFITE, NiAsS. Synonym: nickel glance. Cobalt- and iron-rich varieties are known.

Chemical composition. Ni 35.4%, As 45.3%, S 19.3%. Ni content usually varies from 26 to 40%, As 37 to 56%, S 6 to 19%. Common impurities are Co, Fe, Sb, etc.

System, cubic; symmetry, pentagonal tritetrahedral $3L^24L^3$. Space group $P2_13(T^4)$. $a_0 = 5.719$. **Crystal structure**, similar to that of pyrite. **Habit**, octahedral or cubic. Most common forms are: {100}, {111}, {110}, {210}, {311}. Rare twins are along (111). Occurs mostly in granular aggregates.

Colour, silver white to steel grey. **Streak**, grey-black. **Lustre**, metallic.

Hardness, 5.5. Brittle. **Cleavage**, sometimes parallel to (111). **Specific gravity**, 5.6 to 6.2. Good conductor of electricity.

Diagnostic features. Hardly distinguishable superficially from a number of arsenious minerals, such as smaltite ($CoAs_{2-3}$), chloanthite ($NiAs_{2-3}$), ullmannite (NiSbS), arsenopyrite (FeAsS), etc.; hence the need for microscopic examination and chemical tests for Ni, As, and S; and in the presence of the isomorphs of Fe, Co, Sb, also for quantitative determinations of at least the principal elements.

Before the blowpipe on charcoal fuses into a globule which gives the nickel reaction. Decomposes in nitric acid with separation of S and As_2O_3. The solution is green, indicating the presence of Ni.

Genesis and occurrence. Gersdorffite is a mineral occurring predominantly in *hydrothermal* deposits. It is associated paragenetically with arsenides and sulphides of nickel, such as niccolite, millerite, chloanthite, rammelsbergite, ullmannite, etc. Other possible associates are various sulphides, and also carbonates (calcite, ankerite, dolomite), and quartz. In the oxidised zone, gersdorffite, as other nickel arsenides, turns into bright green annabergite ($Ni_3[AsO_4]_2 \cdot 8H_2O$).

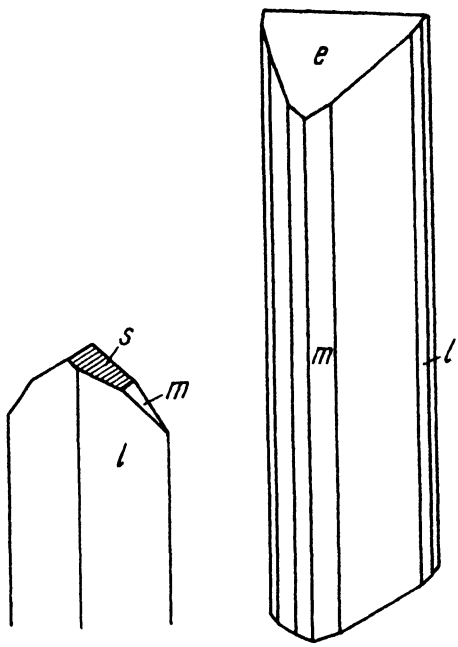


Fig. 125. Löllingite crystals, *m* {110}, *u* {140}, *e* {101}, *s* {120}, *l* {101}.

In the U.S.S.R., gersdorffite has been found in very few localities and in negligible quantities. At the *Berezovskoye* gold mines in the Urals has been observed in small grains in coarse-crystalline dolomite, and also in the *Berikul* gold deposit, Western Siberia, in association with rammelsbergite, niccolite, etc.

The largest finds have been made at *Hartz* (Germany), the *Erzgebirge mountains* (Saxony) and at some other localities.

Uses. Not very important commercially, since it usually occurs only as an accessory in the sulphide-arsenious ores of nickel and cobalt.

LÖLLINGITE, $FeAs_2$. Named after the town of Lölling in Carinthia, Austria. Was first described by Mohs.

Chemical composition. Fe 27.2%, As 72.8%. The Fe:As ratio is somewhat variable. Often contains minor amounts of S (up to 6%) and Sb (up to 5%). Certain varieties are enriched in cobalt (glaucopyrite), which suggests a continuous series of solid solutions: löllingite-safflorite ($FeAs_2$—$CoAs_2$). In addition to cobalt, nickel is usually present in minor amounts.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Pnnm(D_{2h}^{12})$. $a_0 = 5.227$, $b_0 = 5.959$, $c_0 = 2.894$. **Crystal structure,** similar to that of marcasite, though in the type of coordination of As around Fe, it differs somewhat from both marcasite and arsenopyrite. According to V.I. Mikheyev, the structure is retained when iron is replaced by cobalt. With increasing (Co+Ni):Fe ratio, the size of the unit cell gradually increases along the *c* axis, while the length of the other two edges of the cell remains about the same.

Habit, predominantly prismatic (Fig. 125). Also occurs massive.

Colour, silver-white to steel-grey. **Streak**, grey-black. **Lustre**, metallic.

Hardness, 5 to 5.5. Brittle. **Cleavage**, sometimes along {010} and {110} distinct. Fracture uneven. **Specific gravity**, 7.0 to 7.4 (much higher than that of arsenopyrite). **Other properties.** Good conductor of electricity.

Diagnostic features. Externally very similar to arsenopyrite for which it is often mistaken. The minerals differ most sharply in specific gravity. Some differences are also observed in polished sections under the microscope.

Is less fusible in the blowpipe flame than arsenopyrite. In the closed glass tube, yields only metallic arsenic, unless it contains a considerable admixture of sulphur. Dissolves in nitric acid with separation of As_2O_3.

Genesis and occurrence. Is more rare in nature than arsenopyrite, and usually is found in minor amounts. Confined exclusively to *hydrothermal* vein and metasomatic deposits, often associated with arsenopyrite, iron and copper sulphides, Co arsenides, as well as with calcite, siderite, quartz, etc.

In the oxidised zone, decomposes to scorodite ($Fe\cdots[AsO_4]\cdot 2H_2O$).

In the U.S.S.R., löllingite was found in the Caucasus, Urals, Central Asia, Western and Eastern Siberia. Of these the most notable is the *Aguyurm* deposit in Eastern Karategin on the left bank of the Aguyurm river, Central Asia, where it is common in arsenopyrite ores. In the *Sokhondinskoye* tin ore deposits in Kyrin district, Chita Region, the mineral had occurred as continuous masses and veinlets up to 3 cm thick. A characteristic feature is that it forms later than arsenopyrite and overgrows crystals of the latter.

Occurrences of löllingite in Carinthia, Hartz, Saxony, Norway, Canada, and at other places have been mentioned in literature.

Uses. Constitutes an arsenic ore, being an iron arsenide with the richest arsenic content.

ARSENOPYRITE, FeAsS. Synonyms: arsenical pyrites, arsenic iron. Variety: *danaite* which is a cobalt-bearing arsenopyrite; cobalt-rich modifications have the general name of *glaucodot.*

Chemical composition. Fe 34.3%, As 46.0%, S 19.7%. Chemical analyses show frequent deviations from these figures, especially with regard to As and S. Common impurity is Co, more seldom Ni and Sb. In quite a few deposits arsenopyrite is gold-bearing, the gold being present as microinclusions, but for the most part as finely-dispersed phase, i.e., arsenopyrite in this case is in effect a crystallosol.

System, monoclinic; symmetry, prismatic L^2PC. Space group $B2_1/d$ (C_{2h}^5). $a_0 = 9.58$; $b_0 = 5.69$; $c_0 = 6.42$; $\beta = 90°$. **Crystal structure.** Although morphologically arsenopyrite belongs to the marcasite series, X-ray analysis shows that its ideal structure is monoclinic, and appears orthorhombic only due to twinning. Each Fe ion is surrounded

inside the distorted octahedron by three S ions, three apexes of the octahedron being occupied by S and the other three by As. The As and S ions occupy the apexes of the distorted tetrahedron: the As ions are surrounded by three Fe ions and one S ion, and the S ions by three Fe ions and one As ion.

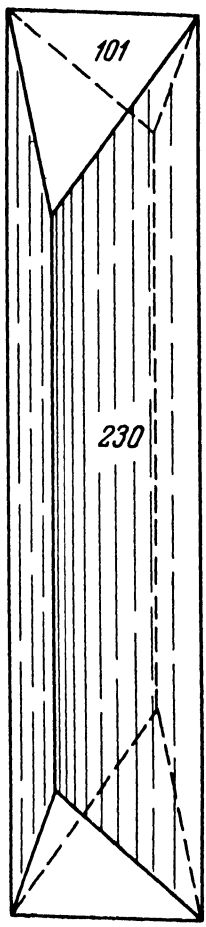


Fig. 126. Arsenopyrite crystal.

Habit. Very often occurs in excellent, usually prismatic, short-columnar to rod-like and acicular crystals (Fig. 126). Also common are pseudodipyramidal crystals formed by the uniform development of prisms of the first and second order. Most common forms are {101}, {230}, {210}, {140}, etc. Characteristically striated faces parallel to the *c* axis. Crystals commonly occur in drusy cavities, but are also frequent in the wall rocks of deposits as metasomatically formed metacrystals. Rather frequent twins, often cruciform (Fig. 127). **Aggregates.** Granular and rod-like when in continuous masses.

Colour, tin-white (crystal faces) to steel-grey (fracture). Often with yellow tarnish. **Streak**, grey-black, sometimes with a brownish tinge. **Lustre**, metallic.

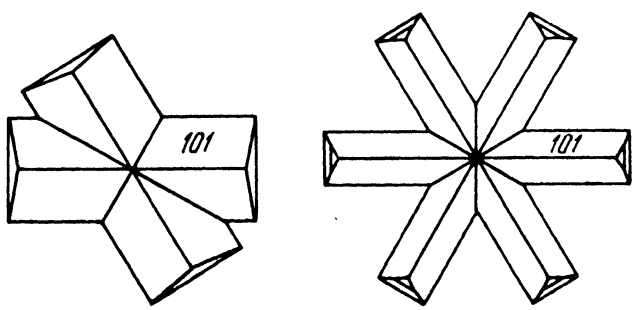


Fig. 127. Arsenopyrite twin and trilling.

Hardness, 5.5 to 6. Brittle. **Cleavage**, rather distinct along {101} and also along {001}. **Specific gravity**, 5.9 to 6.2. **Other properties.** Conductor of electricity. The temperature of decomposition ranges from 430 to 675°, the bond between Fe and As being weaker than that between Fe and S.

Diagnostic features. Identifiable by tin-white crystal faces, high hardness, and the presence of iron, arsenic, and sulphur as principal components. When struck with a hammer, gives off the odour of garlic. Crystal forms are also very characteristic. From löllingite ($FeAs_2$) is distinguished by lower specific gravity. From arsenious compounds of nickel and cobalt (smaltine and chloanthite) is distinguished in granular masses with certainty only by qualitative chemical testing and

microscopic examination of polished sections with microchemical tests.

Fuses in the reducing flame emitting garlic odour; gives a magnetic globule with tombac-brown fracture. In the closed tube, gives a red sublimate of arsenic sulphide and later a black ring of metallic arsenic. Decomposes in nitric acid with separation of S and As_2O_3.

Genesis and occurrence. Arsenopyrite is a mineral of *hydrothermal* origin and one of the most common arsenic bearers in endogenous deposits.

In typical hydrothermal, vein and metasomatically formed deposits, it segregates mostly during the high-temperature stages of mineralisation. Not infrequently forms deposits in its own right, being the principal ore mineral. It also occurs as an accessory in most diverse tin, tungsten, bismuth, copper, lead, zinc, and other deposits. Its most common nonmetallic associates are quartz, tourmaline, feldspars, micas, carbonates, sometimes beryl, topaz, etc.

In the course of oxidation in the weathering zone arsenopyrite decomposes rather rapidly to form scorodite ($Fe\cdots[AsO_4]\cdot 2H_2O$), usually as pale yellowish and greenish loose earthy masses (when mixed with iron hydroxides, it turns brown).

In the U.S.S.R., tens of deposits are known in which arsenopyrite is the chief ore-forming mineral. Of the numerous deposits outside the U.S.S.R. mention should be made of the great deposit at *Boliden* (Sweden) where arsenopyrite bears much gold which is not recovered completely by mechanical concentration.

Uses. Arsenopyrite ores are the principal source of various arsenic compounds used partly in pest control, and also in the manufacture of dyes, leather, and in other chemical industries. The minimum arsenic content making mining worthwhile is commonly accepted at 5 to 6 per cent. In complex concentration of polymetallic ores arsenic may be obtained from its minerals as a by-product, especially from the smelter fumes.

11. SKUTTERUDITE GROUP

This group includes arsenides of Ni and Co of AX_3 and AX_{3-2} composition, in which isomorphs with a high Fe content are present in considerable quantities. All of them crystallise in the cubic system.

X-ray examinations show that these minerals differ fundamentally from those of the foregoing group in crystal structure, though their composition may often be expressed in terms of diarsenides.

A characteristic feature of the skutterudite crystal structure (Fig. 128) is the formation by arsenic atoms of fourfold As_4 groups which occupy the apexes of a *square*. These flat groups are located in the middle of the edges and faces, parallel to the faces of the unit cube. Each Co ion is surrounded by 6 As ions. The crystallochemical formula of skutterudite should be written as $Co_4[As_4]_3$.

The crystal structures of smaltite and chloanthite proved to be absolutely identical with that of skutterudite, despite their lower arsenic content; only their unit cells are slightly larger than those of skutterudite.

It is small wonder, therefore, that these minerals have strikingly similar physical and chemical properties. To avoid repetition, we shall give below a general description of the group.

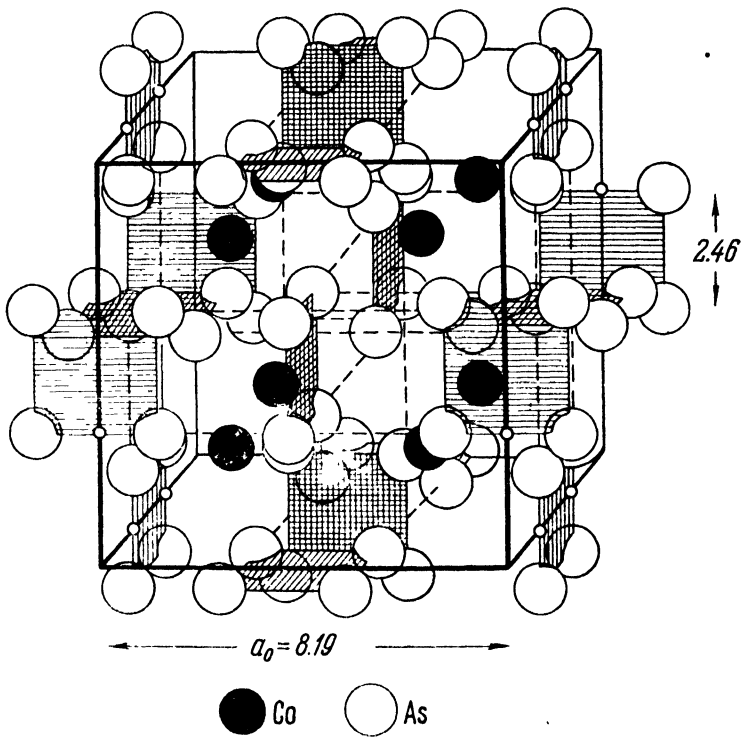


Fig. 128. Crystal structure of skutterudite. Square As_4 groups are shaded.

SKUTTERUDITE, $CoAs_3$. Named after the place of discovery—Skutterud (Norway).

SMALTITE, $CoAs_{3-x}$ where $x = 0$ to 0.5. Synonym: smaltine, grey cobalt. Smalta is a deep-blue cobalt pigment.

CHLOANTHITE, $NiAs_{3-x}$, where $x = 0.5$ to 1.0. "Chloantes" is the Greek for green-colouring. The name was probably given because of the green colouration imparted to acid solutions by nickel compounds or because the oxidation products (annabergite) of the mineral are green, in contrast to cobalt arsenides which yield pink secondary mineral (erythrite).

Chemical composition is variable. The content of individual constituents varies over a wide range (Table 5).

Table 5

Chemical Composition of the Minerals of Skutterudite Group in Weight Percentages

Elements	Skutterudite	Smaltite	Chloanthite
As	76.4 to 72.9	71.6 to 63.4	73.5 to 70.1
S	0 to 1.7	0 to 1.4	0 to 0.6
Co	20.5 to 10.8	24.1 to 13.8	3.6 to 6.3
Ni	0 to 9.4	1.0 to 15.0	21.2 to 14.5
Fe	0 to 5.8	1.2 to 7.3	2.8 to 5.2

Chemical analyses also reveal the presence of Cu, Bi, sometimes Pb and Ag, which most probably are mechanical impurities.

System, cubic; symmetry, didodecahedral $3L^2\,4L^3\,3PC$. Space group $Im3(T_h^5)$. The size of the unit cell increases with increasing Ni and Fe content. $a_0 = 8.189$(for skutterudite), 8.24 (for smaltite), 8.28 (for chloanthite). **Habit,** cubic, cubic octahedral, or octahedral. Occur as dendrites or massive granular aggregates.

Colour, tin-white, sometimes with a grey or iridescent tarnish. **Streak,** grey-black. **Lustre,** metallic.

Hardness, 5.5 to 6. Brittle. **Cleavage,** {100}, {111} distinct. Fracture often conchoidal. **Specific gravity,** 6.4 to 6.8. Conductors of electricity.

Diagnostic features. The minerals are very difficult to identify by external features, especially when they are intimately intergrown with other similar arsenides of nickel, cobalt, and iron. When massive, they resemble externally arsenopyrite, löllingite, gersdorffite, ullmannite, safflorite, and rammelsbergite. May be positively identified only upon microscopic examination of polished sections, and chemical and X-ray analyses.

Before the blowpipe they give a magnetic globule and emit a strong arsenic odour. Cobalt-rich varieties decompose in nitric acid imparting a pink coloration to the solution upon heating, whereas nickel-rich varieties give it a yellow-green colour.

Genesis and occurrence. All these minerals occur in paragenetic association with other arsenides of cobalt and nickel only in *hydrothermal* deposits of the Schneeberg type.

On weathering skutterudite and smaltite decompose to erythrite ($Co_2[AsO_4]_2 \cdot 8H_2O$) which appears as a pink-coloured selvage, while the weathering product of nickel skutterudite and chloanthite is bright-green annabergite ($Ni_3[AsO_4]_2 \cdot 8H_2O$).

Skutterudite has been found along with other cobalt minerals in the arsenic-cobalt deposit of *Ak-Jilga*, the Alai ridge (Southern Kirghizia) and at *Nizhni-Seymchan* in the northeast of the Asian part of

the U.S.S.R., where it associates with glaucodot, cobaltite, arsenopyrite, pyrrhotite, and other minerals in quartz veins.

Notable localities in other countries are *Skutterud*, Norway, where skutterudite was first discovered in association with cobaltite and sphene in mineralised gneisses; *Cobalt*, Ontario (Canada), where, besides skutterudite and nickel skutterudite, chloanthite and smaltine have been found associated with other minerals of cobalt, nickel, and silver; Erzgebirge mountains at *Jachymov* (Czechoslovakia), *Schneeberg*, *Annaberg* (Saxony).

Uses. These minerals sometimes occur together with other arsenides and sulphoarsenides of nickel and cobalt in large amounts, in which case they are of definite economic importance.

CLASS 2.

SULPHOSALTS

This class comprises complex compounds, chemically similar to salt-like compounds, and known as sulphosalts. Like oxysalts, they are subdivided into sulphobases and sulphoanhydrides, i.e., cations and complex anions.

Although the minerals of this class are many and varied, their constituents are few.

In the vast majority of cases, the sulphoanhydrides in sulphosalts are As_2S_3, Sb_2S_3, and Bi_2S_3 which are designated accordingly as *sulphoarsenites*, *sulphoantimonites*, and *sulphobismuthites*.

It should be emphasised that all the three types of sulphosalts have the same metals in their bases: Cu, Ag, and Pb. In other words, the sulphosalts of copper, silver, and lead are the most common in nature. Independent sulphosalts of Tl, Hg, and Fe are extremely rare; only Zn and Mn are found as isomorphous admixtures in any appreciable amounts.

Sulphovanadates, sulphoarsenates, and sulphoantimonates of copper, i.e., sulphosalts having V_2S_5, As_2S_5 and Sb_2S_5 (with pentavalent ions) for sulphoanhydrides are also found in negligible amounts. Less clear is the problem of the existence of the so-called sulphostannates and sulphogermanates (with Sn_2S_3 and GeS_2).

The vast variety of sulphosalts is largely due to the different ratios between sulphobases and sulphoanhydrides in compounds of the same qualitative types. Thus, the following compounds are known under the general designation of silver sulphoantimonites: $12Ag_2S \cdot Sb_2S_3$ $9Ag_2S \cdot Sb_2S_3$, $5Ag_2S \cdot Sb_2S_3$, $3Ag_2S \cdot Sb_2S_3$, $Ag_2S \cdot Sb_2S_3$, and $Ag_2S \cdot 6Sb_2S_3$ or respectively, $Ag_{24}Sb_2S_{15}$, Ag_9SbS_6, Ag_5SbS_4, Ag_3SbS_3, $AgSbS_2$, and $Ag_2Sb_{12}S_{19}$. They are all quite definite compounds occurring in crystals and differing in crystal structure.

Crystal structures of sulphosalts, similarly to oxysalts, differ from simple sulphurous compounds in that their crystal lattices always include structural units in the form of anionic compact groups such a

$[SbS_4]^{5-}$ and $[SbS_3]^{3-}$, etc. Indeed, the simplest cubic and trigonal crystal structures of sulphosalts include anionic groups in the form of obtuse trihedral pyramids (analogous to $[SO_3]^{2-}$ complex anions in sulphites) $[AsS_3]^{3-}$, $[SbS_3]^{3-}$, where As and Sb are trivalent. Examples of these most simple structures are those of proustite (Ag_3AsS_3), pyrargyrite (Ag_3SbS_3), tetrahedrite (Cu_3SbS_3), etc. Furthermore, the structures may include tetrahedral groups such as $[VS_4]^{3-}$, $[AsS_4]^{3-}$, $[SbS_4]^{3-}$, in which V, As and Sb are pentavalent. Complex sulphoanions are less compact than complex oxyanions, this being possibly due to the lower polarising capacity of As^{3+}, Sb^{3+}, Bi^{3+}, V^{5+}, As^{5+} and other cations.

Sulphosalts have somewhat specific physical properties. As compared with simple sulphurous compounds, sulphosalts are generally less hard (especially, the sulphosalts crystallising in the lower systems, i.e., the majority of mineral sulphosalts), poorer reflectivity and lower resistance to acids. These peculiar physical properties are undoubtedly related in some way to the specific crystal structures of these compounds.

The best way to classify sulphosalts would be to divide them into larger groups according to the metals in their sulphobases, followed by subdivision according to the composition of sulphoanhydrides. Then the classification of sulphosalts will be as follows:

A. *Copper sulphosalts*, i.e., compounds of $n Cu_2S \cdot X_2S_3$, where $X = As^{3+}$, Sb^{3+}, and Bi^{3+} and those of the $3Cu_2S \cdot X_2S_5$-type, where $X = V^{5+}$, As^{5+}, and Sb^{5+}. This class would thus include sulphoarsenites, sulphoantimonites, and sulphobismuthites of copper, as well as sulphovanadates, sulphoarsenates, and sulphoantimonates of copper.

B. *Silver sulphosalts*: $n Ag_2S \cdot X_2S_3$, where $X = As^{3+}$, Sb^{3+}, and Bi^{3+}, i.e., sulphoarsenites, sulphoantimonites, and sulphobismuthites of silver.

C. *Lead sulphosalts*: $n PbS \cdot X_2S_3$ where $X = As^{3+}$, Sb^{3+}, and Bi^{3+}, i.e., sulphoarsenites, sulphoantimonites, and sulphobismuthites of lead.

1. TETRAHEDRITE GROUP

The minerals included under this heading comprise a large isomorphous group of so-called fahlite (grey ores) with a common chemical formula A_3XS_3 or $3A_2S \cdot X_2S_3$, where $A_2 = Cu_2$, less often Ag_2, Cu, Zn, Fe, rarely Hg; and X = As, Sb, and rarely Bi (in negligible amounts).

X-ray analyses indicate that the formula $A_{12}X_4S_{13}$ would be the more precise. This agrees well with a certain excess of sulphur shown by precise chemical analyses.

Depending on the prevalent sulphoanhydride in these compounds, the following mineral species are distinguished: tennantite ($Cu_{12}As_4S_{13}$) and tetrahedrite ($Cu_{12}Sb_4S_{13}$). The so-called mixed grey ores of the $Cu_{12}(As, Sb)_4S_{13}$ composition are the most common in nature.

The crystal structure of grey ores is rather complex and generally resembles that of chalcopyrite or sphalerite, except for the size of the unit cell being twice as large.

All the mineral species and varieties included in this group according to their chemical composition have many physical properties in common and hence are described below.

TENNANTITE, $Cu_{12}As_4S_{13}$ or $3Cu_2S \cdot As_2S_3$. Named after the chemist Tennant.

TETRAHEDRITE, $Cu_{12}Sb_4S_{13}$ or $3Cu_2S \cdot Sb_2S_3$. The name derives from the shape of the crystals in which it occurs and which is generally common to the grey ores of different composition.

Chemical composition. The content of individual elements in different grey ores varies as follows (per cent):

Cu . . .22 to 53	Hg . . .0 to 17.0	As . . .0 to 20.0
Ag . . . 0 to 18	Ni . . . 0 to 3.5	Sb . . .0 to 29.2
Zn . . . 0 to 9	Co . . . 0 to 4.2	Bi . . .0 to 4.5 (13.07)
Fe . . . 0 to 13	Mn . . . 0 to 1.5	S . . .20.6 to 29.1

Varieties according to chemical composition are *freibergite*, a silver-rich tetrahedrite; *zandbergite*, a zinc-rich tennantite or tetrahedrite; *ferrotetrahedrite* (up to 13.08% of iron); *ferrotennantite*, etc.

System, cubic; symmetry, hexatetrahedral $3L_4^24L^36P$. Space group $I\bar{4}3m(T_d^3)$. $a_0 = 10.196$ (for tennantite) and 10.400 (for tetrahedrite). In the tennantite-tetrahedrite isomorphous series the size of the unit cell increases as arsenic is replaced by antimony, and copper by silver.

Crystals found in cavities are tetrahedral (Fig. 129) with this combination of forms: {1̄11}, {110}, {112}, {100}, etc. Commonly in continuous masses or impregnations of irregular grains. Often twinned along (111), more seldom along (100).

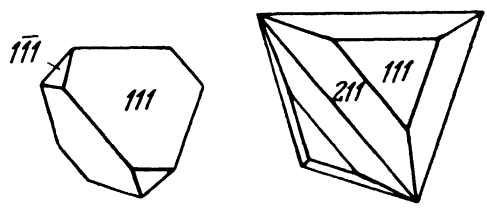


Fig. 129. Tetrahedrite crystals.

Crystal structure. Grey ores have half of the copper ions in fourfold coordination (the same as sphalerite), and the other half in threefold coordination (i.e., without the fourth apex). The As (or Sb) cations are surrounded by three S ions each.

Colour, steel grey to iron black (Fe-rich varieties). **Streak** has the same colour, sometimes with a brownish and even cherry-red tinge (tennantite). Opaque. **Lustre**, metallic or submetallic.

Hardness, 3 to 4. Brittle. **Cleavage**, practically none. **Specific gravity**, 4.4 to 5.4. Arsenious varieties have lower specific gravity than antimonious varieties. **Other properties.** Poor conductor of electricity.

Diagnostic features. Readily identifiable by grey fracture and obvious brittleness (when scratched with a knife, gives a fine powder and no shiny trace is left, as in the case of chalcocite and argentite, that are otherwise rather similar to tetrahedrite). In colour and brittleness, is similar to bournonite ($CuPbSbS_3$) which has a lower hardness and a somewhat stronger lustre.

Before the blowpipe on charcoal fuses readily into a grey globule giving off As_2O_3 and Sb_2O_3. The globule gives the copper and often the iron reaction. Decomposes in nitric acid with separation of S and Sb_2O_3. Behaviour with reagents depends on composition.

Genesis and occurrence. Grey ores, tetrahedrite in particular, are rather widespread in *hydrothermal* copper deposits of different types. They are present in minor amounts in ores of most widely varying composition. Their most frequent paragenetic associate is chalcopyrite, less often sphalerite, galena, pyrite, arsenopyrite, bournonite, and other minerals.

On weathering the ores decompose readily, yielding various alteration products: covellite, malachite, azurite, limonite; the arsenic present in the ores gives rise to scorodite ($Fe[AsO_4]\cdot 2H_2O$); while antimony goes to form various oxides and hydroxides.

Grey ores are widespread in the U.S.S.R. They are found in all copper and lead-zinc deposits, though rarely in large amounts. The richest grey-ore deposits are those known as *Blagodatniye mines*. In these deposits the grey ores are strongly enriched with gold, and also contain antimony and arsenic. They are associated mainly with pyrite, chalcopyrite, and to some extent with galena. Well-formed tetrahedrite crystals are found in drusy cavities at the *Berezovskoye* gold mines. Tennantite crystals have been recorded from hollow fissures in many pyrite deposits of the Middle Urals.

Uses. Grey ores never form large deposits in their own right. Together with other copper-bearing sulphurous compounds in commercial deposits they are a source of copper. In the smelting of copper ores containing tennantite, arsenic volatilises in the form of As_2O_3, a harmful impurity, in the smelter fumes. The same happens in the smelting of ores containing arsenopyrite, enargite, and other arsenious compounds as impurities. At large plants such gaseous arsenic is extracted from the sublimation products which are thus rendered harmless; this may yield a considerable quantity of arsenious material as a by-product.

2. ENARGITE GROUP

This group includes compounds of Cu_3XS_4 or $3Cu_4S\cdot X_2S_5$ type, where X = V, As, and Sb, i.e., pentavalent elements. We shall discuss enargite only.

ENARGITE, Cu_3AsS_4. "Enargis" means distinct in Greek (probably for the distinct cleavage of the mineral).

Chemical composition. Cu 48.3%, As 19.1%, S 32.6%. Impurities: Sb (up to 6.5%), Fe (up to 5.7%), in negligible amounts also Pb, Zn, and Ag (possibly in the form of inclusions of foreign minerals).

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Pnm(C_{2v}^7)$. $a_0 = 6.46$; $b_0 = 7.43$; $c_0 = 6.18$. Crystals mostly columnar, vertically striated, more rarely tabular; consist of combinations of forms {110}, {001}, {100}, {010}, etc. Usually massive granular or disseminated. **Crystal structure**, similar to that of wurt ziteand is regarded as pseudohexagonal.

Colour, steel grey to iron black. **Streak**, grey-black. Opaque. **Lustre**, submetallic, strong.

Hardness, 3.5. Brittle. **Cleavage**, {110} perfect, also {010} rather distinct. **Specific gravity**, 4.4 to 4.5. **Other properties.** Poor conductor of electricity.

Diagnostic features. In external features is very similar to black sphalerite, from which it differs by cleavage which is perfect only in one direction, and by stronger lustre.

Fuses in the blowpipe flame on charcoal giving a coating of As_2O_3. When roasted with soda, gives a copper globule. Dissolves in nitric acid with separation of floating sulphur.

Genesis and occurrence. Sometimes occurs in quantity in *hydrothermal* deposits in association with grey ores, chalcopyrite, galena, pyrite, and other minerals.

Quite common are tennantite pseudomorphs after enargite called "green enargite". A comparison of the chemical formulas of these minerals shows that under endogenous conditions the process is limited to As_2S_5 altering to As_2S_3.

In the oxidised zone of deposits decomposes readily yielding malachite, azurite, olivenite (copper arsenate), and other secondary minerals.

In the U.S.S.R., enargite occurs as an admixture to other minerals. Important commercial deposits of enargite are at *Butte*, Montana, U.S.A.; *Chuquicamata*, Chile; *Tsumeb*, South-West Africa, and elsewhere.

Uses. When found in quantity, enargite is an ore of copper and arsenic.

3. BOURNONITE GROUP

This includes binary sulphosalts of copper and lead of $CuPbXS_3$-type, such as bournonite and aikinite.

BOURNONITE, $CuPbSbS_3$. Synonym: berthonite.

Chemical composition. Cu 13.0%, Pb 42.5%, Sb 24.7%, S 19.8%. Impurities: Fe (up to 5%), Ag (up to 3%), traces of Zn and Mn.

System, orthorhombic; symmetry, rhombic dipyramidal $3L_23PC$. Space group $Pnmm(D_{2h}^{13})$. $a_0 = 8.19$; $b_0 = 8.67$; $c_0 = 7.74$. Well-formed crystals are found only in cavities and often are pseudotetragonal and thick-tabular (Fig. 130) with developed faces of forms {001}, {010},

{100}, {011}, {110}, etc. Frequently twinned along (110). Recurrent cruciform or wheel-like twins. Usually occurs in irregularly-shaped grains or massive. **Crystal structure**, as yet undeciphered.

Colour, steel grey to lead grey, often with tombac-brown tarnish (on crystal faces). **Streak**, grey. Opaque. **Lustre**, metallic.

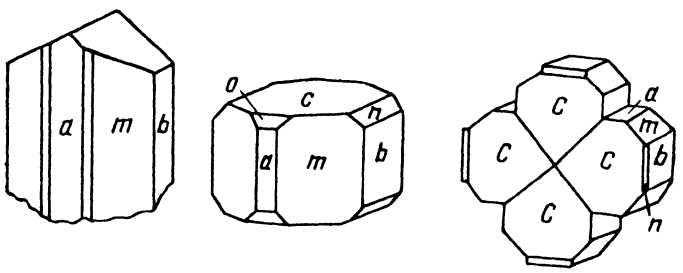


Fig. 130. Bournonite crystals and twin
a {100}, *n* {101}, *m* {110}, *b* {010}, *c* {001}, *o* {101}.

Hardness, 2.5 to 3. Brittle. **Cleavage**, {010} imperfect. **Specific gravity**, 5.7 to 5.9. **Other properties.** Non-conductor of electricity.

Diagnostic features. Externally has some resemblance to grey ores, except for stronger lustre.

Before the blowpipe on charcoal with soda fuses readily into a black bead which upon removal of all lead (by careful ignition with boric acid) yields *with difficulty* a copper globule. The black bead on roasting with KI gives a yellow-green coating of PbI_2. Dissolves in nitric acid with separation of S and Sb_2O_3.

Genesis and occurrence. Occurs in *hydrothermal* lead-antimony ore deposits. Generally is closely associated with tetrahedrite and galena, sometimes is found as selvages on the boundary between them.

In the oxidised zone of deposits decomposes readily, sometimes altering to malachite, cerussite ($PbCO_3$), and antimony oxides.

In the U.S.S.R., bournonite occurs in appreciable amounts in the quartz veins of the *Nagolny Ridge*, the Ukraine, in association with galena, grey ores, boulangerite, jamesonite, etc., also at the *Darasun* gold deposit (Eastern Trans-Baikal Region) in grey ores, galena, etc.

Outside the U.S.S.R., occurs in large amounts at *Přibram*, Czechoslovakia; *Clausthal* and *Andreasberg*, Harz, Germany, and in many deposits in the U.S.A., Mexico, Peru, Chile, and elsewhere.

Uses. When found in quantity has economic value as an ore of lead and copper.

AIKINITE, $CuPbBiS_3$. Was first discovered in the Urals near Sverdlovsk early in the last century. Synonym: patrinite.

Chemical composition. Cu 11.0%, Pb 36.0%, Bi 36.2%, S 16.8%. Impurities: Te and Au (the latter as inclusions).

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Pnmm$ (D_{2h}^{13}). $a_0 = 11.364$; $b_0 = 11.832$; $c_0 = 8.05$. Often found in acicular and rod-like crystals in quartz, sometimes massive. Faces often vertically striated.

Colour, lead grey to steel grey, often with dark-brownish or brownish tarnish. **Streak**, grey-black, shiny. Opaque. **Lustre**, metallic.

Hardness, 2 to 2.5. Brittle. **Cleavage**, {010} imperfect. **Specific gravity**, 6.1 to 6.7.

Diagnostic features. Characteristic acicular or rod-like crystals, but without chemical tests for Bi, Pb and Cu the mineral is hard to identify.

Fuses readily in the blowpipe flame, gives off fumes and leaves a white and yellow coating on charcoal. Gives a metallic bead which in turn yields with difficulty a copper globule when roasted with boric acid. Gives the reaction for Bi with KI. Dissolves in nitric acid with separation of $PbSO_4$ and sulphur.

Genesis and occurrence. It is a rare mineral occurring in quartz veins of *hydrothermal* origin in association with pyrite, chalcopyrite, grey ores, galena, arsenopyrite, native gold, sometimes scheelite, wolframite, and other minerals.

Well-known are the rod-like and acicular crystals of aikinite in the transparent or translucent crystals of quartz occurring at the *Berezovskoye* gold deposit, north-east of Sverdlovsk. It is often paragenetically associated with galena, grey ores, pyrite, chalcopyrite, and especially with native gold.

In the oxidised zone it is unstable. Decomposes into earthy yellow or green-yellow masses of the so-called bismuth and lead ochres.

Uses. In itself it is of purely mineralogical interest. At the Berezovsk ore deposit its presence in veins is a good guide to gold.

4. PROUSTITE GROUP

The group comprises sulphoarsenites and sulphoantimonites of silver of the Ag_2XS_3 type where X = As and Sb.

Proustite and pyrargyrite are the most common minerals of this group. Although both minerals have analogous chemical formulas and crystallise in the same symmetry, chemical analyses show that they do not form a continuous series of isomorphous mixtures. As has been shown by experiments, these compounds can be intermixed infinitely only at high temperatures.

We shall also describe here the rare sulphosalts of silver – stephanite and polybasite.

PROUSTITE, Ag_3AsS_3. Named after Proust, the chemist, who was the first to recognise two separate ruby-silver ores: arsenical and antimonial.

Chemical composition. Ag 65.4%, As 15.2%, S 19.4%. Analyses show that Ag content ranges from 63.4 to 67.6%, As from 12.3 to 20.2%, and S from 13.1 to 20.2%.

System, trigonal; symmetry, ditrigonal pyramidal $L^3 3P$. Space group $R3C(C_{3v}^6)$. $a_0 = 10.77$; $c_0 = 8.67$. **Crystal structure.** The AsS_3 groups occupy every corner and the centre of the rhombohedral cell. Each such group is a low pyramid with an As apex. The apexes of all the pyramids are oriented parallel to the threefold axis. **Habit.** Commonly occurs in scalenohedral crystals with acute rhombohedrons (Fig. 131). The principal forms are hexagonal prism $\{11\bar{2}0\}$ and ditrigonal pyramids $\{21\bar{3}1\}$, $\{11\bar{2}4\}$, etc. Faces are striated obliquely. Occurs mostly as disseminated grains, sometimes massive.

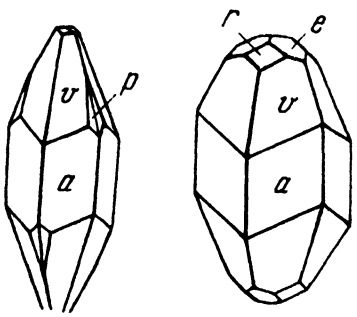


Fig. 131. Proustite crystals $a\ \{11\bar{2}0\}$, $v\ \{21\bar{3}1\}$, $v\ r\ \{10\bar{1}1\}$, $e\ \{01\bar{1}2\}$, $p\ \{15\bar{6}2\}$, $u\ \{10\bar{1}4\}$.

Colour, scarlet-vermilion (like cinnabar). **Streak**, vermilion. Translucent. **Lustre**, strong adamantine. For Li-light: $n_y = 3.088$, $n_z = 2.792$.

Hardness, 2 to 2.5. Brittle. **Cleavage**, $\{10\bar{1}1\}$ distinct. Fracture conchoidal. **Specific gravity**, 5.57 to 5.64. **Other properties.** Non-conductor of electricity.

Diagnostic features. Externally can hardly be distinguished from pyrargyrite. Usually is somewhat lighter in colour than the latter. Crystals have fewer faces than crystals of pyrargyrite. However, the main difference between the two is in the As and Sb contents.

Other minerals similar to proustite in colour and lustre are miargyrite ($AgSbS_2$), cinnabar, cuprite (Cu_2O), and zincite (ZnO). Miargyrite, if not in crystals, can be distinguished from proustite only by the As : Sb ratio, which is determined by chemical analysis. Cinnabar is easily identified by its behaviour before the blowpipe (volatilises completely). Cuprite is identified by its octahedral crystals, dark brownish-red streak, and also paragenetic association with native copper and other copper minerals. Zincite has an orange-yellow streak and high hardness (4 to 4.5).

Before the blowpipe fuses readily, gives off the arsenic odour, and yields a coating of As_2O_3 and Sb_2O_3 (when antimony is present). When roasted in the reducing flame on addition of soda its bead yields silver. Dissolves in nitric acid with separation of S and As_2O_3 (in the case of pyrargyrite, Sb_2O_3 is separated).

Genesis and occurrence. Is widely distributed in *hydrothermal* veins of lead-zinc-silver ores (of the so-called noble quartz-calcite formation). Occurs with minerals formed in the latest stages of hydrothermal processes, such as pyrargyrite. Common paragenetic associates of these minerals are galena, sometimes native silver, and also sulphoarsenites and sulphoantimonites of lead, silver, and copper of different composi-

tion. In some deposits they are associated with arsenides of nickel and cobalt.

In the oxidised zone proustite and pyrargyrite decompose, sometimes forming native silver and argentite. But usually silver, in the unstable form of Ag_2SO_4, is capable of migrating, especially in the presence of free sulphuric acid and ferric sulphate. In a number of instances, this gives rise to silver enrichment of the lower parts of the oxidised zone.

In the lead-zinc deposits of the U.S.S.R., proustite and pyrargyrite are mostly found as minute segregations visible in polished sections under the microscope. They occur most frequently in a number of lead-zinc-silver deposits of the *Western Verkhoyanye*: Bezymyanskoye, Verkhne-Endybalskoye, Berezinskoye, and other deposits.

The richest deposits of these two minerals are in Mexico (Zacatecas, Guanajuato, etc.), Chile, Peru, Bolivia, and elsewhere.

Uses. Proustite and pyrargyrite are the most widespread silver-bearing minerals, and therefore are important ores of silver.

PYRARGYRITE, Ag_3SbS_3. From the Greek words "pyros"—fire, and "argyros"—silver. Synonyms: dark ruby-silver ore (Fig. 132).

Many physical properties of this mineral are similar to those of proustite. We shall mention those that are peculiar to pyrargyrite. Colour in reflected light is dark red to iron black; the corners of crystals and fragments are translucent. Streak, dark cherry-red. Specific gravity, 5.77 to 5.86 (higher than that of proustite). Other diagnostic features have been described earlier (see "Proustite").

Its mode of occurrence is the same as that of proustite but mostly associated with antimony-bearing minerals.

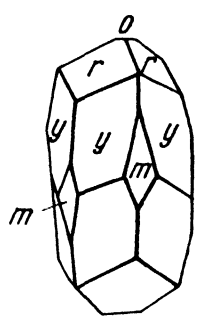


Fig. 132. Pyrargyrite crystal, *o* {0001}, *r* {10$\bar{1}$1}, *m* {$\bar{1}$010}, *y* {3$\bar{2}$51}.

STEPHANITE, Ag_5SbS_4 or $5Ag_2S \cdot Sb_2S_3$. Ag content 68.5%. System, orthorhombic. Occurs in short-prismatic crystals and massive.

Colour, grey-black. Streak, black. Lustre, metallic. Hardness, 2 to 2.5. Brittle. Cleavage, {010} distinct. Specific gravity, 6.2 to 6.3.

Fuses and decripitates in the blowpipe flame on charcoal, giving a coating of Sb_2O_3. With soda yields a silver globule. It is decomposed by dilute nitric acid with separation of S and Sb_2S_3.

Occurs together with other silver minerals, usually in very small amounts, in veins of hydrothermal origin. Has been recorded from deposits of Saxony and Harz, Germany; Mexico, and elsewhere.

POLYBASITE, $(Ag, Cu)_{16}Sb_2S_{11}$ or $8(Ag, Cu)_2S \cdot Sb_2S_3$. Ag content 62.1 to 74.9%, Cu 3 to 10%. System, monoclinic. Occurs in tabular or short-prismatic crystals of pseudohexagonal habit.

Colour, grey-black. Streak, black with a reddish tinge. Lustre, metallic. Hardness, 2 to 3. Cleavage, parallel to {001}. Specific gravity, 6.27 to 6.33.

Fuses readily in the blowpipe flame on charcoal into a metallic globule, giving off fumes, and produces a coating of Sb_2S_3. Fused with a phosphate, gives a greenish-blue bead (copper).

Occurs together with other silver sulphosalts in low-temperature hydrothermal veins in several localities: Jachymov and Přibram, Czechoslovakia; Schemnitz, Hungary; Zacatecas, Guanajuato and Durango, Mexico, and elsewhere.

5. LEAD SULPHOSALTS

The compounds included in this group are mostly sulphoarsenites, sulphoantimonites, and sulphobismuthites of lead. All of them behave differently from the sulphosalts of copper and silver, only in a few instances forming binary compounds with them. The chemical constitution of many of them has not yet been finally established.

We shall review only two minerals: boulangerite and jamesonite.

BOULANGERITE, $Pb_5Sb_4S_{11}$ or $5PbS \cdot 2Sb_2S_3$.

Chemical composition. Pb 55.4%, Sb 25.7%, S 18.9%. Pb content varies from 54 to 58%, part of it being due to the presence of galena as a mechanical impurity. Sometimes contains up to 1% of copper.

System, monoclinic; symmetry, prismatic. Crystals very rare. Usually occurs in fine-granular or felted aggregates.

Colour, lead grey to iron black. **Streak**, grey-black with a brownish tinge. Opaque. **Lustre**, metallic.

Hardness, 2.5 to 3. Brittle. **Cleavage**, {100} distinct. **Specific gravity**, 6.23.

Diagnostic features. Identifiable usually by fine-fibrous aggregates and brownish streak. Cannot be distinguished positively from a number of other, rarer, sulphoantimonites of lead, without chemical and X-ray analyses.

Fuses readily before the blowpipe. On charcoal with soda yields a lead globule and a thick white coating of Sb_2O_3 near the assay. Dissolves in nitric acid and hot hydrochloric acid.

Genesis and occurrence. Occurs in *hydrothermal* deposits of lead-zinc ores together with copper and lead sulphoantimonites, galena, sphalerite, pyrite, arsenopyrite, etc.

In the oxidised zone decomposes readily, forming cerussite ($PbCO_3$) and antimony hydroxides. In the U.S.S.R., occurs in the *Nagolny Ridge*, the Ukraine, associated with sphalerite, galena, bournonite, grey ore, and other minerals; also found in several deposits in the Nerchinsk district (Eastern Trans-Baikal region): the *Algachinskoye* (in large amounts), *Klichkinskoye*, *Darasunskoye*, etc.

Uses. When found in large masses, is an ore of lead.

JAMESONITE, $Pb_4FeSb_6S_{14}$ or $4PbS \cdot FeS \cdot 3Sb_2S_3$. A variety which does not contain iron is called *plumosite.*

Chemical composition does not always agree exactly with the formula. Pb content 40 to 50%, Fe up to 10%, Sb about 30%, S about 20%. Frequent impurities are copper, zinc, and silver.

System, monoclinic. Often occurs in acicular and capillary crystals, sometimes as ingrowths in crystals of quartz, sphalerite, and other late-crystallising minerals in drusy cavities.

Colour, lead grey. **Streak**, grey-black. Faces sometimes show a bluish-grey tarnish. **Lustre**, metallic.

Hardness, 2 to 3. Brittle. Fracture uneven. **Cleavage**, {001} distinct. **Specific gravity**, 5.5 to 6.0.

Diagnostic features. Indistinguishable to the naked eye from other sulphoantimonites of lead occurring in acicular forms. Chemical and X-ray analyses are necessary for positive identification.

Fusible in the blowpipe flame. On charcoal yields a lead globule. Roasted with soda, gives a white coating of Sb_2O_3. Dissolves readily in nitric acid.

Genesis and occurrence. Occurs relatively rarely in *hydrothermal* deposits of lead-zinc ores in association with quartz, galena, sometimes sphalerite, and other minerals in drusy cavities. In the U.S.S.R., has been recorded from the deposits of *Nagolny Ridge*, the Ukraine, in association with calcite, at *Darasunskoye* (Trans-Baikal region). A notable locality is Zimapan, Mexico, where it has been found in quantity.

General. Beginning with this type of compounds we shall deal with minerals sharply differing in properties from any we have reviewed before. These are predominantly compounds with typical ionic bonding, imparting altogether different properties to the minerals. Their most typical representatives are halides of metals.

	H 1																
He 2	**Li** 3	**Be** 4	**B** 5	**C** 6	**N** 7	**O** 8	**F** 9										
Ne 10	**Na** 11	**Mg** 12	**Al** 13	**Si** 14	**P** 15	**S** 16	**Cl** 17										
Ar 18	**K** 19	**Ca** 20	**Sc** 21	**Ti** 22	**V** 23	**Cr** 24	**Mn** 25	**Fe** 26	**Co** 27	**Ni** 28	**Cu** 29	**Zn** 30	**Ga** 31	**Ge** 32	**As** 33	**Se** 34	**Br** 35
Kr 36	**Rb** 37	**Sr** 38	**Y** 39	**Zr** 40	**Nb** 41	**Mo** 42	**Tc** 43	**Ru** 44	**Rh** 45	**Pd** 46	**Ag** 47	**Cd** 48	**In** 49	**Sn** 50	**Sb** 51	**Te** 52	**I** 53
Xe 54	**Cs** 55	**Ba** 56	**TR** 57-71	**Hf** 72	**Ta** 73	**W** 74	**Re** 75	**Os** 76	**Ir** 77	**Pt** 78	**Au** 79	**Hg** 80	**Tl** 81	**Pb** 82	**Bi** 83	**Po** 84	**At** 85
Rn 86	**Fr** 87	**Ra** 88	**Ac** 89	**Th** 90	**Pa** 91	**U** 92											

Fig. 133. Elements characteristically forming halides (bold type).

From the chemical standpoint, the minerals concerned are salts of hydrofluoric, hydrochloric, hydrobromic, and hydroiodic acids. Accordingly, the minerals are classified as *fluorides*, *chlorides*, *bromides* and *iodides*. Moreover, there exist hydrous salts and more complex compounds which contain additional oxigenated anions such as $[OH]^{1-}$, O^{2-}, rarely $[SO_4]^{2-}$ and $[IO]^{1-}$. These are the so-called oxihalide compounds transitional to typical oxygen compounds.

According to the table (Fig. 133), the principal halide-forming elements, in contrast to what we had for the minerals reviewed previously, occupy the left-hand half of the periodic table, mostly groups I and II. Halide compounds of heavy metals are on the contrary almost of no importance in the mineralogy of natural formations and are formed under special conditions.

The specific crystallochemical features of halides. Crystal structures have been studied exhaustively only for some simple anhydrous compounds of AX and AX_2 types which crystallise in the cubic system.

Thus, it has been found that the halides of light metals possess structures with a typical *heteropolar* (ionic) bonding, whereas halides of heavy metals whose cations are strongly polarising develop *homopolar* (covalent) bonding (or bonds of a transitional type) between ions. These peculiarities in the structure of minerals determine their physical properties.

Since halides with a typical ionic bonding contain weakly charged light-metal cations with big ionic radii and, therefore, of low polarising capacity, it is but natural that these minerals are transparent, colourless (occasional colouring is, as a rule, allochromatic), have low specific gravity, high water solubility, low refractive indices, and consequently a weak vitreous lustre.

On the other hand, in the case of cations of heavy metals with an 18-electron outer shell (e.g., Cu, Ag), which tend to polarise the surrounding anions rather strongly and to form crystal structures with a covalent type of bonding, the properties of the halides will differ substantially: high specific gravity; the fact that a number of compounds possess, though weak, but idiochromatic colouring; materially higher refractive indices; much lower solubility.

Now we shall consider the properties dependent on the principal halide anions such as F^{1-}, Cl^{1-}, Br^{1-}, and I^{1-}.

First, it should be noted that the size of the F^{1-} anion is materially different from that of the other anions, as will be seen from the comparison of the lengths of their radii (angstroms):

F^{1-}	Cl^{1-}	Br^{1-}	I^{1-}
1.33	1.81	1.96	2.19

This difference has much to do with the selection of compound-forming cations (in conformity with coordination numbers and types of crystal structure), with the stability of the compounds, and hence with their physical and chemical properties. No wonder, therefore, that the bulk of fluorine in the earth's crust is combined with Ca and partly with Al and Si (in binary compounds), whereas chlorine and the far less common bromine and iodine are combined chiefly with Na, K, (Rb), (Cs), and Mg (in hydrous salts). As different from the chlorides, bromides, and iodides of heavy metals (Au, Ag, and Hg), their fluorides do not occur in nature. Chlorides of light metals are highly soluble in aqueous media, whereas their fluorides are for the most part immune to the action of water. Table 6 given below shows how great is the disparity in the solubility of these two types of compounds.

The melting and boiling points of fluorides are incomparably higher than those of the chlorides of the same metals. For instance, the boiling point of SnF_4 is 705°, whereas that on $SnCl_4$ is 114°; that of AlF_3 is 1000°, and that of $AlCl_3$ only 81°, etc.

Specific features of the behaviour of halides in nature. Most interesting are the specific features of the behaviour of F, Cl, Br, and I halides in the course of geological processes.

Table 6

Solubility of Halides in Water at 18°C

(moles per litre of saturated solution)

Anions	Cations							
	Li	Na	K	Mg	Ca	Sr	Ba	Pb^{2+}
F	0.11	1.06	12.4	0.02	0.03	0.001	0.03	0.003
Cl	13.1	5.42	3.9	5.1	5.4	3.0	1.7	0.05
Br	12.6	6.9	4.6	4.6	5.2	3.4	2.9	0.02
I	8.5	8.1	6.0	4.1	4.8	3.9	3.8	0.02

Magmatic processes do not provide conditions for these elements to concentrate in any large amounts. Fluorine and chlorine enter into the composition of a number of minerals, mainly silicates and phosphates, only as additional anionic constituents (mostly in pegmatites and contact-metasomatic formations). The bulk of these elements, evidently as volatile metal compounds, passes into hydrothermal solutions. That chlorine and fluorine are a part of the volatile magmatic constituents is additionally confirmed by the emanation of HCl and HF, sometimes abundant, in the gaseous products of volcanic eruptions. Thus, in 1919 in the Valley of Ten Thousand Smokes, Alaska, as estimated, 1,250,000 tons of gaseous HCl and 200,000 tons of HF emanated together with water vapours.

Many hydrothermal formations abound in such halides as fluorite (CaF_2) and contain some Al fluorides; metal chlorides are not found there, except for very rare microscopic crystals in the droplets of solutions occluded in some minerals (quartz and galena).

Under exogenous conditions, on the other hand, chlorides of Na and, to a lesser extent, those of K, Mg, and other metals are formed, frequently in enormous masses, in land-locked bodies of salt water together with sulphates, borates, and other water-soluble compounds. In this respect, bromides and iodides stand next to chlorides. Today 70 to 75 per cent of the total chlorine (and probably bromine) and over 90 per cent of iodine in the earth's crust are dissolved in oceanic waters. Contrary to this, fluorides are practically absent from salt-bearing sediments. Oceans and seas are gigantic collectors of dissolved chlorides. At the same time the fluorine content of sea water is as low as 0.8 g per cu m. It has been established that this element is partly assimilated by higher organisms entering into the composition of their skeletons, especially the dental enamel which is composed almost exclusively of calcium fluoride.

The migration of fluorine under exogenous conditions has another peculiarity. In the process of rock and ore weathering, much fluorine is liberated along with chlorine. However, having a very strong affinity

with calcium, fluorine, on its way to the sea, in the main precipitates from the solutions in the form of poorly soluble CaF_2 compound which is retained in continental sediments. That explains the insignificant fluorine content in sea water.

Classification of halides. Thus, the properties of halides as well as their geochemical role in the mineral formation processes allow their division into two classes:

Class 1. Fluorides.

Class 2. Chlorides, bromides, and iodides.

CLASS 1.

FLUORIDES

Fluorides as minerals occur rather sparsely in nature, though as many as 15 elements are capable of combining with fluorine. The most important fluoride is that of calcium, CaF_2, which occurs as an independent compound. Much less important are B, Al, and Si. Other elements enter into the composition of some very rare fluorides.

The most widely distributed fluorides recognised so far are confined mostly to hydrothermal formations, whereas the rare fluorides are found in sublimation products of volcanic activity. Judging by parageneses of minerals they must be formed at relatively high temperatures. Only CaF_2 in newly-formed disseminated crystals occurs frequently in the oxidation zones of ore deposits and in certain sedimentary rocks.

We shall review here fluorite and cryolite – two of the natural compounds of the fluoride group.

FLUORITE, CaF_2. "Fluorum" is the Latin name of the element F. Synonym: fluorspar*. Like other fluorine-rich minerals, it is a good flux for ores, accelerating smelting.

Chemical composition. Ca 51.2%, F 48.8%. Occasionally contains Cl (mostly yellow varieties) as an isomorphous impurity or bituminous substances with a characteristic odour. Among other impurities are Fe_2O_3, rare earths, in rare instances uranium (up to a few per cent), fluorine, and helium.

System, cubic; symmetry, hexoctahedral $3L^44L_6^36L^29PC$. Space group $Fm3m(O_h^5)$. $a_0 = 5.450$. **Crystal structure** is typical of many AX_2-type compounds (Fig. 134). It has two coordination numbers: 8 for Ca and 4 for F. The F^{1-} ions occupy the corners, while the Ca^{2+} ions occupy the centres of all the smaller cubes (Fig. 135). **Habit.** In cavities may occur as well-formed cubic crystals (Fig. 136), less often as octahedral and dodecahedral crystals. Besides {100}, {111}, and {110} forms, {210}, {421}, etc., forms may sometimes be present. The cube faces are usually smooth, while the octahedral ones appear frosted. Some-

* The term "spar" is applied in mineralogy to crystalline substances without metallic lustre but with perfect cleavage in two or more directions.

times, the cube faces carry a parquet-like pattern (Fig. 17). Twinning frequent along (111). **Aggregates.** Mostly found as impregnations or granular masses, less often as earthy masses (ratofkite).

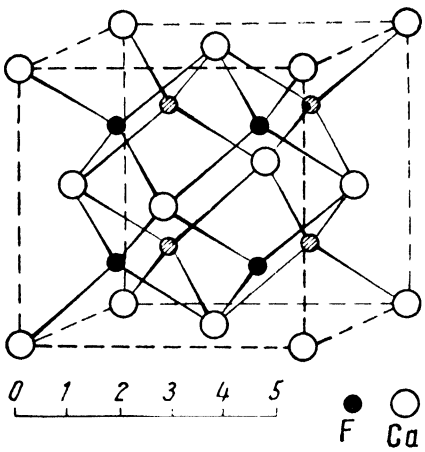


Fig. 134. Crystal structure of fluorite.

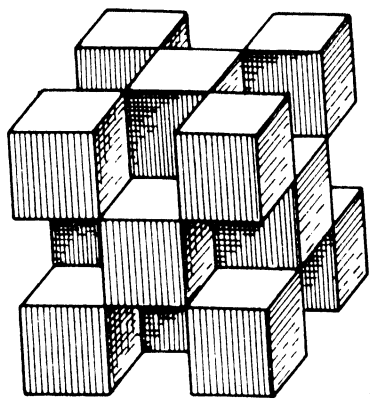


Fig. 135. Crystal structure of fluorite. The apexes of each cube are occupied by F and the centres by Ca.

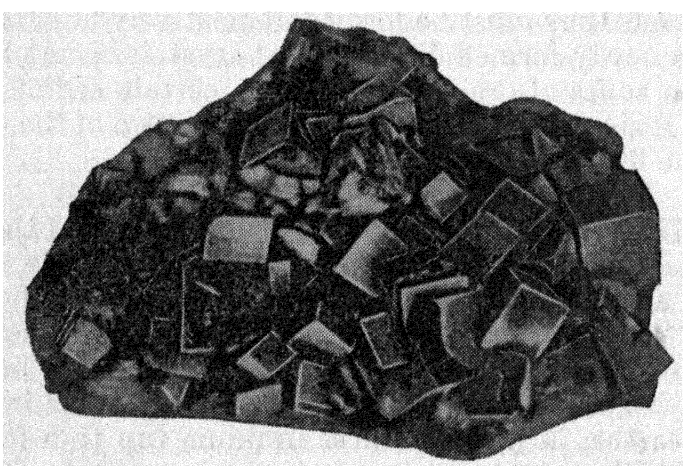


Fig. 136. Druse of cubic fluorite crystals.

Colour. Rarely colourless or water-transparent; commonly yellow, green, blue, violet to violet-black. Curiously, the colour disappears on heating and reappears on exposure to X-rays. In colourless crystals, a violet colour may be induced by the vapours of metallic calcium and electric discharges. This suggests that in a number of cases the colouring is caused by the appearance of electrically neutral Ca and F atoms in the crystal structure. **Lustre**, vitreous. $n = 1.434$.

Hardness, 4. Brittle. When subjected to prolonged unidirectional pressure, shows plastic deformations. **Cleavage**, perfect octahedral not rhombododecahedral, contrary to the concept that cohesion should be

the weakest between the planar nets that are farthest from each other. This is explained by the fact that among the (111) planar nets each net of Ca ions is interlaid by two nets of similarly charged F ions, and hence it is between these that cohesion is the weaker. **Specific gravity**, 3.18 (for impure varieties ranges from 3.0 to 3.2). **Other properties.** Often displays fluorescence (the very term originated from the name of this mineral). In cathode rays, fluorite usually gives a violet luminescence with a peculiar bluish-green hue. Fluorescence also appears on heating (thermoluminescence).

Diagnostic features. With practice, is rather easily identified by crystal forms, octahedral cleavage, weak and somewhat dull vitreous lustre, and hardness.

Before the blowpipe decrepitates, fluoresces; the edges of fragments are rounded with difficulty (at 1270°). On complete evolution of all fluorine, an infusible calcium oxide (CaO) residue remains. Water solubility is very poor. Decomposes completely only in strong sulfuric acid with separation of HF. Much less soluble in nitric and hydrochloric acids.

Genesis and occurrence. Forms mainly in the course of *hydrothermal* processes, being often an accessory of ore mineral in veins. May occur in association with most diverse minerals of hydrothermal origin.

Found also in some *sedimentary* rocks, but does not form large masses with a high F content. As a compound poorly soluble in water, CaF_2 is among the first to precipitate, sometimes in the amorphous state from salt solutions. No wonder, therefore, that the rare fluorite accumulations are confined to early chemical sediments, e.g., to deposits of gypsum, anhydrite, calcite, and dolomite. As rare neogenic formations, it occurs in the oxidised zone of ore deposits, e.g., as minute crystals on goethite sinters.

As an accessory, fluorite occurs in numerous deposits of non-ferrous and rare metals. In the U.S.S.R., fluorite is the principal mineral in the *Kalanguy* deposit (Trans-Baikal region) where it occurs as a thick breccia vein in sandstones and schists and is composed of concentrically-zonal and rod-like aggregates of various tints (white, yellow, and reddish-yellow). Earthy fluorite of sedimentary origin (ratofkite) has been found in dolomitised limestones on the banks of the Ratofka River near the town of Vereya (Moscow Region), on the right bank of the Osuga River (Kalinin Region), and elsewhere.

Uses. The bulk of fluorite (about 70 per cent) is used in steal making as a flux. The chemical industry uses fluorite as a basic ingredient of a number of fluoric compounds, such as fluoric acid for etching glass, for obtaining hydrogen peroxide from sodium peroxide, etc.; artificially produced cryolite (Na_3AlF_6) is used for obtaining electrolytically metallic aluminium from alumina, also for preparation of enamels and glazes. Transparent and colourless crystals are used in optics for making microscope lenses without spherical and chromatic aberrations.

CRYOLITE, Na_3AlF_6. "Cryos" is the Greek for ice, "lithos"—stone. Has been evidently named for ice which it closely resembles in lustre and refractive index.

Chemical composition. Al 12.8%, Na 32.8%, F 54.4%. Sometimes contains $Fe^{\cdots}$ as an impurity.

System, monoclinic, symmetry, prismatic L^2PC. Space group $P2/m$ (C_{2h}^2). $a_0 = 5.39$; $b_0 = 5.59$; $c_0 = 7.76$; $\beta = 90°11'$. Pseudocubic; at 500° becomes cubic. **Habit**, cube-like (Fig. 137) with best developed faces {001} and {010}. Commonly occurs in masses comprised of large individuals.

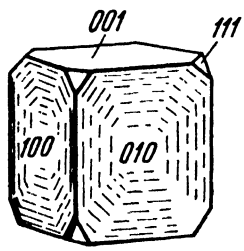


Fig. 137. Cryolite crystal.

Colour. Colourless but more often grey-white, yellowish or reddish, rarely black. **Lustre**, vitreous. $n_x = 1.34$.

Hardness, 2 to 3. Brittle. No **cleavage. Specific gravity**, 2.95 to 3.01. **Other properties.** On slight heating shows yellow luminescence.

Diagnostic features. Characteristic crystal forms and weak vitreous lustre. Accurate identification possible only by blowpipe analysis and by measuring optical constants.

Readily fuses before the blowpipe, and even in the flame of a candle imparting a reddish-yellow coloration to the flame and yielding a transparent bead which turns into white enamel on cooling. Gives the fluorine reaction in the glass tube. On prolonged roasting on charcoal gives an alumina deposit which turns blue when moistened with cobalt nitrate. Completely soluble in strong nitric acid.

Genesis. Occurs in pegmatites in which it is formed from residual solutions enriched with fluorine. An important economic deposit is at *Ivigtut*, Western Greenland, where it occurs in granite that has been converted to greisen and has the shape of a large vertical stock extending to a great depth. Cryolite is found there in coarse-crystalline masses together with other complex fluorides, rare sulphides, cassiterite, etc. In the *Ilmen Mountains* (Southern Urals) cryolite has been recorded from a topaz working and was accompanied by chiolite, amazonite, and other minerals.

Uses. Cryolite is usually obtained artificially, and used in the metallurgy of aluminium, in the manufacture of milk-white glass, enamel for kitchenware, and for other purposes.

CLASS 2.

CHLORIDES, BROMIDES, and IODIDES

Chlorides, in contrast to fluorides, are widely distributed in nature. Chlorine compounds are known for the following 16 elements: H (as HCl in gaseous volcanic emanations), N (in HN_4), Na, Mg, Al, K, Ca, (Rb), (Cs), Fe, (Ni), Cu, Ag, Hg, Pb, and Bi.

The most important of these are Na and Mg chlorides which under exogenous conditions often form, together with other soluble salts, thick salt deposits of sedimentary origin. The heavy metal (Cu, Ag, and Pb) compounds are of secondary importance. The rest of the elements form rarely occurring minerals.

It should be noted that under exogenous conditions potassium and sodium play different parts geochemically. In marine basins where concentration of chlorous salts takes place, the NaCl content is 3.5%, while that of KCl is hardly 0.6% to 0.7%, although their clarks (average content) in the lithosphere are roughly the same (see Table 2) and upon weathering of rocks these elements pass into solutions in roughly equal amounts. Chemical analyses of soils and continental deposits show that while the bulk of sodium in the surface and river waters reaches lacustrine and marine basins, potassium is, to a considerable degree, adsorbed in the upper parts of the weathering crust (soils, argillaceous rocks) and assimilated by plants. As known, the ash of plants is always rich in potassium. Hence it is clear why sodium compounds are sharply predominant over potassium compounds in the crystallisation products of drying salt-water basins.

Bromides are known only for Ag and are found very seldom in the oxidised zones of silver-bearing sulphide deposits in arid and hot climate. The bulk of bromide is disseminated as an isomorphous impurity in widespread chlorides of light metals, especially in bishofite ($MgCl_2 \cdot 6H_2O$), together with which it is accumulated in land-locked lacustrine and marine basins, mainly in the residual brines.

The bromine content of sea water is 0.008%. Sometimes is found in large quantities in mineral springs.

Iodides are also rare, but occur in more mineral species. Iodides exist for Ag, Cu, and Hg (?), i.e., metals whose ions are strongly polarising. They occur in the same conditions as bromides.

Although chlorides of Na, K, and Mg vary widely in iodine content, it remains negligible in all of them. In larger quantities it is present in the products of life activity of algae from the ash of which it is extracted. It is also found in waters of oil reservoirs and in volcanic muds. The very high solubility of iodine salts limits their accumulations to regions of arid climate. Such is, for instance, the great saltpeter ($NaNo_3$) deposit in the Atacama desert, Chile, where iodine is present in the form of iodates, its content being 0.05 per cent.

Thus, chlorides are the most abundant of the halides.

Two groups of minerals of this class will be discussed: the halite group and the cerargyrite group.

1. HALITE GROUP

Included in this group are chlorides of univalent metals Na and K, as well as the binary hydrous chloride of K and Mg.

HALITE, NaCl. "Halos" is the Greek for sea, salt. Synonyms: rock salt (when it occurs in coarse-crystalline masses in rocks) and solar salt (as friable crystalline aggregates at the bottom of bodies of salt water).

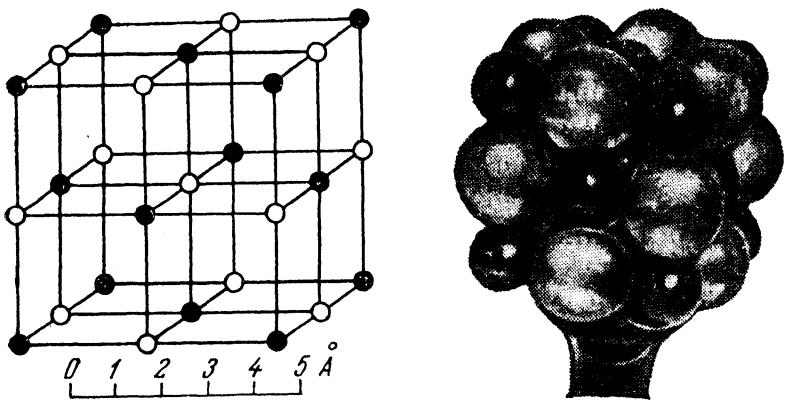


Fig. 138. Crystal structure of NaCl.

Right: model of structure. Black circles—sodium ions, white circles—chlorine ions (or vice versa).

Chemical composition. Na 39.4%, Cl 60.6%. Impurities are mostly mechanical such as droplets of brine, gas bubbles, and also inclusions of clayey and organic matter, gypsum, KCl, $MgCl_2$, etc.

System, cubic; symmetry, hexoctahedral $3L^44L_6^36L^29PC$. Space group $Fm3m(O_h^5)$. $a_0 = 5.6287$. **Crystal structure** is characterised by the closest cubic packing of the Cl^{1-} anions, with the Na^{1+} cations filling all the octahedral spaces between (Fig. 138). The Na^{1+} and Cl^{1-} ions alternate at the corners of the small cubes. Coordination number of the two ions is 6, i.e., each negative chlorine ion is surrounded by six positively charged sodium ions, and vice versa.

Habit. As a rule cubic. Faces {111} and {110} occur very seldom (when crystallised from solutions of complex composition). Twins are rare, always along (111). Solar salt crystals sometimes hopper-shaped with stepped depressions on (100) faces.

Aggregates. Solar salt occurs as loose or compact crystalline-granular crusts or beds at the bottom of enclosed basins, and also as druses of crystals, which are sometimes very large.

It is noteworthy that when the water evaporates rapidly and the weather is quiet, numerous (Fig. 139) hopper crystals float at the surface of salt brines and their upturned base keeps constantly growing. The boats are white, owing probably to occluded microscopic air bub-

bles. When the water is disturbed, it fills the boats which settle to the bottom and continue to grow, forming normal transparent crystals. Frequently, however, they retain inside milk-white portions with a herring-bone or envelope-like pattern.

Rock salt developing by cumulative crystallisation in the course of metamorphism forms unusually coarse-crystalline masses, as evident from the size of cleavage planes. Characteristically, recrystallisation

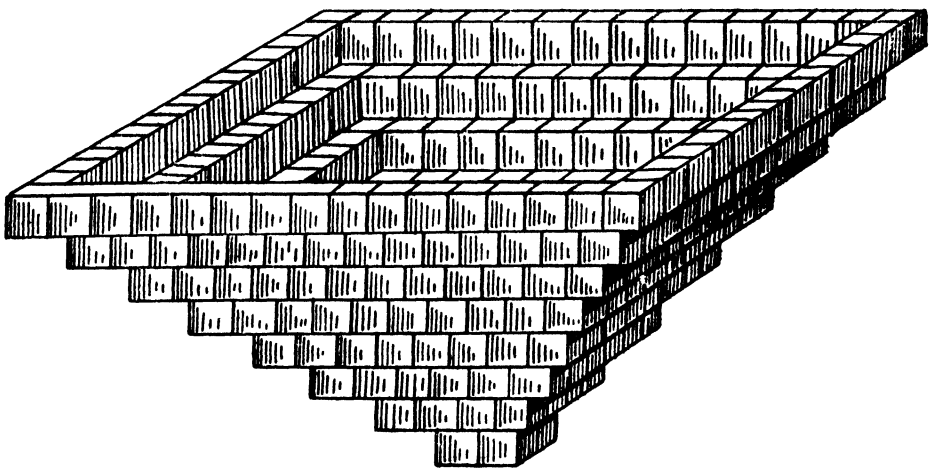


Fig. 139. Crystalline boat of NaCl.

may yield perfectly transparent masses of halite (the occluded liquids and gases evidently being "expelled" towards the perimeter of the crystal grains).

Colour. Pure masses of halite are transparent and colourless or white, but some pigments often produce different colours: grey (usually clayey particles), yellow (iron hydroxides), red (red hematite), dark brown to black (organic matter which disappears on heating), etc. Rock salt has sometimes a very peculiar intense blue colouring distributed in spots and bands, especially in those portions which have suffered considerable deformation. Such colour is obtained artificially by exposing rock salt to X-rays, or by impregnating it with metallic sodium vapours, especially after the specimen has been subjected to unidirectional compression. On heating to 200°, the colour disappears and the salt becomes colourless. The colouring is attributed to the fact that the Na^{1+} ions acquire free electrons (β-particles of radioactive radiation) and thus become electrically neutral atoms. The occurrence of blue salt in those portions where potassium-containing chlorides are also present suggests that K and its usual associate Rb—both capable of emitting β-particles (electrons)—could cause the blue colouring.

Lustre, vitreous, greasy on the surface of slightly weathered varieties. $n = 1.544$ (much higher than that of sylvite).

Hardness, 2. Brittle. Prone to plastic deformation upon continued unidirectional pressure. **Cleavage**, excellent cubic (cf. Fig. 23), which agrees well with the crystal structure of the mineral. **Specific gravity**, 2.1 to 2.2. **Other properties.** Poor conductor of electricity, but extremely good conductor of heat. Highly soluble in water: up to 35 per cent at room temperature (solubility changes but slightly as temperature rises the first few tens of degrees). Taste saline. Hygroscopic, but much less so than potassium and magnesium chlorides.

Diagnostic features. Readily identifiable by low hardness, excellent cleavage, solubility in water, and salty taste.

Easily fusible before the blowpipe on charcoal (at 800°), usually decrepitates and colours the flame yellow. On addition of $AgNO_3$ to a solution slightly acidified with nitric acid, gives a white flocculent AgCl precipitate.

Genesis and occurrence. The bulk of halite, as well as of other water-soluble salts, is formed in the course of *exogenous* processes through the drying of salt lakes or shallow lagoons and bays cut off from the sea by sand bars, in conditions of hot arid climate. In summer in such shallow bays, the evaporation of water over a vast area will cause the concentration of salts in solution to increase continuously over that in the main body of water. The resulting drop of water level will cause more water to flow from the main body adding more salt to the solution.

With the advent of cold weather, different salts are precipitated from the saturated solutions, depending on the concentration of the constituents. If a basin is cut off from the sea entirely and has no fresh water tributaries, salt may precipitate even in summer, when the solution becomes supersaturated due to evaporation.

The composition of water in inland saline lakes varies widely. This depends not only on the composition of inflowing water, i.e., of surrounding rocks, but also on the stage of the drying of the lake and on the corresponding relative concentration of constituents in the brine. In many such lakes NaCl is precipitated along with other salts.

In rock salt deposits formed in the past geologic ages halite occurs in continuous masses. In the course of orogenic movements, the salt beds emplaced in sedimentary rocks change their shape readily in view of their great proneness to plastic deformation. In this way there are often formed thick domes of complicated shape and structure, which sometimes protrude through the overlying sedimentary rocks. In this process, thin lamellar salt deposits frequently undergo very complex crumpling.

The deserts abound in salt efflorescences, which practically always contain NaCl. They disappear after periods of rain and reappear in dry weather.

Finally, halite occurs together with other chlorides as a sublimation product on the walls of volcanic craters and in the cracks in lava flows. With very few exceptions, such accumulations are small. It should be

noted that in this case halite usually contains a great deal of KCl, which, as has been shown experimentally, at high temperatures enters into it in the solid-solution state.

The largest reserves of halite are concentrated in rock-salt deposits. Formed in different geologic epochs, the largest deposits, however, are confined to sediments of the Permian period notable for its prolonged hot continental climate (on the territories of Europe, Southern Asia, America, etc.).

In the U.S.S.R., the most important halite deposits are the following: the *Slavyansk-Artemovsk* at Bakhmut, the Ukraine, where 18 rock-salt strata are interbedded with clays, anhydrites, and limestones; the *Iletskaya Zashchita* where a huge rock-salt stock is overlain with only a thin blanket of drift, and rock-salt strata alternating with anhydrites are badly crumpled; *Solikamsk* (in the upper reaches of the Kama River)—the world's largest deposit of potassium and magnesium salts, enclosing also thick beds of rock salt, gypsum, etc.

The well-known *Lake Baskunchak* is an important deposit of solar salt of recent formation. The lake is located at the northern slope of a salt dome buried under a gypsum series. The crystalline salt deposits lie beneath the brine of the lake.

Notable foreign localities are *Wieliczka* rock salt deposit south-east of Krakow (Poland)—one of the oldest known, the working of which started as early as the XI century; a huge rock-salt stock near *Suez*; enormous deposits of rock salt are known in *Northern India*, along the Himalayas, in Punjab, etc.

Uses. Halite has a great variety of uses. Besides being an essential element of the diet and food-preserving agent, it is extensively used in the chemical industry for manufacture of hydrochloric acid, chlorine, bicarbonate of soda, caustic soda and a number of salts. Moreover, it is a raw material for metallic sodium employed in the production of antifriction alloys (sodium-calcium babbits); in the production of sodium peroxide used as a bleach in the textile industry; as a catalyst in the synthesis of complex organic compounds; as a reducing agent and desulphuriser in ferrous and non-ferrous metallurgy; as an absorber of moisture and oxygen in the purification of noble gases (helium, neon, and argon, etc.); in electrical engineering in sodium-vapour filled discharge lamps, and in electrical cables with sodium "cores" sheathed with copper, etc.

SYLVITE, KCl. **Chemical composition.** K 52.5%, Cl 47.5%. Often contains occluded liquids and gases, chiefly nitrogen, less often carbon dioxide, hydrogen, methane, and, what is most interesting, helium. Frequent mechanical impurities are NaCl and Fe_2O_3. Almost always present as isomorphous admixtures are KBr (up to 0.1%) and negligible amounts of RbCl and CsCl.

System, orthorhombic; symmetry, hexoctahedral $3L^44L_6^36L^29PC$. Space group $Fm3m(O_h^5)$. $a_0 = 6.278$. **Crystal structure**, analogous to

that of halite: face-centred cube (cf. Fig. 138). The unit cell is much larger than that of halite. **Habit**, cubic. Occurs fairly often in cubes truncated by octahedral faces. Twins along (111) are frequent. **Aggregates.** Usually granular massive, sometimes with laminated texture.

Colour. Pure varieties are water-transparent and colourless. May be milk-white due to minute occluded gas bubbles. Bright-red and pink sylvites are also crystallosols containing minutest scales of hematite (Fe_2O_3) as a coarsely-dispersed phase which precipitates on dissolution. **Lustre**, vitreous. $n = 1.490$ (lower than for halite).

Hardness, 1.5 to 2. Brittle. Shows signs of plasticity under continued unidirectional pressure. **Cleavage**, {100} excellent. **Specific gravity**, 1.97 to 1.99 (lower than that of halite). **Other properties.** Taste, bitterly salty. Heat conductivity high. Readily soluble in water. Hygroscopic. Transparent varieties transmit light rays of short wavelengths well; hence their use in spectroscope prisms.

Diagnostic features. Resembles halite, with which often yields granular intergrowths. Differs from it in taste and by the violet colour which it imparts to the flame. This is visible through a blue filter to filter out the yellow sodium flame. Under the microscope differs from halite in the refractive index.

Readily fusible in the blowpipe flame (at 800°). Addition of $AgNO_3$ to a sylvite solution acidified with nitric acid gives a white AgCl precipitate.

Genesis and occurrence. Like halite, sylvite is formed in drying salt lakes. However, it is far less common than halite and occurs only in few rock-salt deposits. It is largely adsorbed by soils from migrating surface solutions. Being among the last salts to crystallise from brines, it usually occurs in the upper salt accumulations. Sometimes it is a product of decomposition of carnallite which is formed under the same conditions.

As a sublimation product it is found on the walls of volcanic craters and in the cracks of solidified lavas.

The world's largest deposit of sylvite is at *Solikamsk*, 35 km north of Perm. It was discovered in 1925. The thick lower horizon of sylvinite (halite-sylvite rock) lies at a depth of 150 to 300 m on a body of rock-salt and is overlain by a zone of carnallite mixed with halite. The sylvinite contains from 10 to 35 per cent of KCl. The upper sylvinite horizon is a decomposition product of the carnallite zone (from which $MgCl_2$ has been leached out) and is comprised of a coarse-grained mass of variegated colour in which milk-white sylvite associates with colourless, blue, deep-blue, and greyish rock salt.

Before the Solikamsk discovery the best known deposits of sylvite were those at *Stassfurt* and other localities in Western and Northern Germany, where salt deposits are of the same Permian age and comprise a rather complex variety of halides, sulphates, and boron com-

pounds. Comparatively younger—Tertiary—sylvinites are mined in *Alsace* (France).

Uses. Potassium salts are predominantly used as fertilisers. Only about 5 per cent are used in the chemical industry for the manufacture of KOH, K_2CO_3, KNO_3, $KClO_3$, $KMnO_4$, KCN, KBr, KI, and other compounds, which have numerous applications: in medicine, photography, in the manufacture of perfumes, fireworks, paper, glass (cut-glass ware and Bohemian glass), varnishes and paints, etc.

CARNALLITE, $MgCl_2 \cdot KCl \cdot 6H_2O$. **Chemical composition.** Mg 8.7%, K 14.1%, Cl 38.3%, H_2O 38.9%; negligible amounts of isomorphous impurities—Br (up to 0.2%), Rb and Cs (hundredths of per cent), rarely Li and Tl. Common mechanical impurities are NaCl, KCl, $CaSO_4$, Fe_2O_3, clayey matter, droplets of brines, and often abundant occluded gas bubbles (mixture of nitrogen, hydrogen, and methane).

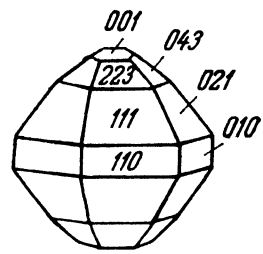


Fig. 140. Carnallite crystal.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Pban(D_{2h}^4)$. $a_0 = 9.54$; $b_0 = 16.02$; $c_0 = 22.52$. Crystals extremely rare, of pseudohexagonal habit (Fig. 140). Commonly granular massive.

Colour. Colourless when pure. Commonly pink or red owing to inclusions of finely-dispersed iron oxides. Dark brown or yellow when iron hydroxides are present. **Lustre**, vitreous on fresh fracture, on exposure to air quickly becomes greasy. $n_x = 1.494$, $n_y = 1.475$ and $n_z = 1.466$.

Hardness, 2 to 3. Brittle. **Cleavage**, none. **Specific gravity**, 1.60. **Other properties.** Unusually hygroscopic. Deliquesces, decomposing to KCl and $MgCl_2 \cdot 6H_2O$ and forming a thick brine. Taste salty disagreeably bitter. Intensely fluorescent. Dissolving in water is accompanied by a crackle similar to the crunch of footsteps on the frozen snow. This is due to the presence of occluded gas bubbles under high pressure, more frequent in carnallite than in other salts.

Diagnostic features. Occurs in paragenetic association with rock salt and sylvite. Deliquescent in moist atmosphere. Can be distinguished from bishofite ($MgCl_2 \cdot 6H_2O$) and tachydrite ($2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$), which are also deliquescent, only with the aid of microchemical reactions (contains K), and by the violet colour it imparts to the flame. This is best observed through a blue filter. When scratched with the point of a knife, emits a characteristic crackle, due to sudden expansion of the occluded gas bubbles.

Readily fusible before the blowpipe flame. Like many other water-abundant crystallohydrates, grains of carnallite, when heated on glass, dissolve in their own crystallisation water. On slow drying, small KCl cubes are formed.

Genesis and occurrence. One of the last salts to be formed from salt-lake brines, it is enriched with potassium and magnesium. Therefore, it occurs in the upper horizons of buried sedimentary salt beds and overlays sylvinite strata. Sometimes segregates on the walls of dry mine workings from the brines which trickle down from overlying strata.

In the U.S.S.R. occurs in enormous amounts at *Solikamsk* which has already been mentioned (see sylvite). Large masses also found at *Stassfurt* (Germany), *Kalush* (Western Ukraine), and elsewhere.

Uses. Like sylvite and other potassium salts, is used for fertilisers.

Electrolysis of dehydrated carnallite in closed baths produces floating metallic magnesium; potassium-enriched residues are utilised in the production of fertilisers.

Refined metallic magnesium goes to make light and strong alloys with aluminium (duraluminium, magnalium) for the aircraft industry, and as a reducing agent for obtaining metallic titanium. Other uses are in flares and flashlight powders for photography, etc.

Bromine extracted from the brines by chemical processes is used in medicine (potassium bromide), photography, etc.

2. CERARGYRITE GROUP

This group comprises normal chlorides, bromides, and iodides of Ag, Cu, Hg, and Pb occurring in the oxidised zones of ore deposits under the conditions of hot and arid climate. We shall review only cerargyrite.

CERARGYRITE, AgCl. "Ceras" is the Greek for horn, "argyros", silver. Synonym: horn silver (its fracture often appears horny).

Chemical composition. Ag 75.3%, Cl 24.7%. May contain Hg and Br as impurities.

System, cubic; symmetry, hexoctahedral. Space group $Fm3m(O_h^5)$. $a_0 = 5.547$. **Crystal structure** resembles that of NaCl. Crystals are rare, habit cubic. Twinning along (111). Usually occurs as incrustations, crystalline coatings, horny and waxy sinter masses.

Colour. Freshly-exposed specimens colourless or slightly yellowish, bluish-greenish, and brownish. On exposure to light turns first violet-grey and later even black (possibly owing to segregation of finely-dispersed Ag). **Lustre**, adamantine for crystals and waxy for cryptocrystalline compact masses. $n = 2.07$.

Hardness, 1.5 to 2. Can be cut with a knife. Malleable. **Cleavage**, none. **Specific gravity**, 5.55. **Other properties.** Insoluble in water.

Diagnostic features. Characterised by low hardness, high refractive index, insolubility in water, and chemical reactions.

Before the blowpipe on charcoal fuses readily (450 to 500°) and boils. Roasted with soda in the reducing flame, readily yields metallic silver.

Almost insoluble in acids (partly dissolves in HCl). Forms a solution only with ammonia, which is a highly characteristic feature.

Genesis. Occurs in the oxidised zones of silver-lead ore deposits, being formed in the course of oxidation of silver minerals by chlorine-bearing water seeping down from the surface. In larger amounts occurs in localities with a hot and arid climate. Pseudomorphs after native silver have been recorded.

In the U.S.S.R., cerargyrite occurs in the oxidised zones of a number of deposits in the Southern Urals (Mikhaylovsky mine in the Baimak district), Kazakhstan, and Altai. The world's largest deposits of cerargyrite and other halide silver compounds are in the Atacama desert (Chile), and also in Bolivia, Mexico and Australia.

General. This section covers the simplest compounds of metals and metalloids with oxygen and hydroxyl. Oxygen salts will be discussed separately.

As known, oxygen plays an outstanding role in the chemical processes in the earth's crust; this concerns both inorganic and organic mineralogy. Oxygen compounds, from simple oxides to various oxysalts, are sharply predominant throughout the earth's crust. We might recall that the mean oxygen content in the earth's crust is 47.0 per cent by weight.

	H 1																
He 2	**Li** 3	**Be** 4	**B** 5	**C** 6	N 7	O 8	F 9										
Ne 10	Na 11	**Mg** 12	**Al** 13	**Si** 14	P 15	S 16	Cl 17										
Ar 18	K 19	Ca 20	Sc 21	**Ti** 22	V 23	**Cr** 24	**Mn** 25	**Fe** 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	**As** 33	Se 34	Br 35
Kr 36	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	**Sn** 50	Sb 51	Te 52	I 53
Xe 54	Cs 55	Ba 56	TR 57-71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85
Rn 86	Fr 87	Ra 88	Ac 89	Th 90	Pa 91	**U** 92											

Fig. 141. Elements characteristically forming natural oxides and hydroxides (bold and medium type).

Forty different elements, in some form or other, combine with oxygen into the simplest compounds (Fig. 141).

The total weight of free oxides in the lithosphere (hydrosphere and atmosphere excepted) is about 17 per cent. The share of silica alone is 12.6 per cent. Iron oxides and hydroxides constitute 3.9 per cent. Other important oxides and hydroxides are those of aluminium, manganese, titanium, and chromium.

The atmosphere contains oxides in the form of carbon dioxide and water vapour which extend in appreciable quantities up to a height of

12 km from the surface of the earth. The hydrosphere, as its name implies, is chiefly water.

Genesis and chemical features of compounds. The bulk of oxides and hydroxides of most diverse composition is concentrated in the uppermost parts of the earth's crust, i.e., on the border with atmosphere which contains free oxygen. The depth of intense penetration of free oxygen into the earth's crust is controlled mainly by the ground-water table. The crust of weathering, together with the oxidised zones of ore deposits, is the principal arena of chemical reactions which produce new formations, among which the oxides and hydroxides of metals play the dominant role.

An essential role is played in these processes not only by free oxygen of the air which penetrates from the surface into the crust of the earth, but also by percolating rain water which carries dissolved oxygen and carbon dioxide. Air-saturated rain water contains on the average from 25 to 30 cu cm of gas per litre. The gas consists of 30 per cent oxygen, 60 per cent nitrogen, and 10 per cent carbon dioxide. Thus rain water is heavily saturated with oxygen and particularly with carbon dioxide.

As the water percolates toward the ground-water table, its oxidising power gradually diminishes, the free oxygen being consumed in oxidation. This depletion is especially intense in the oxidation of sulphides and similar compounds, resulting at the first stage in formation of sulphates, arsenates, etc.

Also rather easily oxidised are oxygen compounds entering into the composition of minerals and ores containing low-valent metals, such as Fe^{2+}, Mn^{2+}, V^{3+}. In the course of oxidation these metals are replaced by ions of higher valency, but of smaller size, and hence the bonds of the crystal structure become weaker. In the end the oxidised crystalloids completely break down which is followed by the formation of new compounds, some soluble and some insoluble in water.

The salts, (sulphates, carbonates, etc.) forming during the first stage of these processes react with water, being subjected to *hydrolysis*, as a result of which a number of metal cations precipitate in the form of hydroxides of low water solubility.

It is well known that the behaviour of ions in solution depends on the ionic potentials, whose values are expressed in terms of the charge-to-ionic-radius ratio ($W : R_i$). The cations yielding poorly water-soluble hydroxides are presented graphically (Fig. 142) in the order of increasing valencies (across) and increasing ionic radii (down). The region of cations likely to produce oxides and hydroxides is confined between the dashed lines.

To the left of this region are the cations of strong metals with an 8-electron outer shell, i.e., alkalis and, to some extent, alkali earths (with ionic potentials below 2.0). We know from chemistry that these ions are easily retained and transported in aqueous solutions. In nature, they precipitate from solution only as salts of various acids. The only

exception are strongly polarising cations with an 18-electron shell (Cu^{1+} and Pb^{2+}) occurring in nature in the form of oxides.

Cations with very high ionic potentials (over 10), small ionic radii and high charges are at the top of the graph (Fig. 142). All of them are

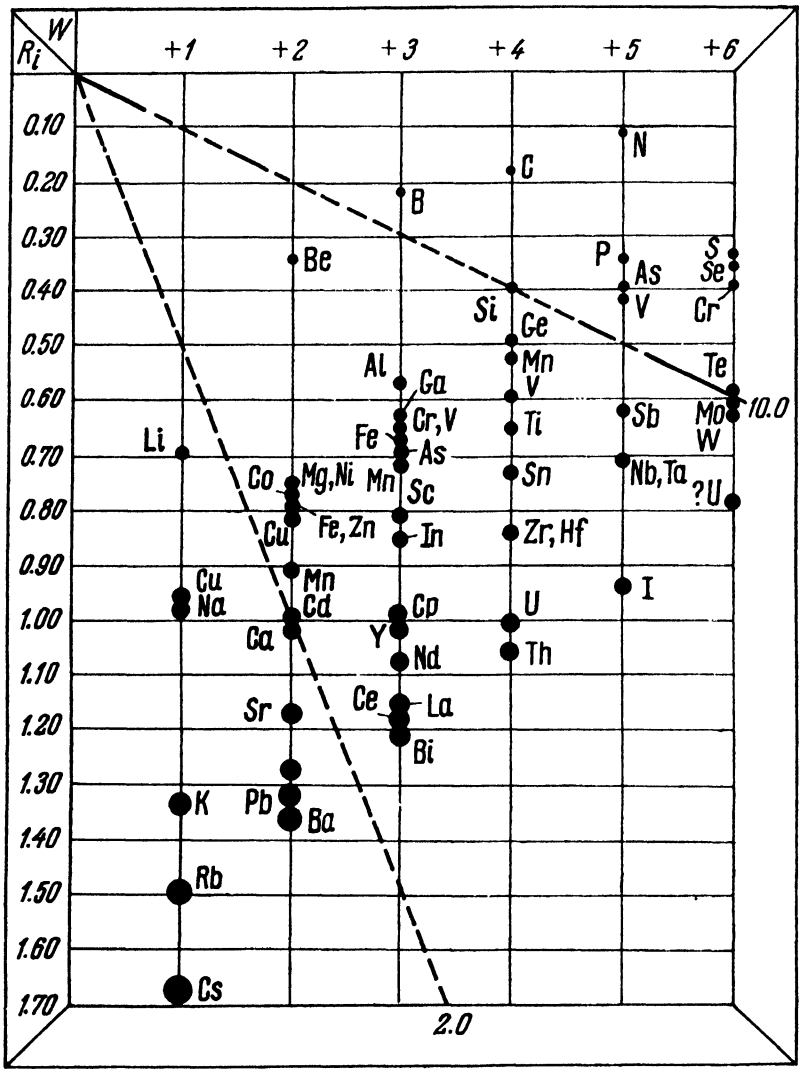


Fig. 142. Cations prone to forming hydroxides (between dotted lines).

known to yield stable complex anions with covalent bonding: $[BO_3]^{3-}$, $[CO_3]^{2-}$, $[SO_4]^{2-}$, $[PO_4]^{3-}$, etc., which, combining with corresponding cations, give various salts capable of precipitating from solutions.

Thus, the graph shows lucidly the difference in the chemical properties of cations in relation to their potentials, which determine the specific behaviour of the cations in solutions, depending on the acidity or alkalinity of the latter.

Among the oxide- and hydroxide-forming cations with which we are concerned (on the left-hand side of the region confined between the

dashed lines) Mg^{2+}, Fe^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+} are easily transported in acid solutions, while in strongly alkaline solutions they precipitate as crystalline hydroxides or basic and neutral salts. The cations with higher ionic potentials, Al^{3+}, Fe^{3+}, Mn^{4+}, Si^{4+}, Ti^{4+}, and Sn^{4+} precipitate readily from slightly alkaline or slightly acid solutions as a result of hydrolysis of the salts, mostly in the form of poorly soluble hydroxides (combined with OH anions).

The bulk of hydroxides forms in the oxidised zone of ore deposits and in the *crust of weathering* of rocks in general. Because the majority of hydroxides are poorly soluble in water, in the course of intense oxidation processes they are capable of giving strongly supersaturated solutions. It is natural, therefore, that they are usually found in the form of cryptocrystalline or colloidal masses.

Metal hydroxides (principally of iron, manganese, silicon) are also widespread in *bodies of water* such as marshes, lakes, and seas. Thus, in many contemporary fresh-water lakes in the northern regions (Karelia, Finland, Sweden, Canada) accumulations of iron and manganese hydroxides occur in the shallow near-shore zone as scattered concretions of different sizes and shapes: globular, ellipsoidal, flattened, and various irregular forms. The concretions almost always contain, along with Fe and Mn hydroxides, humic matter, and sometimes Ni, Co, etc.

Irrespective of their mode of formation, hydroxides, especially in air-dry conditions, with time lose their capillary and adsorbed water, and form compounds chemically associated with hydroxyls, and even anhydrous oxides (Fe_2O_3 and MnO_2), especially in regions with a sharply continental climate. In the course of regional metamorphism at moderate depths hydroxides are also converted to crystalline granular masses of anhydrous oxides.

Turning to the question which elements in general form simple anhydrous oxides in the course of *endogenous* processes of the formation of minerals (magmatic, pneumatolitic, and hydrothermal), we shall see that their list matches exactly that of the cations that tend to form water-insoluble hydroxides in the process of hydrolysis of salts (Fig. 142). Such are, for instance, quartz, rutile (TiO_2) cassiterite (SnO_2), corundum (Al_2O_3), hematite (Fe_2O_3), braunite (Mn_2O_3), and many others. The divalent cations adjoining this principal cationic group (Fig. 142) occur much more seldom as simple anhydrous oxides, but characteristically rather often occur as binary oxides (minerals of the spinel group, the so-called titanates, and tantaloniobates). If we mention in conclusion gaseous carbon and sulphur oxides (CO_2 and SO_2) as well as water (H_2O), this will exhaust the list of elements relating to the class of minerals under consideration.

Peculiar features of crystal structure. Almost all the compounds included in this section have crystal structures characterised by ionic bonding of the structural units.

The crystal structures contain the following anions: O^{2-} (in oxides) and $[OH]^{1-}$ (in hydroxides). The ionic radii of the two are approximate-

ly equal (about 1.36 Å). Consequently, the entire variety of crystal structures depends in the main on the radii of the cations, their valencies, and the chemical bonds between ions.

In the crystal structures of these compounds, the cations are always surrounded by oxygen or hydroxyl anions, and the coordination numbers of the crystal structures are an important characteristic of these minerals.

Comparing the known structures of *simple oxides* we shall see the different variants of the coordination numbers, from high-coordination ionic structures to the rather rare molecular ones with low coordination numbers and van der Waals bonding. The oxides of divalent metals, characterised by typically ionic bonding, crystallise in the NaCl-type structure, i.e., with coordination numbers 6 and 6. Only the oxides of strongly polarising ions with an 18-electron outer shell have structures of lower coordination, e.g., ZnO (4 and 4) and Cu_2O (4 and 2). The crystal structures of oxides of tri- and tetravalent metals, whose cations are smaller, have lower coordination numbers, which decrease as ionic bonding approaches the covalent type: Al_2O_3 (6 and 4), UO_2(8 and 4), TiO_2(6 and 3), SiO_2(4 and 2). In compounds with molecular structures, the coordination numbers are lower still: 3 and 2 for Sb_2O_3 (cenarmontite), 2 and 1 for CO_2 (solid carbon dioxide).

As to *complex oxides* which comprise metal cations of different sizes, the coordination numbers of each such compound may be either the same or different. For instance, in $FeTiO_3$ (ilmenite), both cations, Fe^{2+} and Ti^{4+}, are surrounded by six oxygen anions. A different picture is presented by compounds of the perovskite ($CaTiO_3$) type: the Ti^{4+}, Nb^{5+}, and other cations are surrounded by the same six anions, whereas the coordination number of the Ca^{2+} and Na^{1+} cations, whose ionic radii are larger, is 12. In compounds of the spinel type ($MgAl_2O_4$) X-ray investigation establishes the coordination numbers of 4 for Mg^{2+}, and 6 for Al^{3+}.

The list of cations and their coordination numbers in the investigated structures of simple and complex oxides is given in Table 7.

Hydroxides containing hydroxyl groups $(OH)^{1-}$, for instance $Mg[OH]_2$, and also oxides containing hydrogen H^{1+} as the cation, for instance $HAlO_2$, differ materially in structure from typical oxides. It should be noted that replacement of O^{2-} ions by dipole anions $[OH]^{1-}$ results in the formation of typical layered structures with ionic bonding within the layers and van der Waals bonding between them. This diminishes the symmetry of the crystalline lattice. MgO, for instance, crystallises in the cubic system of the NaCl type, whereas $Mg[OH]_2$ does so in a hexagonal layered structure. In the same way, Al_2O_3 crystallises in the trigonal system, and $Al[OH]_3$ in the monoclinic, etc. Strongly polarising cations of the cupro type do not form hydrates of their own, but only enter as constituents into the composition of complex salts, which will be considered in the next section.

Table 7

The Principal Cations and Their Coordination Numbers in Natural Oxides

Coordination numbers	Cations
4	Be^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Si^{4+}
6	Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}, Ti^{4+}, Zr^{4+}, Sn^{4+}, Ta^{5+}, Nb^{5+}
8	Zr^{4+}, Th^{4+}, U^{4+}
12	Ca^{2+}, Na^{1+}, Y^{3+}, Ce^{3+}, La^{3+}

All these specific features of the crystal structures of oxides are reflected in the physical properties of the minerals. Compounds characterised by ionic bonding possess stable crystal structures, which on the whole are much stronger than in the case of halogens and sulphides. This is an expression of the strong chemical affinity with the oxygen of the metals forming such oxides. The strength of the crystal structures is reflected in the high hardness of these oxides (6, 7, 8 and 9 on the Mohs scale), high chemical stability, infusibility, very low solubility, etc.

Hydrates possessing layered crystal structures are much less stable structurally due to the weak bonding between the layers. They are notable for their ability to split into thin folia along their basal cleavage. The hydrates of divalent metals have low hardness; when these ionic groups are replaced by cations of trivalent metals, hardness increases, especially in the presence of $[OHO]^{2-}$ ionic groups in the structures (e.g., diaspore).

The colouring of minerals also has its peculiarities. The compounds in which ions of the noble-gas type (Mg^{2+}, Al^{3+}, etc.) take part are, as a rule, either colourless or allochromatic. However, the vast majority of minerals in which the cations are asymmetrical ions (Fe, Mn, Cr, etc.) are of intense dark colours, black being most prevalent. Many of them are opaque or translucent in thin fragments or polished sections, having predominantly brown or red tinges. This also accounts for their submetallic lustre. Their magnetic properties are likewise definitely more pronounced.

Classification of minerals. It is customary to divide all the minerals under this section into (1) anhydrous oxides and (2) hydroxides and oxides containing hydroxyl and hydrogen ions. This classification has been adopted in the present course since it fully agrees with the principles of crystal chemistry.

Either category, besides simple compounds, includes binary or more complex compounds, that formerly were treated as separate classes, such as binary oxides of $RO \cdot R_2O_3$ type, the so-called titanates, niobates, and tantalates, i.e., "salts" of hypothetical titanic, niobic, and tantalic acids. As we shall see later, X-ray investigation of these compounds shows that their crystal structures have nothing in common with the typical salts of oxygen acids. Far from that, they reveal features definitely placing them with the oxides.

Thus this section should include two classes of compounds:

Class 1. Simple and complex oxides.

Class 2. Hydroxides or hydroxyl-containing oxides.

CLASS 1.

SIMPLE AND COMPLEX OXIDES

Included in this class are both simple and complex oxides without hydroxyl ions. There is no point in setting the complex oxides apart, since their crystal structures are either analogous or very similar to those of the simple oxides.

These minerals have mostly rather simple crystal structures. The only group having more complex structures, and therefore standing somewhat apart, is that of quartz SiO_2.

The oxygen cation-to-anion ratios in these minerals may range from 2 : 1 (A_2X) to 1 : 2 (AX_2). Furthermore complex oxides may have different cation ratios, usually 1 : 1 and 1 : 2. Only some rare compounds exhibit more complex ratios.

1. ICE GROUP

As known, water may be in three states: solid (ice and snow); liquid (rain, mineral springs, rivers, lakes, seas, and oceans); and gaseous (water vapour in the atmosphere and in volcanic exhalations). For its properties water stands apart from oxides of metals and metalloids. Water plays a tremendous part in the chemical processes occurring in the earth's crust, since chemical reactions take place mostly in aqueous solutions. Without water, just as without oxygen, no organic life could exist on the Earth.

We shall review this compound here only in its solid and liquid states as the most common in nature.

ICE, H_2O. Chemical composition. H 11.2%, O 88.8%. May contain gaseous and solid mechanical impurities.

System, hexagonal; symmetry, dihexagonal pyramidal. Space group $C6mc(C_{6v}^4)$. $a_0 = 7.82$; $c_0 = 7.36$. **Crystal structure.** Molecular, close to that of the diamond (each H_2O molecule is in fourfold coordination). The H_2O molecule itself has a peculiar structure, viz., H^{1+} protons,

being ions without electrons of their own and possessing infinitesimal dimension, deeply imbed themselves within the oxygen ion (Fig. 143). The oxygen atomic nucleus is accordingly somewhat displaced away from the protons. Therefore, although the H_2O molecule is electrically neutral, it carries weak residual charges (positive in the area of the protons and negative on the opposite side). This is why in the structure of ice the weakly bonded H_2O molecules are oriented with their positively charged areas towards the negatively charged areas of other H_2O molecules. As for the general arrangement of molecules, the structure of ice is analogous to that of wurtzite (cf. Fig. 96) with the only difference that the places of Zn and S are occupied by H_2O molecules. In such structure (with a coordination number as low as 4) the structural units are far from being closely packed (the spacings are too large), on account of which the specific gravity of ice is lower than that of water. **Habit.** The crystals of snowflakes with their hexagonal symmetry exhibit a great variety of hexactinal forms of growth. Well-known are the dendrites and lace-pattern ice formations. In ice caves, ice crystals occur in regular hexagonal plates, tabular individuals, and intergrowths of complex forms. N.N. Stulov has described ice crystals of unique size and clear-cut faces (up to 40 cm long and up to 15 cm wide) found in permafrost in mine workings in north-eastern Asia. In one case, they were found in the cavities of a thick zone of crushing at a depth of 55 to 60 m where the temperature of enclosing perpetually frozen rocks was 3 to 4°. According to the readings of a contact goniometer, the predominant crystal faces were the hexagonal dipyramid and the pinacoid. In another case, very large columnar ice crystals were found in abandoned mine workings in the oxidised zone of a sulphide deposit. The workings were filled with a solid mass of ice. The ice had cavities with mineralised water and gases under high pressure. The largest ice crystals were 60 cm long and 15 cm across, and occurred as hexagonal prisms truncated by the faces of hexagonal dipyramids.

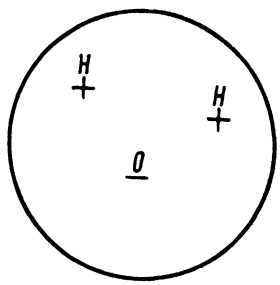


Fig. 143. Structure of H_2O molecule.

H^{1+} protons are located inside the oxygen ion (circumscribed).

Aggregates. Often composes massive aggregates of crystalline grains (compact snow and firn in glaciated regions). Glacier ice is composed of very large irregularly-shaped crystalline grains. Familiar to everyone are the stalactitic icicles forming from supercooled water, i.e., from melted snow on the shady side of roofs, as well as in ice caves (stalactites and stalagmites). In the form of hail ice often has a concentrically-banded structure. On a cold autumn morning the ground is often coated with ice efflorescence (hoar-frost).

Colour. Colourless or slightly bluish when in large masses. **Lustre,** vitreous. Optically positive. Refractive indices as low as $n_x = 1.310$ and $n_y = 1.309$.

Hardness, 1.5. Brittle. **Cleavage**, none. **Specific gravity**, 0.917 (less than that of water). A decrease in specific gravity on crystallisation is characteristic also of metallic bismuth.

Genesis. Formed on the surface of water basins on the cooling of the water. The slush that is formed first freezes into a floating crust onto which crystalline individuals extending vertically parallel to the axes of sixfold symmetry grow from below. Snow is formed from water vapour in the cold regions of the atmosphere. Under the same conditions cooled objects are coated with hoar-frost. In low-temperature ice caves, water percolating from the surface through cracks and fissures turns into ice.

In the permafrost regions with their severe climate and long winters with little snow, the so-called icings are formed during the cold season. These are enormous sheets of ice spreading at times over vast areas. River icings develop when the river freezes to the bottom in shallow places. Running water seeks an escape to the surface and soaks the snow blanket. In other instances, icings are formed by ground waters emerging from below the permafrost layer in the form of non-freezing springs. The origin of glaciers and glacier ice will not be discussed here.

Deposits of ice are well known to everyone. Notable among the ice caves in the regions of cold long winter and short summer is the *Kungur Cave* (Perm Region) which attracts numerous tourists by the beauty of crystals glittering on the walls and the ceiling. Another famous ice cave is at *Dobsina* (Slovakia) where over 7,000 sq m are covered with ice. The total volume of ice in the cave is 120,000 cu m, and the ice walls rise to the height of 15 m.

Uses. Ice is used for refrigeration and for different other industrial and domestic applications. In very cold regions where in winter there are no sources of potable water, the latter is obtained by melting river and lake ice.

WATER, H_2O. According to chemical composition and genesis, natural waters may be divided into the following principal varieties: (1) sea water containing dissolved chlorides and sulphates of Na, Mg, etc. (about 3.5%); (2) fresh river and lake water; (3) surface rain and ground waters; (4) underground waters; (5) the waters of mineral springs classified according to their mineral content as carbonated, sulphuretted, chalybeate, and other waters. Underground waters rich in calcareous salts are known as hard, in contrast to those poor in these salts, called soft.

Physical and chemical properties. Pure water has the highest specific gravity of 1 at 4°. Water vapour pressure relative to air is 0.62. The critical temperature of pure H_2O is 374°, and the critical pressure is 217 kg/sq cm. The presence of poorly volatile dissolved constituents greatly reduces vapour pressure and raises the critical point.

Water is an environment for and a most important agent in the chemical reactions that take place in the earth's crust. Its dissolving

capacity is a fundamental factor in the transportation of chemical compounds of elements either in true or colloidal solutions (sols) in the course of endogenous and exogenous processes of mineral formation. Its evaporation and temperature drop are the controlling factors in the precipitation of crystalline sediments from saturated solutions. In a number of instances crystallisation water enters into the composition of crystallohydrates in definite stoichiometric ratios.

The electrolytic dissociation of water into H^{1+} and $[OH]^{1-}$ ions plays an essential part in the processes of hydrolysis of dissolved salts with consequent formation of hydroxides, basic and acid salts.

Water is a most important constituent of hydrogels, being adsorbed on the surface of finely dispersed colloidal particles.

Water, just as carbon dioxide, is a mineralising agent in all metamorphic processes. Even an insignificant water content in solid environments facilitates the processes of recrystallisation of minerals.

Genesis. In the course of *exogenous* processes, both at the earth's surface and in the atmosphere, enormous masses of water are in constant circulation, evaporating from the surface of seas, oceans, and especially through vegetation, into the atmosphere and returning as atmospheric precipitation. The surface or so-called vadose waters include soil, ground, artesian, and underground waters as well as many fresh-water and mineral springs.

Great quantities of water also take part in the *endogenous* processes of mineral formation. During volcanic eruptions, large masses of superheated water vapour escape into the atmosphere. The crystallisation of magmas deep in the interior of the earth also releases tremendous amounts of water saturated with diverse dissolved compounds. These so-called juvenile waters are probably the source of some hot mineral springs (in regions of recent volcanic activity, such as California).

Uses. The enormous importance of water in the life of the organic world and in human activity is well known. Thus, to support plant life, soils must contain from 40 to 60 per cent of moisture. The human body contains 70 per cent water and man has to consume on the average 2.5 to 3 litres of water a day. Water resources are used extensively by man for most diverse technical purposes (for steam and hydraulic power plants, irrigation, ore concentration, chemical industry, navigation, etc.). Many mineral springs possess curative properties. Examples are the carbonated mineral springs of Narzan, Karlovy Vary, Baden, etc.; the chalybeate waters of Zheleznovodsk; the sulphuretted waters of Matsesta, etc.

2. CUPRITE GROUP

Cuprite or cuprous oxide (Cu_2O) is the only known metal oxide of A_2O type to occur naturally. An artificial product crystallising in the cuprite structure is Ag_2O which has never been found in nature.

CUPRITE, Cu_2O. From the Latin "cuprum" meaning copper. Synonym: ruby copper ore. A brick-coloured ore (due to an admixture of iron hydroxides) and pitchy copper ore (due to admixture of silica and iron hydroxides) are essentially colloidal mineral mixtures.

Chemical composition. Cu 88.8 per cent. Native copper is often found as mechanical impurity, and in cryptocrystalline varieties, Fe_2O_3, SO_2, and H_2O.

System, cubic; symmetry hexatetrahedral $3L^44L_6^36L^29PC$. Space group $P43m(T^1d)$. $a_0 = 4.26$. **Habit**, octahedral (Fig. 144), less often cubic or dodecahedral. Crystals usually small. Occasionally fine slender needles or fibres are found. Occurs more often in massive granular, sometimes earthy (mixed with impurities), aggregates.

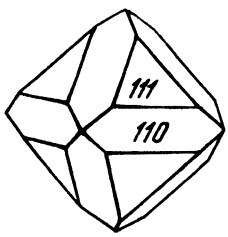


Fig. 144. Cuprite crystal.

Colour, red to lead-grey (in fine-granular or cryptocrystalline aggregates). **Streak**, brown-red or dark brownish red (when rubbed against another plate turns yellow). **Lustre**, on fracture, adamantine or submetallic. Thin fragments are translucent. $n = 2.85$.

Hardness, 3.5 to 4. Brittle. **Cleavage**, {111} distinct. **Specific gravity**, 5.85 to 6.15.

Diagnostic features. Identifiable by adamantine lustre, red streak, and especially by paragenetic association with native copper, occasionally with other secondary copper minerals—malachite and azurite. From cinnabar, proustite, and pyrargyrite differs in streak (bright red for cinnabar, red turning green on rubbing for proustite and pyrargyrite, and brown-red for cuprite), but mostly by behaviour before the blowpipe.

In the blowpipe flame on charcoal turns black, then fuses quietly, and in the reducing flame yields a copper globule. When held in pincers, colours the flame light green, and when moistened with HCl, imparts pleasant blue tinge to the flame. Readily dissolves in nitric acid, colouring the solution green. On addition of excess of ammonia the solution turns blue.

Genesis. Cuprite is formed almost exclusively through *exogenous* oxidation of chalcocite and less often of bornite ores, occurring in the zone of secondary sulphide enrichment of copper ore deposits (below the ground-water table).

Massive development of cuprite is liable to occur when for some reason or other (e.g., lowering of the base level of erosion) the ground-water table sinks and the previously formed chalcocite-rich zone comes within the oxidation zone. Oxidation of chalcocite in the course of dissolution of the evolving sulphuric acid in water may be expressed as follows:

$$Cu_2S + 2O_2 + H_2O \rightarrow Cu_2O + H_2SO_4$$

It will be easily seen that in the case of oxygen deficiency, the reaction would yield metallic copper, either instead of or in addition to

Cu_2O, which is often actually observed in specimens of cuprite (recognized by the hackly appearance of fracture).

Occasionally cuprite occurs together with native copper in certain sedimentary rocks containing vegetal remains. In this case it is in all probability the product of the reduction of cuprous sulphate by organic matter in the presence of some oxygen according to the following reaction:

$$Cu_2SO_4 + C + O \rightarrow Cu_2O + CO_2 + SO_2$$

In solutions strongly saturated with carbon dioxide cuprite becomes unstable. Pseudomorphs of malachite, more rarely of azurite, after cuprite are quite common.

In the U.S.S.R., cuprite occurs in quantity and in well-formed crystals at *Gumeshevskoye*, *Mednorudyanskoye*, and *Turya* mines in the Urals, at a number of localities in the Altai, and elsewhere, associated with malachite, azurite, iron hydroxides, etc. A notable foreign deposit is at *Chessy* near Lyons (France) where crystals up to 2-3 cm across have been found.

Uses. Cuprite is one of the best ores of copper. In the remote past, the cuprite ores along with native copper must have been worked intensely. At present large cuprite bodies are comparatively rare.

3. ZINCITE GROUP

This group includes relatively simple oxides of the AX type, i.e., of divalent metals (Mg, Ni, Fe, Mn, Cd, Ca, Be, Zn) as well as Cu, Pb, Pd. We shall discuss here only zincite and tenorite.

ZINCITE, ZnO. Zn 80.3%, O 19.7%. System hexagonal; symmetry, dihexagonal dipyramidal. Crystal structure of the wurtzite type. Occurs as impregnations and massive.

Colour, orange-yellow to dark red. Streak, orange-yellow. Lustre, adamantine. Optically positive. $n_x = 2.029$ and $n_y = 2.013$.

Hardness, 4. Cleavage {1010} distinct. Specific gravity, 5.66.

Infusible in the blowpipe flame. Soluble in acids. Has rectifying properties.

Is found in quantity at the well-known contact-metasomatic deposit at *Franklin*, New Jersey (U.S.A.) in calcite masses associated with willemite, Zn_2SiO_4, and franklinite, $(Zn, Mn)Fe_2O_4$. Crystals are very rare, and are observed only in more recent calcite veins. Finds also recorded from the Olkusz (Poland) lead-zinc deposit, Saravezza (Tuscany, Italy), and other localities.

TENORITE, CuO. Cu 79.9%, O 20.1%. Synonym: melaconite (massive variety).

System, monoclinic. A rare mineral. Commonly occurs in fine-scaly or earthy aggregates.

Colour, black to grey-black. Streak, grey-black. Lustre, submetallic. Strongly anisotropic in polished sections.

Hardness, 3.5. Brittle. Specific gravity, 5.8 to 6.4.

Infusible in the blowpipe flame. Readily soluble in acids.

Occurs in the oxidised zones of copper-sulphide deposits in association with cuprite, limonite, chrysocolla, malachite, manganese hydroxides, and other hypergene minerals. In the U.S.S.R., occurs in the area of the Turya copper mines (Northern Urals), Mednorudyanskoye deposit near Nizhny Tagil. Found in quantity in the copper deposits near Lake Superior, Michigan (U.S.A.), and the Atacama desert, Chile. Occurs as thin scales on lava at the Vesuvius and Etna, associated with alkali and copper chlorides.

4. CORUNDUM-ILMENITE GROUP

Besides dimorphic oxides of the A_2X_3 type (Al_2O_3 and Fe_2O_3), this group, according to X-ray data, includes complex (binary) oxides of ABX_3 type (where A = Mg, Fe··, Mn·· and B = Ti) crystallising in the corundum-type structure. It should be noted that at high temperatures Fe_2O_3 and $Fe{\cdot\cdot}TiO_3$ form a continuous series of solid solutions which disintegrate on cooling.

All the minerals of the group crystallise in the trigonal system and have crystal structures of the same Al_2O_3 type (Fig. 145). Only Fe_2O_3 occurs in nature in two modifications, viz., α-Fe_2O_3 in the trigonal system, and γ-Fe_2O_3 in the cubic system. The symmetry of the $FeTiO_3$-type binary oxides is of a lower order as compared with simple oxides of the Fe_2O_3 type, since their cations are not equivalent. They are formed at relatively high temperatures.

CORUNDUM, Al_2O_3. The name of the mineral comes from India. For Al_2O_3, the following polymorphous modifications are known: (1) α-Al_2O_3 (corundum), trigonal and the most stable in nature; formed over a wide range of temperatures (500 to 1500°); (2) β-Al_2O_3, hexagonal, stable at very high temperatures; the conversion of α-Al_2O_3 into β-Al_2O_3 occurs at temperatures from 1500 to 1800°; this modification forms in the course of very slow cooling of the Al_2O_3 melt; (3) γ-Al_2O_3, cubic with the crystal structure of the spinel type (as in the case of maghemite); it is obtained artificially by ignition of aluminium hydroxide (hoemite) up to 950°; at higher temperatures it becomes unstable and alters to α-Al_2O_3.

Chemical composition. Al 53.2%. Crystal varieties are of very pure composition. Traces of Cr render it red, of Fe···—brown (mixed with Mn) and pink, of Ti—blue, and a mixture of Fe·· and Fe···—black.

System, trigonal; symmetry, ditrigonal scalenohedral $L_6^3 3L^2 3PC$. Space group $R\bar{3}c(D_{3d}^6)$. $a_0 = 4.76$; $c_0 = 13.01$; $a_0 : c_0/2 = 1 : 1.363$. **Crystal structure** is shown in Fig 145 as Al_2O_3 groups at the corners of two rhombohedra composing the unit cell. Although it seems complex, the

cell structure is rather simple in fact. The oxygen ions are in closest hexagonal packing with their sheets perpendicular to the threefold axis (Fig. 146) and superimposed on each other. The Al cations are located between two such sheets, in the form of hexagons (with unoccupied centre), and fill two-thirds of the octahedral spaces (i.e., spaces between the six oxygen anions, three of which belong to one oxygen-ion sheet, and three to the other, the latter anions being turned through 180° in respect of the first three). The groups of three oxygen ions each form a common face shared by two adjacent octahedra in the neighbouring sheets. It should be noted that the oxygen sheets are superimposed on each other so that in each column of octahedra two occupied octahedra alternate with an unoccupied one, the pairs of occupied octahedra forming spiral threefold axes in a vertical plane.

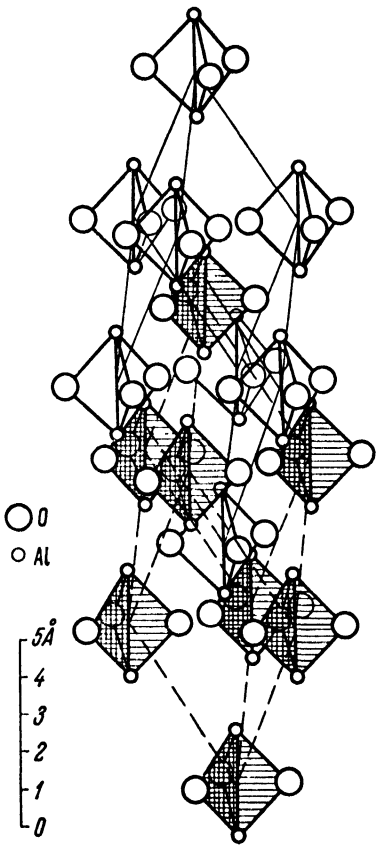


Fig. 145. Crystal structure of corundum presented as Al_2O_3 groups.

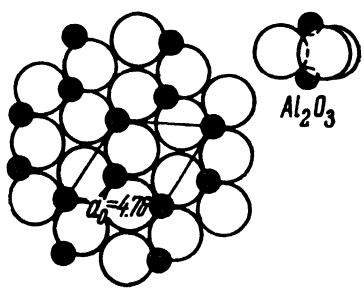


Fig. 146. One layer of closest-packed oxygen ions with Al cations in octahedral hollows, projected on (0001).

In a hexagonal cell six Al-O layers are located one on top of another. Top: side view of Al_2O_3 groups.

Habit. Common are well-formed barrel-shaped, columnar, pyramidal, and tabular crystals, sometimes as large as 10 cm across. Most common forms of faces are the hexagonal prism $\{11\bar{2}0\}$; hexagonal dipyramids $\{22\bar{4}1\}$, $\{22\bar{4}3\}$; rhombohedron $\{10\bar{1}1\}$; and pinacoid $\{0001\}$ (Fig. 147). The faces of the prisms, dipyramids, and pinacoids commonly have oblique striations. Sometimes the striations are horizontal due to pinacoidal twinning. Corundum usually occurs disseminated in rock, but in some deposits it is granular massive.

Colour, commonly bluish- or yellowish-grey (in translucent varieties). Occurs in transparent crystals of different colour. Transparent gem quality varieties are: colourless *leucosapphire*, blue *sapphire*, red

ruby, yellow *oriental topaz*, violet *oriental amethyst*, green *oriental emerald*, and *asteriated corundum* showing a six-rayed star on the basal pinacoidal plane when the crystal is turned which is due to oriented mechanical microinclusions. **Lustre**, vitreous. $n_y = 1.767$ and $n_z = 1.759$.

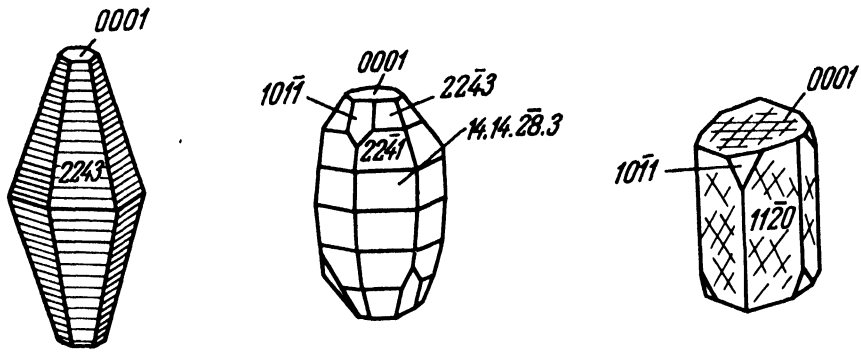


Fig. 147. Corundum crystals.

Hardness, 9. **Cleavage**, practically none. Displays only parting after pinacoid, sometimes after the unit rhombohedron (due to polysynthetic twinning). **Specific gravity**, 3.95 to 4.10. The melting point of artificial corundum is 2040°.

Diagnostic features. Readily identifiable by crystal form, striations, often by characteristic bluish-grey colour and high hardness. Differs from similar disthene (Al_2SiO_5) by the absence of perfect cleavage and by high hardness. Ruby differs from red spinel by crystal form. In irregular grains can be distinguished only under the microscope. Infusible in the blowpipe flame. Insoluble in acids.

Genesis and occurrence. Occurs in alumina-rich and silica-poor plutonic *magnetic* rocks such as corundum-syenites, and anorthosites, associated with feldspars; more rarely in other rocks (andesites and basalts). Corundum-bearing syenite *pegmatites* of economic importance are also known.

Contact-metasomatic corundum deposits in which the gem varieties (ruby and sapphire) are usually found are formed in crystalline limestones in the vicinity of igneous rocks. Corundum deposits sometimes develop by vigorous action of pneumatolytic agents upon alumina-bearing sedimentary and igneous rocks. In such cases, corundum associates with such minerals as andalusite, sillimanite, and also rutile, diaspore, etc.

Regional metamorphism of alumina-rich sediments (bauxites), without any direct relation to igneous rocks, may also give rise to corundum-bearing rocks. In the course of these processes the rocks are usually converted to crystalline schists.

Being very inert chemically, corundum often turns up in *placers*.

In the course of hydrothermal processes the earlier formed corundum is sometimes hydrated into diaspore ($HAlO_2$). This phenom-

enon never occurs near the surface, with very rare and doubtful exceptions.

In the U.S.S.R., a most notable location for high-grade corundum is *Semiz-Bugu* in the Bayan-Aul district of Kazakhstan, where it occurs in pocket-like bodies which are almost solid granular dark-blue or grey corundum, separated from surrounding quartzites by andalusite zones. The corundum is paragenetically associated with muscovite, hematite, rutile, and other minerals. A number of corundum deposits are also known on the eastern slope of the Urals, namely in the Kyshtym district, in the upper reaches of the *Borzovka river*, where it occurs as plagioclase corundum veins in ultrabasic rocks; on the eastern shore of the Irtyash Lake where metamorphic rocks, such as marbles, enclose lenticular and irregular bodies of emery containing chloritoids and sulphides.

Famous foreign localities are the deposits of transparent gem corundums (ruby and sapphire) in India, *Upper Burma* (in the contact zone of marbles and granites), Tailand (in placers, mostly sapphire), and others.

Uses. Due to its high hardness, the chief application of corundum is as an abrasive. Made into wheels, disks, emery papers and powders, it is employed for polishing and grinding (chiefly in metalworking). The transparent coloured varieties are used as gemstones.

Of late, in the countries where electricity is cheap, corundum (alundum) is made artificially by electric melting of alumina-rich bauxites. Artificial corundum is superior to natural in purity and coarse-granularity. By melting powdered Al_2O_3 with 2.5 per cent Cr_2O_3 rubies identical to natural ones are obtained, while addition of Ti, and also of Co gives sapphires.

HEMATITE, Fe_2O_3. From the Greek "hematicos" meaning sanguine. Two natural polymorphs of iron oxide are known: trigonal stable α-Fe_2O_3 and cubic and unstable γ-Fe_2O_3 which will be reviewed separately. Synonyms: iron glance, specularite, red iron ore (compact cryptocrystalline variety), micaceous hematite (red pulverulent variety). Pseudomorphs of hematite after magnetite are called martite.

Chemical composition. Fe 70.0%. May contain isomorphous admixtures of Ti (titanhematite) and Mg. Contains water in negligible quantities (hydrohematite, usually in colloform state). Cryptocrystalline compact masses often contain silica and alumina as mechanical impurities.

System, trigonal; symmetry, ditrigonal scalenohedral $L_6^3 3L^2 3PC$. Space group $R\bar{3}c(D_{3d}^6)$. $a_0 = 5.029$, $c_0 = 13.73$. **Crystal structure,** analogous to that of corundum (Fig. 145). **Habit.** Commonly in platy, rhombohedral, and tabular crystals (Fig. 148) forming in cavities. Most common forms are rhombohedral $(10\bar{1}1)$, $(10\bar{1}4)$, and pinacoidal {0001}, hexagonal dipyramidal $(22\bar{4}3)$, etc. Owing to polysynthetic twinning along the rhombohedron $\{10\bar{1}1\}$, pinacoidal planes, like those of co-

rundum, often show triangular markings (Fig. 148), while rhombohedral planes {10$\bar{1}$1}, show parallel diagonal striation. Simple twinning is rare, mostly along the rhombohedron as well as along the prism. Occasionally occurs as accumulations of slightly curved platy crystals intergrown in planes close to the pinacoid (so-called *iron roses*). **Aggregates.** Commonly massive cryptocrystalline, or in foliated or scaly aggregates. Large kidney-shaped forms of radial-fibrous structure are called

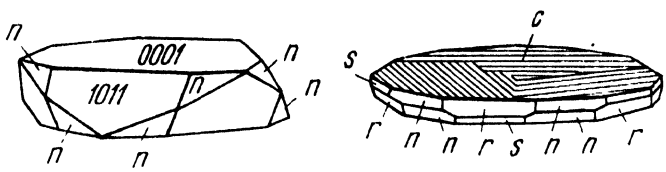


Fig. 148. Hematite crystals
n {22$\bar{4}$3}, *r* {10$\bar{1}$1}, *s*{02$\bar{2}$1}, *c* {0001}.

kidney ore (Fig. 46). Very often finely-dispersed anhydrous iron oxide imparts an intense colour to the surrounding minerals and rocks, as in the case of jaspers (siliceous rocks), red marbles, and red clay shales.

Colour of crystalline varieties of hematite is iron black to steel grey. Very thin translucent plates transmitting deep-red light. Earthy finely-dispersed varieties bright red. **Streak**, cherry-red. **Lustre**, submetallic. Sometimes a bluish tarnish is observed.

Hardness, 5.5 to 6. Brittle. **Cleavage**, none. Characteristic rough parting on rhombohedron {10$\bar{1}$1}. **Specific gravity**, 5.0 to 5.2.

Diagnostic features. Readily distinguished from similar minerals (ilmenite, magnetite, goethite, etc.) by cherry-red streak, high hardness, platy and scaly aggregates, and the absence of magnetic properties.

Infusible in the blowpipe flame. A characteristic feature is that in the reducing flame at high temperature it becomes magnetic (turns into magnetite). Slowly soluble in hydrochloric acid.

Genesis and occurrence. Hematite is formed under oxidising conditions in deposits and rocks of widely different origin. The temperature of its formation may vary within a wide range, but at high temperatures it is unstable.

1. Occasionally occurs in negligible amounts as a constituent of *igneous*, mostly acid, rocks (granites, syenites, andesites, etc.). Relatively rare in *pegmatites* where it develops at the hydrothermal stage of mineral formation.

2. In certain *hydrothermal* deposits it is found in large masses in association with quartz, barite, sometimes magnetite, siderite, chlorite, and other minerals. Quite common in later reduction to magnetite. The reverse, however, may be observed at other places, i.e., the transformation of magnetite into hematite (the process of martitisation). These phenomena are evidently connected with changes in

the oxidation-reduction potential after the deposition of the minerals from hydrothermal solutions.

3. As *a sublimation product*, usually in small amounts, in crystals and crusts on the walls of craters and in cracks in lavas. Thus, in 1871 a body of hematite about 1 m thick was deposited within 10 days in a fissure on Mount Vesuvius. Most probably it is a decomposition product of iron chloride sublimates.

4. In *the crust of weathering* in hot and arid climate hematite and hydrohematite are formed as a result of dehydration of earlier iron hydroxides. This irreversible process is easily demonstrated artificially by gradually dehydrating goethite. The two minerals are fairly often associated with aluminium hydroxides—diaspore and boehmite (in ferruginous bright-red bauxites).

Also known are reniform hematite-hydrohematite formations with concentrical conchoidal structure and hackly fracture (kidney ore). Some of the concentrical zones are composed of radial-fibrous masses of hematite or hydrohematite, sometimes goethite. The conditions of their formation still remain obscure. They may be the products of dehydration of limonite of similar shape.

It should be noted in conclusion that in a hot climate in the upper zones of magnetite deposits extensive martitisation is often observed, i.e., oxidation of magnetite masses into hematite according to the reaction:

$$4Fe_3^{\text{II}}O + {}^{\text{V}}O = 6Fe_2O_3$$

5. In the course of *regional metamorphism* at high temperatures and pressures large masses of hematite are often formed in sedimentary deposits of limonite through the dehydration of the latter. Such is the origin, for instance, of oölitic red iron ores, specularite-bearing schists, and ferruginous quartzites in which bands of quartzite alternate with those of scaly compact hematite. Such quartzites may enclose huge bodies of massive hematite-magnetite ores.

As a higher oxide of iron, hematite is chemically inert in the oxidised zone. Occasionally, however, hematite masses are subject to mechanical weathering (disaggregation). Crystalline hematite varieties are converted into hydroxides extremely rarely, under very specific conditions and on a most limited scale.

The largest deposits of high-grade hematite-magnetite ores in the U.S.S.R. are at *Krivoi Rog* in Pre-Cambrian ferruginous quartzites that are a product of regional metamorphism of originally sedimentary ferruginous deposits repeatedly and steeply folded. An example of hydrothermal formations is the deposit at *Kutim* where the ores occur in Paleozoic dolomites and consist of crystalline masses of coarsely tabular hematite, in places altered to magnetite. Beds of oölitic red iron ores are widespread on the western slope of the Middle Urals—in the *Kusye-Alexandrovsk* and *Pashyisk* districts.

Notable foreign deposits of hematite are those of *Lake Superior* in the U.S.A. where they are found in Pre-Cambrian metamorphosed series and at *Minas Geraes*, Brazil. Highly interesting mineralogically is a contact-pneumatolytic deposit on the island of *Elbe*. Excellent iron glance crystals from this locality are exhibited in many mineralogical museums.

Uses. Hematite ores are a most important ore smelted for iron and steel. The iron content of massive hematite ores usually varies from 50 to 65 per cent. Pure varieties of pulverulent hematite are used as pigments and in the manufacture of red pencils.

ILMENITE, $FeTiO_3$ or $FeO \cdot TiO_2$. Named after the Ilmen mountains, Southern Urals, where it was first discovered. Synonym: titanic iron ore.

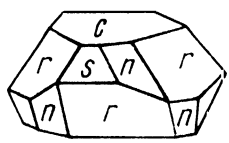


Fig. 149. Ilmenite crystal c {0001}, n {$22\bar{4}3$}, r {$10\bar{1}1$}, s {$02\bar{2}1$}.

Chemical composition. Fe 36.8%, Ti 31.6%, O 31.6%. May contain isomorphous admixture of Mg, sometimes in large amounts (picroilmenite), occasionally Mn (up to a few per cent). Forms continuous isomorphous $FeTiO_3 - MgTiO_3$ and, probably $FeTiO_3 - MnTiO_3$, series.

System, trigonal; symmetry, rhombohedral L_3^6C. Space group $R\bar{3}(C_{3i}^2)$. $a_0 = 5.083$; $c_0 = 14.04$. **Crystal structure** is analogous to that of corundum with the difference that the sites of Al are alternately occupied by Fe^{2+} and Ti^{4+}. Such replacement by different ions results in lowering the symmetry of the crystal lattice. **Habit**, thick tabular (Fig. 149), rhombohedral, sometimes lamellar. The most common forms are pinacoid {0001}, rhombohedrons {$10\bar{1}1$}, {$02\bar{2}1$}, {$22\bar{4}3$}, etc. Twins are on rhombohedron {$10\bar{1}1$}. Commonly occurs as irregular impregnated grains, rarely granular massive. Under the microscope ilmenite, in the form of platy segregations is found in some hematite varieties, as a product of disintegration of solid solutions. Much more often, however, it is found in the so-called titanomagnetites, occasionally in titanious augites, and in other minerals, also as a product of disintegration of solid solutions.

Colour, iron to steel grey. **Streak**, generally black, sometimes dark brown to brownish red (for varieties containing hematite inclusions). **Lustre**, submetallic. Opaque.

Hardness, 5 to 6. **Cleavage**, on rhombohedron {$10\bar{1}1$} very imperfect. **Specific gravity**, 4.72. Slightly magnetic.

Diagnostic features. Resembles hematite. In crystals identifiable by crystal form (there are only rhombohedrons, no hexagonal dipyramid-

al faces). Massive ilmenite is distinguishable from hematite by streak and weakly magnetic character.

Infusible in the blowpipe flame. In the reducing flame becomes definitely magnetic. In powdered form dissolves with difficulty in concentrated hydrochloric acid with separation of titanium oxide. When boiled with tin after fusion with $KHSO_4$, imparts a bluish-violet coloration to the solution, which when diluted with water turns pink (titanium reaction).

Genesis. Occurs as impregnations in basic igneous rocks (gabbros, diabases, pyroxenites, etc.), often associated with magnetite, and also in alkaline rocks. Occasionally occurs in quantity in certain pegmatites (syenitic), in paragenesis with feldspars, biotite, ilmenorutile, etc.

In hydrothermally altered igneous rocks, usually decomposes into the so-called leucoxene. Cases are known of ilmenite decomposing into a mechanical hematite-rutile mixture with the external crystal shape of ilmenite being preserved.

In the U.S.S.R., some rather large crystals of ilmenite are found ingrown in pegmatites in the *Ilmen Mountains* near Miass, Southern Urals, among nepheline-syenites. Widespread as inclusions in titanomagnetites in many deposits.

Important foreign localities are *Ekersund-Zoggendhal* (Norway), where ilmenite occurs in veins in norites (basic igneous rock), and *Kragerö*, from which crystals weighing up to 6 and even 7 kg, have been recorded, and elsewhere.

Uses. In large accumulations ilmenite is a source of titanium ore, used in the form of TiO_2 as white pigment (titanium white with high covering power), in iron alloys, ferrotitanium, with 10 to 15 per cent of Ti, in some special steels, etc.

Its heat and corrosion resistance, welding capacity, and low specific gravity make metallic titanium an important material of the aircraft industry.

5. BRAUNITE GROUP

This group includes oxides of Mn, which may contain Fe and differ materially from the corundum minerals in crystal structure.

BRAUNITE, $Mn{\cdot\cdot}Mn{\cdot\cdot\cdot\cdot}O_3$. The formula is often abridged to Mn_2O_3.

Chemical composition. MnO 44.8%, MnO_2 55.2%. Often contains up to 8 per cent silica and an excess of manganese oxide against the formula. In addition, braunite often contains iron, sometimes up to 10 per cent. The presence of B and Ba is also detected spectroscopically. The presence of the latter element may be explained by the fact that barite is a common accessory of braunite.

System, tetragonal; symmetry, ditetragonal dipyramidal L^44L^25PC. Space group $14acd$ (D_{4h}^{20}). $a_0 = 13.44$; $c_0 = 18.93$. Structure still ob-

scure. Crystals have octahedral habit (Fig. 150); the tetragonal dipyramid, approaching the octahedron at the corners, sometimes occurs in combination with prismatic and pinacoidal faces. More often found in granular aggregates.

Colour, black. **Streak**, brownish black. **Lustre**, submetallic. Opaque. **Hardness**, 6. **Cleavage**, {111} distinct. **Specific gravity**, 4.7 to 5.0. Nonmagnetic.

Diagnostic features. Similar to many black manganese minerals. High hardness and brownish-black streak are characteristic features, but positive identification is possible only in polished sections under the microscope and by X-ray analysis.

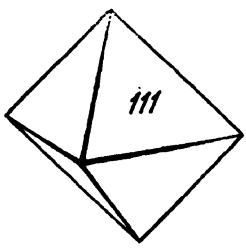


Fig. 150. Braunite crystal.

Infusible in the blowpipe flame. With borax gives the Mn reaction. Dissolves with difficulty in hydrochloric acid, evolving chlorine and leaving a residue of gelatinous silica. In nitric acid decomposes into MnO and MnO_2.

Genesis and occurrence. Is formed under reducing conditions, but remains stable within a certain range of the oxidation-reduction potential. In more strongly reducing conditions is replaced by hausmannite, Mn_3O_4. Occurs in some *contact-metasomatic* deposits, and also in *hydrothermal* veins in association with various manganese and iron minerals, barite, quartz, etc. Large masses occur in *regionally-metamorphosed* sedimentary manganese deposits.

In the oxidation zone, braunite is unstable: gradually oxidising to the highest Mn valency, is converted to psilomelane, and then to pyrolusite, MnO_2, which is more stable in the presence of oxygen.

In the U.S.S.R., large masses occur in a number of metamorphosed sedimentary deposits of Central Kazakhstan: at *Jezdy*, Karsakpai district; in this locality it has also been observed as massive granular aggregates in small hydrothermal veins; at *Karajal*, Atasuy district, etc. At *Sapal*, in the Urals, there is a hydrothermal deposit in limestones, where braunite is associated with hausmannite, hematite, magnetite, jacobsite, and sulphides of Fe, Pb, etc.

Outside the Soviet Union, large metamorphosed deposits of braunite are known in India, Brazil, and South Africa (Postmasburg) and elsewhere.

Uses. Braunite ores are an important ore of manganese which go to make ferromanganese, a flux used in steel smelting. Manganese-poor ores are added to blast furnace charges.

6. SPINEL GROUP

The spinel minerals of the $RO \cdot R_2O_3$ type should be regarded, according to X-ray data, as binary oxides, not as salts of oxygen acids, i.e., not as aluminates, ferrates, etc. The group abounds in isomorphous

mixtures. The trivalent metals substituting for each other are Fe^{3+}, Al^{3+}, Cr^{3+}, and Mn^{3+}; the divalent metals are mainly Mg^{2+}, Fe^{2+}, sometimes Zn^{2+}, Mn^{2+}; and occasionally, in smaller quantities Ni^{2+} and Co^{2+}. Characteristically, the divalent ions of Pb, Sr, Ca, and Ba with longer radii and also the univalent ions Na and K never enter into the composition of the minerals of this group. Depending on the combination of the elements listed above there are distinguished many mineral species which have much in common in crystal forms, physical features,

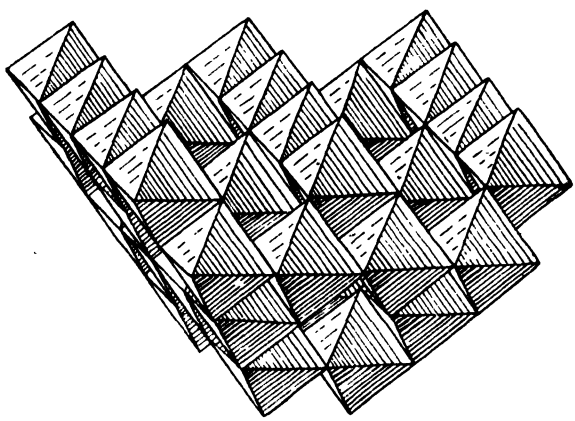


Fig. 151. Crystal structure of spinel.
Basic pattern of octahedra with vertical fourfold axis arrangement.

and conditions of formation (mostly developing at high temperatures and pressures).

The vast majority of these minerals crystallise in the cubic system forming crystals of octahedral habit which persists even in those that crystallise in the tetragonal system. Apart from these stands chrysoberyl, a compound of analogous chemical formula. The ionic radius of Be^{2+} is so small that the compound has an entirely different structure, and crystallises in the orthorhombic system.

The crystal structure of the spinel minerals is rather complex. The oxygen ions are closely packed on the planes parallel to the octahedral faces. The divalent cations (Mg^{2+}, Fe^{2+}, etc.) are surrounded by four tetrahedrally located oxygen ions, whereas the trivalent cations (Al^{3+}, Fe^{3+}, Cr^{3+}, etc.) are surrounded by six oxygen ions occupying the octahedral apexes. Each oxygen ion is bonded to one divalent and three trivalent cations. Figure 151 shows the basic structure of spinel, Al_2O_4, in which the unit octahedra are spaced round a vertical fourfold axis. All the vacant columns of the structure are occupied by bands of MgO_4 tetrahedra.

Thus the structure is characterised by the combination of isometric "structural units" – tetrahedra and octahedra, each apex being shared by a tetrahedron and three octahedrons.

These structural features explain very well such properties of the minerals as optical isotropy, the absence of cleavage, chemical and thermal stability of compounds, high hardness, etc.

SPINEL, $MgAl_2O_4$. The origin of the name is unknown. Transparent beautifully coloured varieties (red, pink, green, blue, violet, etc.) are known as gem spinels.

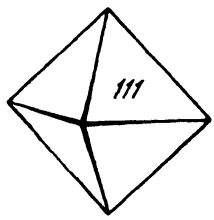


Fig. 152. Crystal of spinel. The common form for all spinellids.

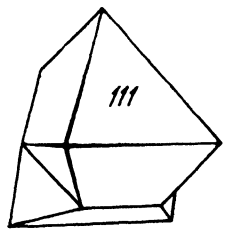


Fig. 153. Twin according to spinel law.

Chemical composition. MgO 28.2%, Al_2O_3 71.8%. Impurities: Fe_2O_3, which imparts a bottle-green colour (chlorospinel); FeO together with Fe_2O_3, which colours spinel brown or black; sometimes ZnO, MnO, and Cr_2O_3.

System, cubic; symmetry, hexoctahedral $3L^44L_6^36L^29PC$. Space group $Fd3m(O_h^7)$. $a_0 = 8.86$. Crystal structure is typical and has been described above. **Habit.** Mostly occurs as intergrown octahedral crystals (Fig. 152), usually small, but sometimes as large as 25 cm across. Twins parallel to (111)—planes of the closest packing of oxygen ions. Hence the term "spinel law twinning" (Fig. 153).

Colour. Colourless varieties are rare. Spinel most often has different colouring. **Lustre**, vitreous. Optically isotropic. $n = 1.718$ to 1.75.

Hardness, 8. The presence of Fe_2O_3 and Cr_2O_3 lowers it to 7.5. to 7. **Cleavage**, {111} indistinct. **Specific gravity**, 3.5 to 3.7 (the lowest for the group). Melting point 2150°.

Diagnostic features. The most characteristic features are the octahedral habit and high hardness. Under the microscope in polarised light, powdered isotropic spinel is easily distinguished from birefringent varieties of corundum similar to spinel in colour and shape. Differs from the other minerals of the spinel group by having the lowest specific gravity.

Infusible in the blowpipe flame. Insoluble in acids.

Genesis and occurrence. Spinels occur most frequently in *contact-metasomatic* formations in dolomites and magnesial limestones as the product of the action on the latter of the pneumatolytic agents of the magma at high temperatures. Minerals of the same origin are found in paragenetic association with spinels, viz., garnets, pyroxenes, chlorine-bearing silicates, etc.

Spinel occurs occasionally in *pegmatites* and *magmatic* rocks. Some finds have been recorded from strongly metamorphosed rocks, such as gneisses and schists.

At the earth's surface, spinel is perfectly stable and is therefore often found in placers.

In the Soviet Union, individual emerald-green spinel specimens were found in placers in the *Kamenka River* valley, in Kochkar district. In this case, spinel, along with some other gemstones, is evidently the product of weathering of local pegmatites. Blue and violet spinels have been found near *Baikal Lake*, and red varieties in the *Shungan* mines in Ferghana (near the Afghan border). Huge deposits of red gem spinel exist on *Ceylon* and *Kalimantan* (Borneo) where it is found in gold placers, and also in Burma, Thailand, Afghanistan, and elsewhere.

Uses. Only perfectly transparent flawless crystals are used as gemstones. Spinel is usually mined along with gold or other gemstones (ruby). The ruby mines of Mogon (Northern Burma) annually yielded 10,000 carats of gem spinel, mined together with rubies (50,000 carats). No large accumulations in primary rocks are known.

MAGNETITE, $FeFe_2O_4$. The origin of the name is vague. Thought to be derived from the locality Magnesia, (in Macedonia) or from the name of a shepherd Magnes who by ancient tradition discovered the magnetic stone when the iron ferrule of his stick and the nails of his shoes stuck to it. Synonyms: magnetic iron ore, lodestone.

Chemical composition. FeO 31%, Fe_2O_3 69%. Fe content 72.4%. Usually rather pure. Varieties are *titanomagnetite* containing TiO_2 (up to a few per cent) which at high temperatures enters into the composition of the mineral as a solid solution, and *chromomagnetite* containing Cr_2O_3 (up to a few per cent). Occasionally varieties rich in MgO (up to 10 per cent), Al_2O_3 (15 per cent), etc., are found. Mention also should be made of a rather rare ferromagnetic iron oxide, γ-Fe_2O_3, crystallising in the cubic system, and known as maghemite (combination of the words magnetite and hematite).

System, cubic; symmetry, hexoctahedral. $a_0 = 8.374$. **Crystal structure** analogous to that of spinel.

Habit. Often octahedral, more rarely rhombic-dodecahedral crystals (Fig. 154). Faces {110} often striated parallel to the longer rhombic diagonal. Minute dendrites are observed in basalt glass under the microscope. Twins along (111). **Aggregates.** Mostly massive granular or impregnating igneous, predominantly basic, rocks. Occurs as crystal druses in cavities.

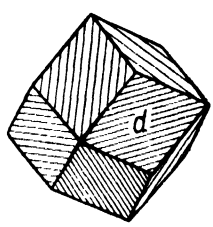


Fig. 154. Magnetite crystal *q* {110}.

Colour, iron black, sometimes crystals show a blue tarnish. **Streak**, black. **Lustre**, submetallic. Opaque.

Hardness, 5.5 to 6. Brittle. **Cleavage**, none. Sometimes parting on {111} is observed. **Specific gravity**, 4.9 to 5.2. **Other properties.** Strongly magnetic, sometimes showing polarity. At red heat (at about 580°) magnetism disappears abruptly, and reappears on cooling.

Diagnostic features. Strong magnetic character and black streak usually readily distinguish it from externally similar minerals (hemat-

ite, goethite, hausmannite, chromite, etc.), but sometimes it cannot be distinguished from other, rarer minerals species of the spinel group, rich in ferric and ferrous oxides: ferrochromite, jacobsite, etc.

Infusible in the blowpipe flame. In the reducing flame first alters to maghemite (γ-Fe_2O_3) and then to hematite, becoming nonmagnetic. With borax and salt of phosphorus gives the iron reaction (bottle-green bead). Powdered magnetite is soluble in hydrochloric acid.

Genesis and occurrence. Magnetite is formed under more strongly reducing conditions than hematite and occurs in ore deposits and rocks of most divers e genetic types.

1. In *magmatic* rocks it is usually observed as an impregnation. Magmatic deposits of titanomagnetite in the form of irregular masses and veins are frequently associated genetically with basic rocks (gabbro).

2. In negligible amounts occurs in many *pegmatites* in paragenetic association with biotite, sphene, apatite, and other minerals.

3. In *contact-metasomatic* formations it is often an important component and is accompanied by garnets, pyroxenes, chlorites, sulphides, calcite, and other minerals. Large deposits have been found at the contact of limestones with granites and syenites.

4. As an accessory mineral, magnetite occurs in *hydrothermal* deposits, mostly in association with sulphides (pyrrhotite, pyrite, chalcopyrite, etc.). Comparatively rarely it forms deposits in its own right in association with sulphides, apatites, and other minerals. The largest deposits of this type in the Soviet Union are located in the Angara-Ilim region in Siberia.

5. *Exogenous* formation of magnetite could have taken place only under exceptional conditions. The presence of magnetite grains in recent marine silts is believed to be due not only to denudation of dry land but also to new in-situ formations from iron hydroxides under the reducing influence of decaying organic matter.

6. In course of *regional metamorphism*, magnetite, as well as hematite, is formed through the dehydration of iron hydroxides (formed in sedimentary rocks exogenously) only under reducing conditions (oxygen deficiency). Of this type are the numerous large beds of hematite-magnetite ores occurring in metamorphosed sedimentary strata.

In the oxidised zone, magnetite is rather stable. On physical weathering of rocks it is freed of the accessory minerals and tends to concentrate in placers. Magnetite is the principal constituent in the black sand residue of panning of gold-bearing sand and gravel.

In conditions of weathering magnetite is highly resistant to hydration, i.e., to conversion into iron hydroxides. The process is observed but rarely and on a comparatively small scale.

The phenomenon of martitisation (formation of pseudomorphs of hematite after magnetite) is observed in hot climatic zones. Some local martitisation of magnetite is also observed in hydrothermal and meta-

morphosed deposits where it is entirely independent of exogenous processes.

We shall mention but a few of the many magnetite deposits in the Soviet Union.

1. An example of magnetic deposits is the *Kusinskoye* titanomagnetite deposit, enriched with vanadium. The deposit (18 km north of Zlatoust in the Urals) comprises veins of solid ore in altered parent igneous rocks of the gabbro formation. Magnetite is closely associated here with ilmenite and chlorite.

2. An example of metasomatic deposits is the well-known *Mount Magnitnaya* (Southern Urals) where thick bodies of magnetite occur in garnet, pyroxene-garnet, and other skarns formed through the action of granitic magma emanations on limestones. In some portions of the ore bodies, magnetite is associated with primary hematite. The ores beneath the oxidised zone contain disseminated sulphides (pyrite, occasionally chalcopyrite, galena, etc.).

Of the same type are the deposits of *Mount Vysokaya* (near Nizhny Tagil), *Mount Blagodat* (Kuvshino district), a cluster of deposits in the Kustanai Region, and also *Dashkesan* in Azerbaijan, etc.

3. The great deposit at *Krivoi Rog*, the Ukraine, belongs to the *regional-metamorphosed* sedimentary type. Besides typical beds, the ferruginous quartzite series contains massive columnar iron ore bodies of a lenticular cross section persisting to very great depth.

Of similar origin are the deposits of the so-called *Kursk magnetic anomaly* (south-east of the city of Kursk); the magnetite-hematite ores in Central Kazakhstan, etc.

Notable foreign localities are *Kirunavaara* and *Luossavaara* (Sweden), where the ores occur in thick vein-like bodies in metamorphosed strata where the magnetite is associated with apatite. Well-known are the great magnetite-hematite deposits in the *Lake Superior* district, (U.S.A.) in very ancient metamorphosed schists, in Labrador (Newfoundland), and elsewhere.

Uses. Magnetite ores often containing up to 60 per cent Fe are a most important raw material for smelting of iron. Undesirable impurities are phosphorus (maximum permissible content for the Bessemer process is 0.05 per cent, and only 0.03 per cent for high-grade steels) and sulphur (maximum content 1.5 per cent). In the Thomas process, in which the phosphorus is removed with the slag, its content should not be below 0.61 per cent and not over 1.5 per cent. The phosphorus slag from this process is used as a fertiliser.

The slag obtained in smelting titanomagnetite ores is a source of vanadium which is a valuable alloying metal for high-grade steels. Vanadium pentoxide is used in the chemical industry as a pigment in ceramics and in other applications.

CHROME-SPINELLIDS with the common formula (Mg, Fe) (Cr, Al, $Fe)_2O_4$. All the mineral species classified under this heading occur in the

same conditions and are so similar in external features that species of different composition cannot be distinguished without chemical analyses. In the prospecting and mining practice they are known under the general name of *chromites*. According to composition the following principal mineral species are recognized: *chromite* proper, ($FeCr_2O_4$) (occurring in meteorites, and very rarely in the earth's crust); magnochromite, (Mg, Fe)Cr_2O_4; alumochromite, Fe(Cr,Al)$_2O_4$; and chromopicotite, (Mg,Fe)(Cr,Al)$_2O_4$. Chromite was first mentioned by Academician Lovits as early as 1797.

Chemical composition. For the most common chrome-spinellids, the Cr_2O_3 content varies within a wide range – from 18 to 62%; that of FeO from 0 to 18%; MgO from 6 to 16%; Al_2O_3 from 0 to 33%; Fe_2O_3 from 2 to 30%. Moreover, there may be isomorphous impurities such as TiO_2, up to 2 per cent; V_2O_3, up to 0.2 per cent; MnO, up to 1 per cent; ZnO, up to a few per cent; NiO, up to tenths, and CoO, up to hundredths of one per cent.

System, cubic; symmetry, hexoctahedral $3L^44L_6^36L^29PC$. a_0 = = 8.305. **Crystal structure** analogous to that of spinel. **Habit.** Occasionally small octahedral crystals, but usually rounded or somewhat irregular grains, or massive granular aggregates.

Colour, black. In polished sections, semi-transparent or deep red to brown-red when viewed in transmitted light. Only varieties rich in FeO and Fe_2O_3 are absolutely opaque. **Streak**, brown. **Lustre**, submetallic. n = 2.07 to 2.16.

Hardness, 5.5 to 7.5. **Cleavage**, none. **Specific gravity**, 4.0 to 4.8. **Other properties.** FeO- and Fe_2O_3-bearing chrome-spinellids show weak magnetism, while varieties rich in these components and poor in Cr_2O_3 are strongly magnetic.

Diagnostic features. The common distinguishing features of the chrome-spinellids are black colour, brown streak, high hardness, and chrome reaction. The minerals occur so constantly in ultrabasic rocks (dunites, peridotites, and serpentinites) that in the field these features alone are sufficient for almost positive identification.

Infusible in the blowpipe flame. The borax or phosphate bead is emerald-green when cold (chrome reaction). Insoluble in acids.

Genesis and occurrence. Almost exclusively confined to *magmatic* ultrabasic rocks both as impregnations and as massive accumulations mostly of irregular pocket-like, lenticular, and columnar shapes. Constantly associated with chrome-spinellids are greenish serpentine (hydrosilicate of Mg and Fe), olivine, (Mg, Fe)$_2SiO_4$, chromium-bearing chlorites, sometimes chromous emerald-green garnets, etc. In some ultrabasic rock masses, chrome-spinellids may be paragenetically associated with platinum and osmiridium minerals.

In the weathering zone the chrome-spinellids are chemically inert. Only in hot climate they are subject to oxidation and decomposition.

In the Soviet Union, most of chrome-spinellid ore deposits are confined to the Ural Mountains. Among them are the deposits of high-

grade chromite ores on the eastern slope of the southernmost part of the Urals ridge known as the *Donskoye* or *Kempirsaiskoye* (Aktyubinsk Region). Another important locality is *Saransk* in the Northern Urals (6 km from Biser Station) comprised of steep vein-like bodies of massive chromite ores of a rather poor grade (high iron content). Smaller deposits are found in Transcaucasia: at *Shorjin*, *Geydarin*, and elsewhere (on the eastern shore of Lake Sevan and south-east of it in Armenia).

Important foreign localities are in *Rhodesia* (South-East Africa), *New Caledonia*, *Turkey*, *Cuba*, and elsewhere.

Uses. Chromite ores are the only source of chrome which is of great value as an alloy metal for making special steels. Moreover, it is extensively used as a coating for protecting various metal articles and machine parts from corrosion. Chromite ores are also used as a material for making stable paints, tanning agents, and certain chemicals (potassium dichromates, etc.). Massive low-grade ores poor in Cr_2O_3 and rich in FeO and Fe_2O_3 go into refractory brick.

HAUSMANNITE, $MnMn_2O_4$. **Chemical composition.** MnO 62.0%, MnO_2 38.0% (Mn 72.0%). Also contains FeO and Fe_2O_3.

System, tetragonal; symmetry, ditetragonal dipyramidal L^44L^25PC. Space group $14amd(D_{4h}^{19})$. $a_0 = 5.75$; $c_0 = 9.42$. **Crystal structure**, the same as that of spinel, though the mineral crystallises in the tetragonal system. Usually massive granular. Crystals occur only in cavities. **Habit** close to octahedral (Fig. 155). Its angle (001) : (011) = 58°57′, while for a regular octahedron it would be 54°44′8″. Often twinned on (112). Very characteristic are polysynthetic twins seen in polished sections with crossed nicols in reflected light.

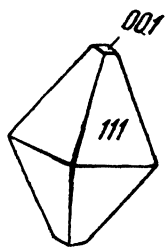


Fig. 155. Hausmannite crystal.

Colour, black. **Streak**, brown to reddish brown. **Lustre** of unoxidised crystals strongly adamantine or submetallic.

Hardness, 5. Brittle. **Cleavage**, {001} perfect. **Specific gravity**, 4.7 to 4.9. Nonmagnetic.

Diagnostic features. In granular aggregates is distinguished with difficulty from other manganese minerals without the aid of the microscope. Differs from braunite by lower hardness and obviously reddish streak. Pyrolusite, MnO_2, has a black streak. The psilomelane minerals have either a black or chocolate-brown streak. Differs from hematite in hardness and structure of aggregates.

Infusible in the blowpipe flame. Borax bead turns violet in the oxidising flame. Dissolves in hydrochloric acid with evolution of chlorine.

Genesis and occurrence. Like magnetite, hausmannite is formed in a more strongly reducing environment than braunite. Like braunite, with which it is often associated, it occurs in certain *contact-metasomatic* and *hydrothermal* manganese deposits. Minerals rich in manganous oxide, MnO, such as tephroite, Mn_2SiO_4, manganosite, MnO, rhodochrosite, $MnCO_3$, manganous garnets, etc., are usually observed in close

association with hausmannite. The most frequent non-metalliferous associate is barite, not quartz, the latter being the common associate of braunite and manganese silicates (rhodonite and bustamite).

In large masses hausmannite together with braunite, jacobsite, magnetite, and other anhydrous oxides of Mn and Fe, is widespread in metamorphosed sedimentary manganese deposits. In conditions of weak regional metamorphism, hausmannite derives from the dehydration of manganese hydroxides and also through reduction from pyrolusite and braunite. Hausmannite pseudomorphs after braunite have been observed.

In the Soviet Union, hausmannite is one of the main ore minerals in the *Sapalskoye* hydrothermal deposit in marbled limestones (Nizhny Tagil). Besides hausmannite, the ores contain braunite, magnetite (probably manganous), hematite, rhodochrosite, iron sulphides, ferruginous chlorites, and other minerals. In Central Kazakhstan, hausmannite occurs in association with braunite in the ores of the *Karajal* metamorphosed sedimentary deposit.

Outside the Soviet Union hausmannite occurs in approximately the same paragenetic associations in contact-pneumatolytic deposits at *Nordmark* and *Langban* (Sweden), in vein deposits at *Ilefeld* near Hartz (Germany), and elsewhere.

Uses. Hausmannite ores, as well as those of braunite, are used for making ferromanganese or as an addition to blast-furnace charges (low manganese—ores).

GAHNITE, $ZnAl_2O_4$. Chemical composition ZnO 44.3%, Al_2O_3 55.7%. Impurities: MgO, FeO, MnO, and Fe_2O_3.

System, cubic; symmetry hexoctahedral. $a_0 = 8.062$. **Habit**, the same as that of spinel. Also occurs in rhombic dodecahedrons and distorted cubes. Sometimes individual crystals attain large dimensions. Twinning according to the spinel law, on (111).

Colour, dark-green, greyish-green to black-green. **Streak**, grey. Translucent. **Lustre**, vitreous. $n = 1.78$ to 1.82.

Hardness, 7.5 to 8. Brittle. **Cleavage**, {111} indistinct. **Specific gravity**, 4.0 to 4.6. Resembles many other spinel minerals.

Diagnostic features. Gahnite may be tentatively distinguished from other spinels by higher specific gravity, refractive index, and paragenetic association with zinc minerals, but positive identification is possible only by blowpipe and chemical analysis.

Infusible in the blowpipe flame. With soda on charcoal yields a ZnO coating. Insoluble in acids and alkalis.

Genesis and occurrence. Occurs comparatively seldom in certain pegmatites and contact-metasomatic deposits in marbled limestones together with other minerals of the same origin, including zinc minerals.

Occasional finds are recorded from strongly altered rocks, such as talc schists.

In the Soviet Union gahnite is found at Altyn-Tau (north-western part of the Kara-Kalpak Autonomous Republic), in the Ukraine, in pegmatites on the western shore of the Sea of Azov, etc.

It is found in commercial quantity in the well-known *Franklin* deposit in New Jersey (U.S.A.) noted for the unusual association of manganese and zinc minerals. There gahnite is associated with zincite, franklinite, and other minerals. It was found also in the talc schists of Falun (Sweden) and in the diamond placers of Brazil.

FRANKLINITE, $(Zn,Mn)Fe_2O_4$. System, cubic; occasionally contains FeO and Mn_2O_3. In many physical properties resembles magnetite. Opaque. Streak reddish-brown. Slightly magnetic. Specific gravity, 5.07 to 5.22. $n = 2.36$. Infusible. With borax in the oxidising flame yields a reddish-violet bead (manganese reaction). On charcoal with soda produces a ZnO coating. Soluble in hydrochloric acid. If Mn_2O_3 is present, chlorine is evolved from the solution.

Forms thick beds in the well-known contact-metasomatic (?) deposit at Franklin, New Jersey (U.S.A.). Associated with it in crystalline limestones are zincite, willemite (Zn_2SiO_4), calcite, less often gahnite, axinite, manganese silicates, apatite, and other minerals.

CHRYSOBERYL, $BeAl_2O_4$. *Chrysos* is the Greek for gold. Varieties: the emerald-green gemstone *alexandrite* (violet-red when viewed under incandescent light).

Chemical composition. BeO 19.8%, Al_2O_3 80.2%. Always contains impurities: Fe_2O_3(3.5 to 6%), sometimes TiO_2 (up to 3%) and Cr_2O_3 (up to 0.4%) responsible for the emerald-green colour.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group *Pmnb*. $a_0 = 5.47$; $b_0 = 9.39$; $c_0 = 4.42$. **Crystal structure.** Already Y.S. Fyodorov, when he was developing his system of classification of crystals according to external form, established that structurally chrysoberyl should be similar to the minerals of the olivine group. X-ray investigations have fully corroborated his conclusion that the arrangement of ions in the chrysoberyl unit cell is perfectly analogous to that in the unit cell of forsterite (Mg_2SiO_4). The oxygen ions actually occupy positions of closest hexagonal packing; the beryllium ions, just as the ions of silicon in forsterite, are surrounded by four oxygen ions, while the aluminium ions are surrounded by six. **Habit**, tabular, sometimes short- or long-prismatic. The closest almost hexagonal packing of the basic oxygen ions results in a pseudohexagonal ratio between the *a* and *b* axes; hence, the frequent pseudohexagonal habit of the crystals (Fig. 156) both with regard to angles and faces. This is especially marked (Fig. 157) in (030) trillings characteristic of alexandrite. The (001) faces are often striated parallel to the *a* axis, which is a sure sign of the trilling intergrowth (Fig. 157). Chrysoberyl has not been observed in granular masses.

Colour, usually yellow or greenish-yellow, rarely colourless. Only the chrome-bearing variety (alexandrite) is emerald-green (violet-red in incandescent light). **Lustre**, vitreous, greasy on fracture. $n_x = 1.753$, $n_y = 1.747$, and $n_z = 1.744$.

Hardness, 8.5. Brittle. **Cleavage**, distinct parallel to (110) and indistinct parallel to (010), (001). Fracture conchoidal. **Specific gravity**, 3.50 to 3.84.

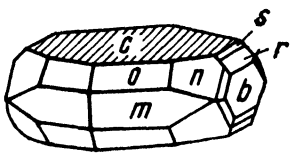


Fig. 156. Pseudohexagonal crystal of chrysoberyl: *c* {001}, *o* {111}, *m* {110}, *b* {010}, *n* {121}, *s* {021}, *r* {031}.

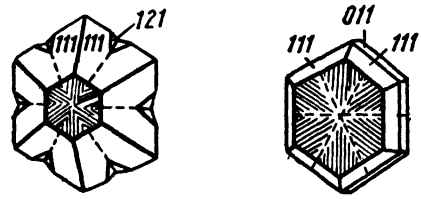


Fig. 157. Penetration trillings parallel to (130), with striations on {001} faces.

Diagnostic features. Occurs exclusively in crystals of very characteristic shape, sharply differing from that of beryl, high hardness, and specific colour.

Infusible in the blowpipe flame. Insoluble in acids. Decomposes only when fluxed in powdered form with KOH or $KHSO_4$. On ignition the melt moistened with cobalt nitrate shows a specific blue colouring.

Genesis and occurrence. This rather rare mineral occurs usually in *pegmatites* and *contact-pneumatolytic* formations at the boundary between schists and granite intrusives. In the oxidised zone it is very stable. Occurs in placers, sometimes as rounded pebbles. Some alexandrite crystals are several centimeters across.

The most remarkable group ever found comprising 22 large crystals and small trillings of alexandrite is on view at the Mineralogical Museum of the U.S.S.R. Academy of Sciences. Chrysoberyl is commonly associated with emerald, feldspars, apatite, and other minerals of mica, chlorite, and talc schists, usually at the contacts of granite pegmatites.

Notable foreign deposits are at *Minas Geraes* (Brazil) where chrysoberyl, associated with topaz, rock crystal, spinel, garnet, tourmaline, and other minerals, occurs in pegmatite veins in gneisses and mica schists; and also in placers on *Ceylon* and *Madagascar*.

Uses. Beautifully coloured transparent varieties are used as gemstones.

7. RUTILE GROUP

This group comprises compounds of the AX_2-type crystallising in the tetragonal system: binary oxides of Ti, Sn, Mn, and Pb. Of these, TiO_2 occurs in three different polymorphous modifications which have

special names, and MnO_2 at least in two. There is some evidence that SnO_2 too is dimorphous.

The principal members of the group are not associated paragenetically, and are formed under different conditions. Although occurring under conditions similar to those under which TiO_2 is formed, SnO_2 behaves in the geological processes quite differently. MnO_2 and PbO_2 are formed under entirely different conditions, almost exclusively in the course of exogenous processes of mineral formation.

The notable feature of the chemical composition of rutile (as well as of brookite and anatase) is the presence of Nb^{5+} and Ta^{5+} together with Fe^{2+} as isomorphous impurities.

The chemical formula for such varieties is $Ti_{3-3x}Nb_{2x}Fe_x^{\cdot\cdot}O_6$ which shows that the two Nb^{5+} ions and one Fe^{2+} ion may replace three Ti^{4+} ions, with the total charge of the replaced ions being preserved. Since the length of the radii of all these ions is approximately of the same order (Fig. 142), the crystal structure of the minerals generally follows the same pattern, but its dimensions increase corresponding to the ionic radii of Nb^{5+}, Ta^{5+}, Fe^{2+} (or Mn^{2+}). Thus, these varieties of rutile are isomorphous mixtures of TiO_2, or rather Ti_3O_6 with $Fe^{\cdot\cdot}Nb_2O_6$ or $Fe^{\cdot\cdot}Ta_2O_6$, i.e., with the minerals mossite and tapiolite crystallising in the same rutile structure.

It should be noted that $FeNb_2O_6$ and $FeTa_2O_6$ are dimorphous and crystallise both in the tetragonal and orthorhombic systems. The crystal structure of the orthorhombic modification of columbite and tantalite is also similar to that of the orthorhombic modification of brookite (TiO_2).

RUTILE, TiO_2. From the Latin *rutilus*, meaning reddish. It is the most stable modification of TiO_2, both at high and low temperatures.

Chemical composition. Ti 60%. Chemical analyses show frequent presence of other elements: Fe (as ferrous or ferric oxide), sometimes Sn^{4+} (up to 1.5%), rarely Cr^{3+}, V^{3+}, and some others. A variety rich in $FeTiO_3$ (in the form of solid solution) is called *nigrine*.

System, tetragonal; symmetry, tetragonal dipyramidal L^44L^25PC. Space group $P4/mnm(D_{4h}^{14})$. $a_0 = 4.58$; $c_0 = 2.95$. **Crystal structure** is typical of the entire group (Fig. 158). It has some peculiar features. Whereas in the corundum-type structure the sheets of most closely packed oxygen ions are perpendicular to the threefold axis, and in the spinel-type structure they are parallel to the octahedron faces (i.e., also to the threefold axis), in the rutile-type structure (as has been shown by N.V. Belov) the closest packing directions in the form of columns are parallel to the principal (fourfold) axis of rutile crystals. Each Ti ion is surrounded by six oxygen ions occupying the corners of an almost regular octahedron. In the rutile crystal structure, the octahedra are elongated parallel to the *c* axis in the form of rectilinear columns (Fig. 158*b*); hence the acicular or rod-like habit

of rutile crystals with cleavage planes parallel to the elongation. The rutile structure differs characteristically from other TiO_2 modifications in that each TiO_6 octahedron shares two edges with adjacent octahedra (Fig. 158*b*). Since the columns of closely packed oxygen ions elongated parallel to the rutile fourfold axis are in the main oriented in one of

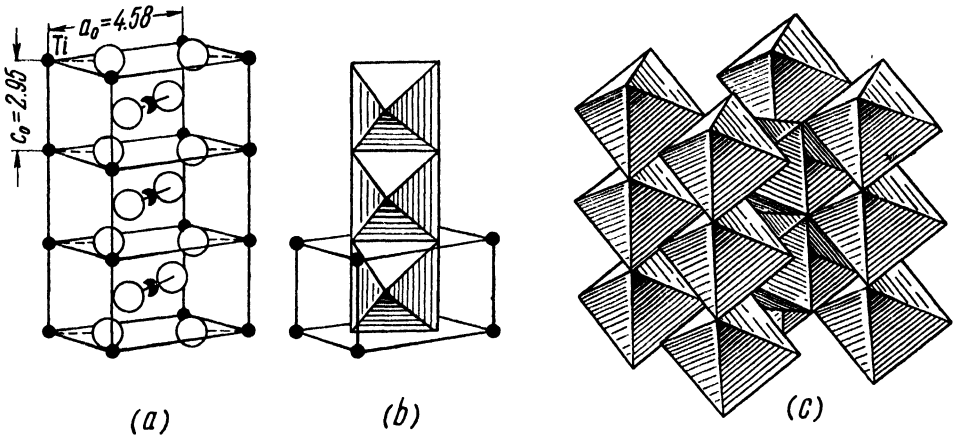


Fig. 158. Crystal structure of rutile.

a – ionic centres: black circles – titanium; white circles – oxygen; three unit cells of rutile are arranged vertically; *b* – TiO_6 octahedra (central column): titanium ions are located inside octahedra; *c* – general view of structure with vertical fourfold axis.

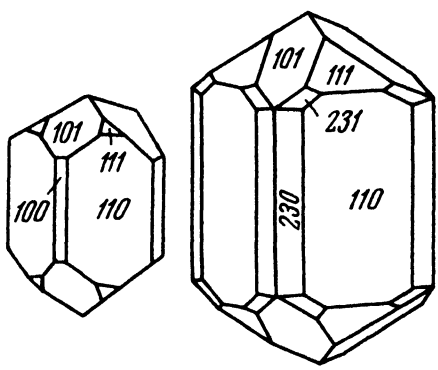


Fig. 159. Rutile crystals.

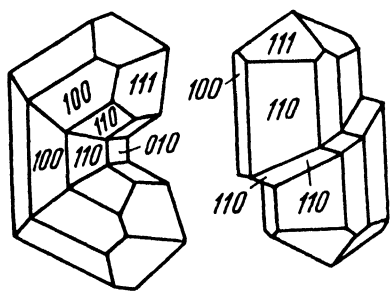


Fig. 160. Rutile twins.

the three possible directions in the plane of the hexagonal closest packing, it is not accidental that the rutile group minerals occur as geniculated penetration twins and trillings (Fig. 160) sometimes at an angle close to 120° (i.e., corresponding to the directions of a hexagonal network). Even ring-shaped sixlings may form in this manner. This is also the cause of ordered (at 120°) growth of extremely thin needles or tiny prismatic crystals of rutile on the basal {0001} pinacoid of hematite (cf. Fig. 148), mica, and other minerals, with faces corresponding to the planes of the closest-packed oxygen ions. **Habit** is very characteristic: prismatic, columnar to acicular. Common forms are {100}, {110}, {101}, {111}, occasionally {001}. Often striated parallel to the princi-

pal *c* axis. Typical crystal forms are shown in Fig. 159. Geniculated twins with a (011) twinning plane are very frequent. Flat reticulated twins of acicular rutile are called sagenite. As has been stated above, ordered intergrowths of tiny crystals of rutile with hematite crystals are common, the fourfold axis of rutile coinciding with a horizontal twofold axis of hematite. Puffs of acicular capillary crystals of rutile are sometimes found occluded in transparent quartz crystals.

Colour, generally dark yellow, brown, red, and black (nigrine). Colourless or faintly coloured varieties are extremely rare. **Streak**, yellow to light-brown. **Lustre**, adamantine to submetallic (black opaque varieties). $n_x = 2.903$; $n_y = 2.616$.

Hardness, 6. Brittle. **Cleavage**, {110} perfect and {100} distinct. **Specific gravity**, 4.2 to 4.3.

Diagnostic features. Tetragonal prismatic crystals and geniculated twins are very characteristic. May be confused with minerals of similar habit: zircon ($ZrSiO_4$) which has a higher hardness (7 to 8), cassiterite (SnO_2) which has a higher specific gravity. Capillary rutile crystals may be mistaken for tourmaline, from which it differs in optical constants.

Infusible and unchangeable in the blowpipe flame. Insoluble in acids, gives the titanium reaction with salt of phosphorous (in the reducing flame yields a violet head).

Genesis and occurrence. In nature rutile is formed under a wide variety of conditions. Occasionally it is a constituent of *igneous rocks* (syenites and less often granites). In small quantities occurs in *pegmatites* and certain *hydrothermal* deposits where it is associated with quartz, minerals of titanium and iron (ilmenite, ilmenorutile, hematite, and magnetite), sometimes with corundum, silicates, and other minerals. Rare finds of neogenesis of rutile have been recorded from the *exogenous* products of decomposition of titanium minerals, occasionally in sedimentary rocks, and in bauxite deposits. Most often, however, rutile is formed in the course of *metamorphic* processes as a result of alteration of titanium minerals, segregating as individual grains in gneisses, mica schists, amphibolites, and other rocks.

Very spectacular are the acicular and capillary crystals in veins of the *Alpine cleft type*, often occluded in rock crystal and hematite crystals; it is often accompanied by brookite and anatase.

In the oxidised zone rutile is chemically inert and therefore often found in placers as rounded grains and pebbles.

In the Soviet Union large crystals of rutile have been found in a number of deposits in mica schists, in the pegmatite veins of the *Ilmen Mountains*, at *Semiz-Bugu* (Central Kazakhstan), where it is associated with corundum, and elsewhere. Moreover, it often occurs in placers, especially in the Middle Urals.

A notable foreign location is in North Caroline (U.S.A.) where excellent rutile crystals of diverse habit are found.

Uses. A source of ferrotitanium for making steels with high impact strength; as a brown pigment for ceramics; as a radio-wave detector;

for the manufacture of titanium white, etc. The uses of metallic titanium see under "Ilmenite".

BROOKITE, TiO_2. **System** orthorhombic; symmetry rhombic dipyramidal $3L^23PC$. Space group $Pabc$ (D_{2h}^{15}). $a_0 = 9.16$; $b_0 = 5.44$; $c_0 = 5.14$.

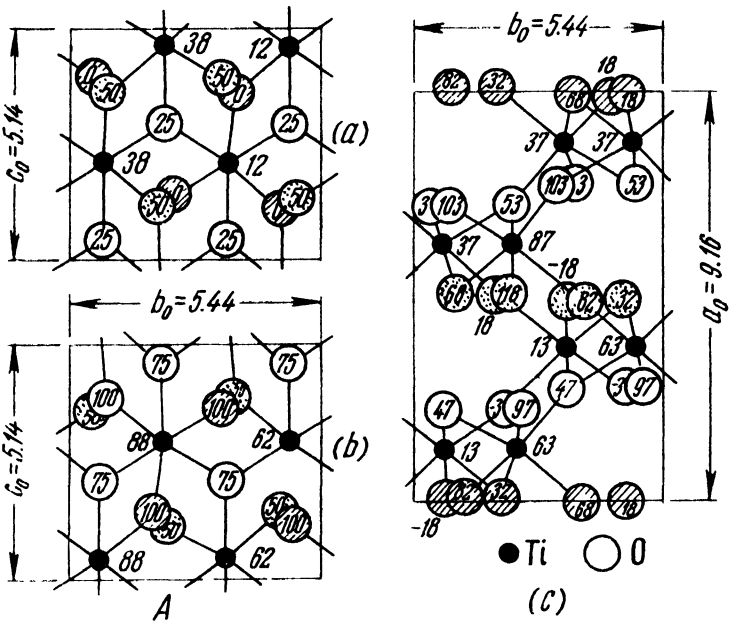


Fig. 161. Crystal structure of brookite (somewhat generalised). *a* and *b* – two portions of structure projected on (100); the lower portion shown above the upper (the oxygen ions marked 50 are shared); right – structure projected on (001) with actual arrangement of oxygen and titanium ions.

Crystal structure is shown somewhat idealised in Fig. 161*a*, projected on plane (100) which is the plane of the closest hexagonal packing of oxygen ions. Figure 161*b* shows the superimposed (over the plane of drawing) sheets of oxygen ions (cf. figures in circles). If the lower drawing is superimposed on the upper one, it will be easily seen that in the general direction of the *a* axis we have a combination of hexagonal and cubic packings (topaz packing); the oxygen ions "75" do not match with the "25" ions, as it should be in the closest hexagonal double-layer packing, but follow the pattern of the cubic closest packing. The Ti ions lie between the sheets of oxygen ions and have a sixfold coordination thus forming zig-zag chains of octahedra in each layer of the closest packing. In contrast to rutile structure, these octahedra share three common edges. Also in agreement with this structure is the flattened (on 100) habit of crystals (Fig. 162), four faces of the prism {021} parallel to the *a* axis and the

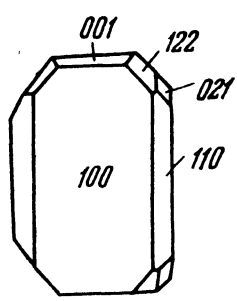


Fig. 162. Brookite crystal.

pinacoids {001} forming an almost regular hexagon in cross-section. No less characteristic is the vertical striation of the faces.

Colour, yellow- or red-brown to black. **Streak**, colourless to greyish- or brownish-yellow. **Lustre**, adamantine. $n_x = 2.741$, $n_y = 2.586$, and $n_z = 2.583$. Some specimens show sharply different refractive indices with a corresponding change in the dispersion of optical axes for different wavelengths.

Hardness, 5 to 6. **Cleavage**, {110} imperfect. **Specific gravity**, 3.9 to 4.0 (lower than that of rutile but higher than in anatase). On ignition specific gravity increases and becomes equal to that of rutile (probably a rearrangement of the crystal structure takes place).

Occurrence. Excellent brookite crystals are found in the Atlyanskaya gold placer near Miass, and in Alpine clefts elsewhere in the Urals.

ANATASE, TiO_2. **System**, tetragonal; symmetry, ditetragonal dipyramidal $L^4 4L^2 5PC$. Space group $I4/amd(D_{4h}^{19})$. $a_0 = 3.73$; $c_0 = 9.37$. **Crystal structure** is characterised by the closest cubic packing of oxygen ions, with a vertical fourfold axis (Fig. 163). Although the coordination numbers are the same as for rutile (6 : 3), the geometry of the coordination is distorted, because the TiO_2 octahedra are joined in such a way that they have four common edges.

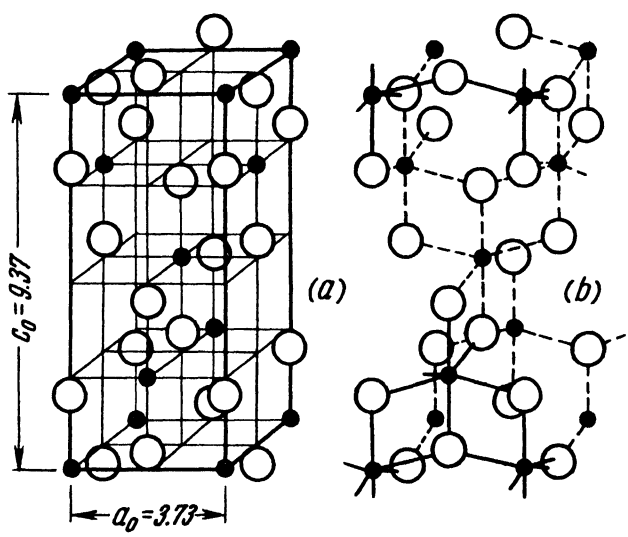


Fig. 163. Crystal structure of anatase. *a* – unit cell; *b* – linkages between Ti and O.

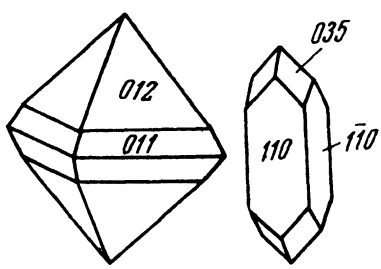


Fig. 164. Anatase crystals.

Crystals are of characteristic dipyramidal habit (Fig. 164); the (011) dipyramid being more acute than the (012) dipyramid which is close to an octahedron in shape. More rarely, anatase occurs in prismatic and tabular crystals.

Colour, brown to black. **Streak**, colourless. **Lustre**, adamantine. $n_y = 2.55$ and $n_z = 2.49$.

Hardness, 5 to 6. **Cleavage**, perfect parallel to (001) and (011), in which it differs from rutile. **Specific gravity**, 3.9 (lower than that of rutile and brookite). Infusible in the blowpipe flame. Insoluble in acids.

Occurs in pegmatites and chlorite and mica schists. Well-developed crystals are fairly often observed on quartz in Alpine clefts in the Alps, Brazil, and in the Northern Urals. The mineral is chemically inert, occurs in placers such as Atlyanskaya placer in the Southern Urals near Miass and elsewhere.

CASSITERITE, SnO_2. *Kassiteros* is the Greek for tin. Synonym: tin stone. The only economically important ore of tin.

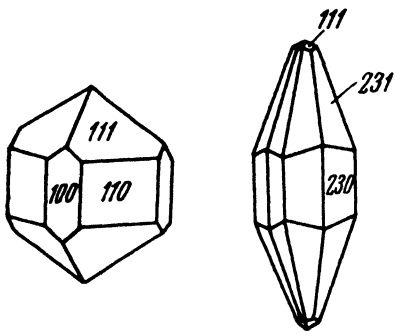


Fig. 165. Cassiterite crystals.

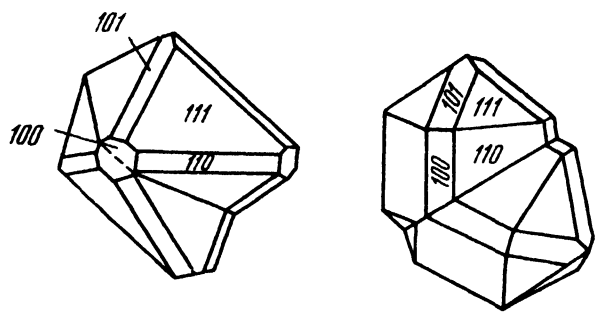


Fig. 166. Cassiterite twins.

Chemical composition. Sn 78.8% (according to the chemical formula). Almost invariably contains impurities. In many cases, especially when occurring in pegmatites, contains Fe_2O_3, Ta_2O_5, Nb_2O_5, TiO_2, MnO, FeO, occasionally ZrO_2 and WO_3. All these metals of different valences are probably present as isomorphous admixtures or the products of disintegration of solid solutions, as in the case of certain varieties of rutile.

System, tetragonal; symmetry, ditetragonal dipyramidal $L^4 4L^2 5PC$. Space group $P4/mnm(D_{4h}^{14})$. $a_0 = 4.72$; $c_0 = 3.17$. However, occasional optically biaxial varieties possibly have a crystal structure close to the orthorhombic. SnO_2 rhombic crystals (specific gravity 6.70) were obtained artificially by Daubrée.

Crystal structure, identical with that of rutile. **Habit**, Well-developed crystals of cassiterite are frequently found in cavities. Crystals are usually small but sometimes may be as large as 10 cm (weighing several kilograms). Mostly of dipyramidal, pyramidal prismatic (Fig. 165) or columnar habit, sometimes acicular. In pegmatites the most common are crystals of dipyramidal habit, often twinned. The grains impregnated through greisens and granites are often irregular. The same is true of the cassiterite grains formed metasomatically in the course of endogenous oxidation of stannite and other sulphurous compounds of tin. Twins are very frequent and, like those of rutile, geniculated. (Fig.166). **Aggregates.** Granular masses are rare. Usually occurs as tiny impregnated crystals or irregular grains. In the cavities of hydrothermal veins, druses of well-formed crystals are found occasionally. The so-called wood tin occurs in nodules and sinters of concentrically-banded structure characteristic of colloidal accumulations. Under the micro-

scope it can be often seen in these cases that some zones are composed of cryptocrystalline aggregates, and some of distinctly granular, columnar, radially-oriented individuals.

Colour. Because of the presence of Fe, Nb, Ta, and Mn impurities, cassiterite is usually dark-brown to pitch-black. Thin polished sections often show a banded structure of individual crystals and grains due to the alternation of zones of different colour intensity. Transparent varieties are extremely rare. **Streak** of dark varieties is usually of light-brown. **Lustre**, adamantine, on fracture pitchy, slightly greasy. Crystal faces are sometimes dull. Opaque black varieties may even have submetallic lustre. $n_x = 2.09$ and $n_y = 1.99$.

Hardness, 6 to 7. Brittle. **Cleavage**, {110} imperfect, sometimes distinct. Fracture often conchoidal. **Specific gravity**, 6.8 to 7.0. **Other properties.** Nonmagnetic, though iron-enriched black varieties are electromagnetic.

Diagnostic features. In crystal form, twinning, and colour resembles rutile, and in light-coloured varieties also zircon. Differs fundamentally from them in specific gravity, hardness (7 to 8 for zircon), and characteristic slightly greasy or pitchy lustre on fracture. In thin sections, small grains of cassiterite may be mistaken for zircon whose birefringence is much lower.

Infusible in the blowpipe flame, but strongly ignited with three volumes of soda on charcoal, in the reducing flame, gives small malleable globules of tin and a white coating of SnO_2. Insoluble in acids. If a drop of hydrochloric acid is placed on cassiterite and touched with a piece of zinc (or better with a specially made zinc needle), after a while, under the reducing effect of intensely evolving hydrogen, a metallic tin coating will appear on cassiterite. This coating becomes shiny when rubbed against a piece of cloth (a very characteristic and almost always successful test for cassiterite).

Genesis and occurrence. Cassiterite deposits are genetically associated with acid igneous rocks, mostly granites.

In granites proper, however, cassiterite occurs very rarely, and when it does, it is in greisenised sections, i.e., those transformed by pneumatolytic agents (F, Cl, B, etc.) into mica-feldspar-quartz rock with topaz, fluorite, lepidolite (lithium mica), tourmaline, and other minerals. Presumably, at high temperatures tin is transported in the form of volatile SnF_4 and $SnCl_4$ compounds, which are later on hydrolised producing an SnO_2 precipitate. It has also been established that alkaline solutions containing hydrogen sulphide vigorously transport tin in a reducing environment.

Cassiterite forms most unevenly distributed accumulations in *pegmatite* dikes associated with tin-bearing intrusions. Unlike hydrothermal cassiterite, the cassiterite found in pegmatites often contains Nb-Ta,Fe, and other metals. Found in paragenesis with it are quartz, micas, albite, tourmaline, sometimes columbite, beryl, spodumene, etc. Cassiterite is also found in some *contact-metasomatic* deposits in close asso,

ciation with different sulphides, which shows that it deposited during the hydrothermal stage.

Hydrothermal cassiterite vein deposits are much more important economically. Of these two types are most important: (1) quartz-cassiterite, and (2) sulphide-cassiterite veins. The first, apart from the predominant quartz and cassiterite, usually contain tourmaline, white mica, feldspars, wolframite, and small amounts of arsenopyrite, pyrite, fluorite, topaz, beryl, and other minerals. Cassiterite mostly occurs as impregnations in a quartz groundmass and in cavities as crystals, which are sometimes very large. In deposits of the second type, which are of economic importance in a number of regions of the Soviet Union, cassiterite is chiefly associated with sulphides: in some cases mainly with pyrrhotite, and partly with sphalerite, chalcopyrite, and stannite; in other cases, it is predominantly associated with sphalerite and galena; and elsewhere with various rare sulphides, such as bismuthinite (Bolivian type). The non-metalliferous associates of cassiterite, besides quartz, are rather abundant black tourmalines and frequently ferruginous chlorites and carbonates.

Owing to its high chemical inertness in the oxidised zones of tin ore deposits, cassiterite passes into placers.

Exogenous cassiterite formed in the course of disintegration of tin sulphides is found in the oxidised zones as porous and earthy masses.

In the Soviet Union cassiterite deposits are found in Eastern and especially in North-Eastern Siberia.

Important foreign localities are the *Malayan* tin-bearing province (Burma, Western Thailand, the entire Malay Peninsula, the southern islands of Banka and Billiton) with widespread cassiterite placers derived from the weathering of primary pegmatite and quartz-cassiterite veins. *Bolivia* has numerous deposits—quartz veins containing cassiterite, tungsten minerals, various sulphides, fluorite, tourmaline, as well as sulphide-cassiterite deposits.

Uses. Cassiterite is the most important ore of tin accounting for practically all of industrial production of tin. Tin has the following applications: (1) in the manufacture of tin plate; (2) in the preparation of fusible acid-resistant alloys with copper (bronze), with zinc, copper, and lead (brass), with lead (solder), etc.; (3) in tinning copper ware; (4) in the production of tin foil; (5) in ceramics (for enamels and pigments) and for other purposes.

COLUMBITE-TANTALITE, $(Fe, Mn)Nb_2O_6$ - $(Fe, Mn)Ta_2O_6$. Form a continuous series of isomorphous mixtures. The name *columbite* derives from the American name for niobium—columbium. Synonym: niobite.

Chemical composition varies greatly. Even in the same deposit the contents of Fe, Mn, as well as of Nb and Ta vary within a wide range. It should be noted that tantalites occur either as almost pure manganotantalites or pure ferrotantalites (intermediate varieties are rare). May

contain as impurities negligible amounts of Sn (1 to 2%, seldom up to 9% in tantalites), W, and Ti. However, unlike other tantalo-niobates, they never have any admixture of such large cations as Na, Ca, U, Th, rare-earths, and yttrium.

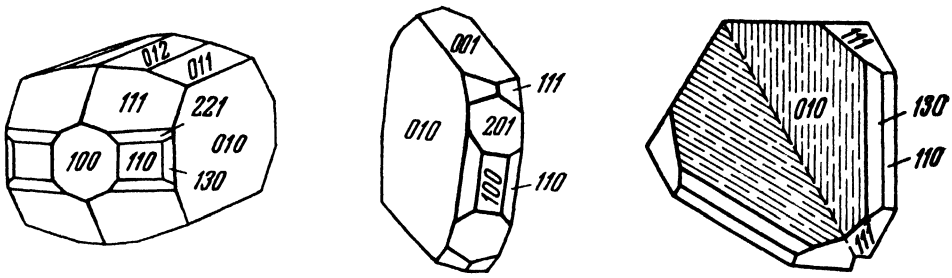


Fig. 167. Columbite crystals.

Fig. 168. Columbite twin.

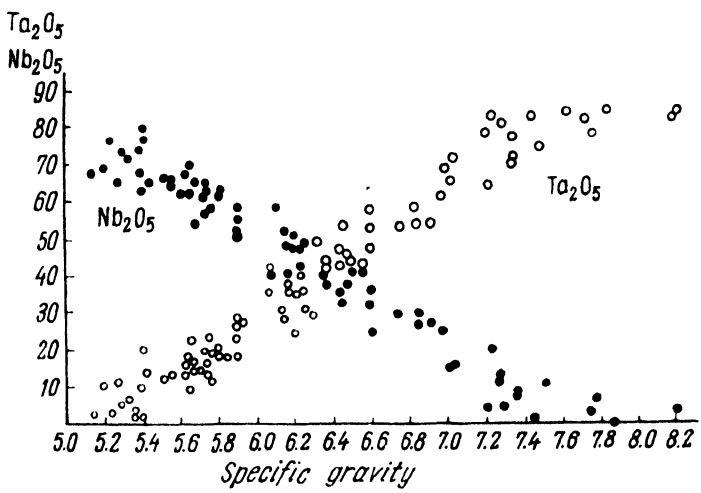


Fig. 169. Dependence between Ta_2O_5 and Nb_2O_5 content on specific gravity.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^33PC$. Space group *Pbcn* (D_{2h}^{14}). $a_0 = 5.08$; $b_0 = 14.24$; $c_0 = 5.73$. **Crystal structure** analogous to that of brookite (cf. Fig. 161). The ions of Nb, Ta, Mn, Fe, W, and possibly of Sn occupy the same positions as Ti ions in brookite, i.e., the centres of the oxygen octahedral groups. **Habit**, lamellar on (010), tabular, sometimes short-columnar (Fig. 167). The most common forms are pinacoids {100}, {010}, {001}; prism {110}, dipyramid {111}, etc. Twins of (201) are often lamellar-cordate with characteristic pinnate striation (Fig. 168). Intergrowths of niobite with samarskite have been described in literature.

Colour, black to brownish-black. **Streak**, red or reddish-brown to reddish-black. **Lustre**, submetallic. Opaque.

Hardness, 6. Brittle. **Cleavage**, {100} rather distinct. **Specific gravity**, 5.15 to 8.20, increases with Ta content (Fig. 169). **Other properties.** Columbite is a conductor of electricity.

Diagnostic features. Columbite and tantalite are almost indistinguishable by external features. They may be mistaken for: (1) ilmenite (distinguished by streak, habit, and negative reactions for Nb and Ta); (2) wolframite, which has a more perfect cleavage on {010} and lower hardness; (3) orthite which has a lower specific gravity (3.2 to 4.2) and light streak; (4) samarskite, aeschynite, euxenite, and other niobates and tantalates containing rare earths and radioactive elements, from which they cannot be distinguished without spectral and radiometric analyses, and microchemical tests.

Infusible in the blowpipe flame. Insoluble in acids. When fused with KOH and treated with dilute hydrochloric and sulphuric acids, on addition of metallic zinc, columbite develops a stable blue colouring. Tantalite, when fused with $KHSO_4$ and treated with hydrochloric acid, colours the solution yellow and yields a heavy white precipitate which also turns bright-blue on addition of Zn; however, on dilution with water, the blue colour disappears.

Genesis and occurrence. Usually occur in *pegmatite* dikes in association with various minerals formed at the later stages of the pegmatitic process: albite, quartz, muscovite, tourmaline, zircon, wolframite, cassiterite, sometimes samarskite, monazite, etc.

Being rather inert in the oxidised zone, they occur in placers.

Important foreign localities are Moss, Kragerö, and Finbo (Norway); near Limoges (France), and also at Ivigtut (Greenland) where very well-formed crystals have been found, etc.

Uses. When found in quantity, these minerals are of economic value as a source of niobium and tantalum used in the production of special steels and in other applications.

PYROLUSITE, MnO_2. *Pyros* is the Greek for fire and *lusios* destructive (it is used as a decolouriser of green glass). Synonym: polianite (the name formerly applied to phanerocrystalline varieties).

Chemical composition. Mn 63.2%. In fine-granular and cryptocrystalline masses usually contains mechanical impurities such as Fe_2O_3, SiO_2, H_2O, etc.

System, tetragonal; symmetry ditetragonal dipyramidal L^44L^25PC. Space group $P4/mnm(D_{4h}^{14})$. $a_0 = 4.38$; $c_0 = 2.85$. **Crystal structure**, analogous to that of rutile. Very seldom occurs in crystals (only in cavities) of acicular or rod-like habit. Usually found in crystalline or cryptocrystalline, often pulverulent, sooty masses, sometimes as pseudomorphs after reniform masses of psilomelane.

Colour, black, sometimes with a metallic bluish tarnish. **Streak**, black. **Lustre**, submetallic. Opaque.

Hardness, for crystal individuals 5 to 6; for aggregates, decreases to 2 (depending on their porosity and friability). Very brittle. **Cleavage**, {110} perfect, very characteristic of pyrolusite. **Specific gravity**, 4.7 to 5.0.

Diagnostic features. Differs from other black manganese minerals with a black streak by characteristic cleavage, brittleness, and rather low hardness.

Infusible in the blowpipe flame. Giving off some of its oxygen (up to 12 per cent by weight) changes to lower oxides and becomes brown. Does not alter on heating up to 500°C but in the interval between 550

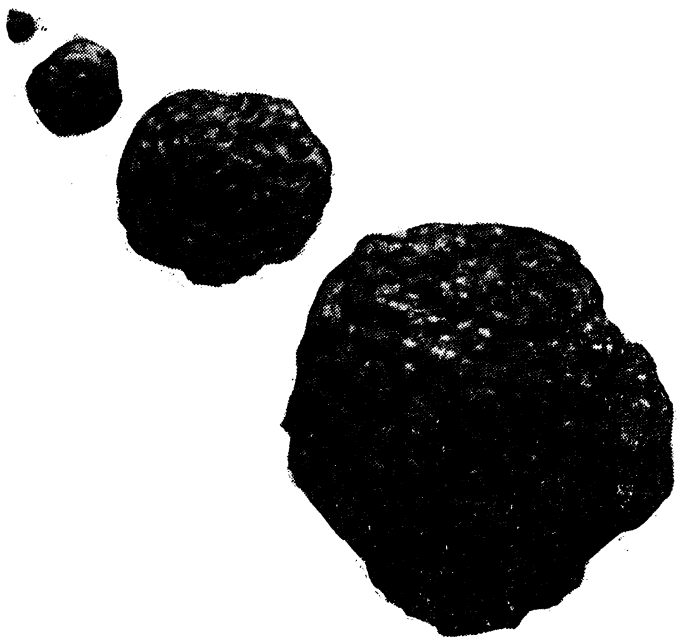


Fig. 170. Pyrolusite concretions.

and 650°, according to X-ray analyses, dissociation takes place with formation of β-braunite (cubic modification); when heated further (940 to 1100°) β-braunite is converted into hausmannite, which is stable at high temperatures.

Dissolves in hydrochloric acid with evolution of chlorine. Extensive use of this property is made by the chemical industry. With borax and salt of phosphorus in the oxidising flame yields a violet bead which becomes colourless on reduction.

Genesis and occurrence. Rather rarely formed in hydrothermal manganese deposits, and then only in an obviously oxidising environment. However, it is widely distributed on the earth's surface as a multiple oxide in near-shore facies of *sedimentary* deposits. It is the most stable manganese oxide in the oxidised zone where it is the end product of alteration of all the manganese minerals containing manganese in low degrees of oxidation. Therefore pyrolusite often occurs in pseudomorphs after manganite, vernadite, psilomelane, hausmannite, etc. Owing to its brittleness, very rarely occurs in placers. Constantly occurs in the so-called manganese hats, i.e., in the oxidised zones as well as in a number of sedimentary deposits. One of the world's largest sedimen-

tary deposits is at *Chiatury* (Georgian Soviet Socialist Republic), where pyrolusite occurs as oölitic nodules or pseudomorphs after manganite oölites in the form of cryptocrystalline soft aggregates (at the outcrops); at *Nikopol* (the Ukraine) where it occurs in larger globular concretions (Fig. 170) with a concentric-banded structure (usually as pseudomorphs after manganite).

Notable foreign localities for pyrolusite are the oxidised zones of metamorphosed deposits in India, Ghana (West Africa), and elsewhere. Well-formed crystals were found at Platten (Czechoslovakia).

Uses. Pure pyrolusite ores have a wide variety of applications: (1) in the making of dry batteries; (2) in making activated components for such batteries; (3) as a decolouriser of green glass; (4) in the manufacture of chemicals for medicinal and other purposes; (5) in the manufacture of special gas masks against carbon monoxide, of catalysts of the hopkalite type to purify the exhaust fumes of automotive engines, etc.; (6) in the production of drying and various other oils, wax, as a tanning agent for chrome leather, in photography, in the preparation of pigments, etc. The ore used for the manufacture of dry batteries should contain not less than 80 per cent of manganese dioxide.

8. PEROVSKITE GROUP

Perovskite, $CaTiO_3$, is similar in chemical formula to ilmenite which crystallises in a structure typical of corundum, but is very different from ilmenite in crystal structure, since the Ca^{2+} ion has a much longer radius than the Mg^{2+}, Fe^{2+}, and Mn^{2+} ions.

The latter feature is also reflected in the association of the elements in the minerals of the perovskite group.

To begin with, isomorphous admixtures to Ca in some minerals are rare earths: Ce, La, and also Yt, which is quite natural (provided that Ca^{2+} is replaced by isometric Na^{1+} ions).

Then, as in the rutile group, Ti^{4+} may be partly or largely replaced by Nb^{5+} or Ta^{5+} provided that the summary charge of all cations is not disturbed, i.e., Ca^{2+} should be replaced by univalent cations. Indeed, in such cases, an isometric Na^{1+} ion appears as an isomorphous admixture to Ca^{2+}. The crystal structure of the compound remains intact. It should be noted that artificial $NaNbO_3$ has the same crystal structure as perovskite; the places of Ca^{2+} are taken by Na^{1+} and those of Ti^{4+} by Nb^{5+} ions. Small amounts of U^{4+} and Th^{4+} may sometimes be present as isomorphous admixtures to Ca.

PEROVSKITE, $CaTiO_3$. Named after L. A. Perovsky.

Chemical composition. CaO 41.1%, TiO_2 58.9%. May contain in negligible amounts the following impurities: Fe (up to 2%), Cr, Al, and TR (knopite).

System, externally cubic; optically, however, perovskite is usually anisotropic with twinning lattices on faces, a sign of its transformation

into a lower-temperature orthorhombic modification. **Crystal structure** is shown in Fig. 171. The centre of the cube is occupied by Ca, the corners by Ti, and the centres of the edges by O. According to N.V. Belov, in the perovskite crystal structure, which follows the closest packing pattern, the calcium cations, being rather large, participate

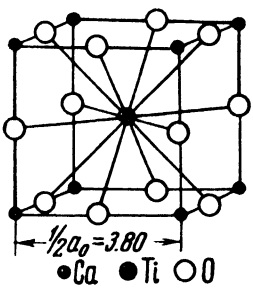


Fig. 171. Crystal structure of perovskite.

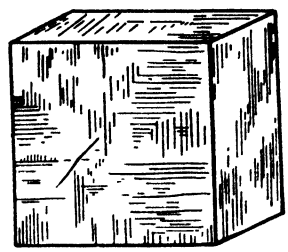


Fig. 172. Perovskite crystal.

in the closest packing of oxygen anions. On the section parallel to (001), the O^{2-} ions are staggered with Ca^{2+} ions as in the NaCl structure. This is why the crystals of perovskite have cubic shape and cubic cleavage.

Habit. Frequent crystals, which are sometimes rather large, have a cubic habit. The cube faces are striated parallel to the edges (Fig.172) which is probably due to twinning in the course of transformation into the orthorhombic modification. Also occurs in reniform masses in which small cubes are discernable.

Colour, greyish black, reddish brown, orange-yellow, and light-yellow. **Streak**, white or greyish-yellow. **Lustre**, adamantine. $n = 2.34$.

Hardness, 5.5 to 6. **Cleavage**, cubic, distinct. **Specific gravity**, 3.97 to 4.04.

Diagnostic features. Perovskite is characterised by the cubic habit of its crystals with faces having perpendicularly oriented short striations (parallel to the edges). Differs from minerals of similar colour and hardness by very faintly coloured or white streak.

Infusible in the blowpipe flame. Soluble only in boiling sulphuric acid or upon fusion with $KHSO_4$.

Genesis and occurrence. Perovskite does not occur in large masses. Is found as impregnations in certain alkali basalts (melilitic, leucitic, etc.), sometimes in titanomagnetite and chromite deposits. Chrome-bearing perovskite has been found in the *Saranovskoye* chromite deposit (the Urals). The best perovskite crystals have been found in contact-metasomatic deposits of unusual origin (associated with basic igneous rocks) in the *Nazyam* and *Shishim* Mountains in the Zlatoust district (the Urals)—in the well-known Akhmatovskaya, Nikolaye-Maximilianovskaya, Melnikovskaya, and other mines, very interesting from the viewpoint of paragenetic mineral associations. Particularly large perovskite crystals were found in the form of metacrystals in

chlorite schists and limestones of the Melnikovskaya mine. They have also formed in hollow fissures in association with crystals of chlorite, magnetite, sphene, garnets, and other minerals.

Perovskite occurs in many localities outside the U.S.S.R., the most notable of which are those in the Zermatt Valley (Switzerland).

Perovskite has no economic importance of its own.

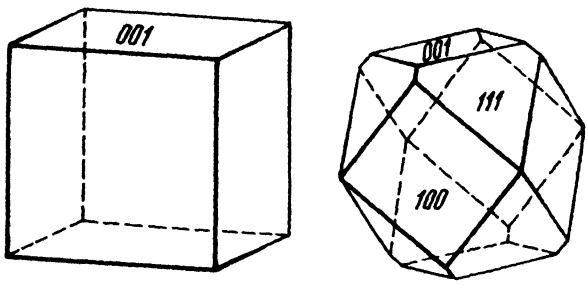


Fig. 173. Loparite crystals.

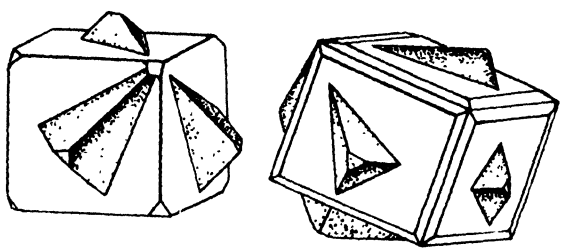


Fig. 174. Loparite twins.

LOPARITE, (Na, Ce, Ca) (Nb, Ti)O_3. First discovered by I.G. Kuznetsov on the Kola Peninsula.

Chemical composition, variable. According to chemical analyses, loparite contains (per cent): TiO_2 39.2 to 40, Tr_2O_3 32 to 34, $(Nb, Ta)_2O_5$ 8 to 10, CaO 4.2 to 5.2, Na_2O 7.8 to 9.0, SrO 2.0 to 3.4, K_2O 0.2 to 0.7, UO_2 hundredth fractions, ThO_2 0.2 to 0.5, SiO_2 0.2 to 0.7; in altered varieties, may contain up to 3.5 per cent of H_2O.

System, cubic; symmetry hexoctahedral $3L^44L_6^36L^29PC$. **Crystal structure**, similar to that of perovskite (Fig. 173). **Habit.** Mostly in cubic crystals, sometimes with truncated {111} faces (Fig. 173), usually very small (1 to 2 mm and occasionally 1.5 cm across). Almost invariably twinned according to the fluorite law (Fig. 174).

Colour, black or greyish-black. **Streak**, brown. **Lustre**, submetallic. Thin polished sections, brownish-red in transmitted light. $n = 2.24$. Occasionally shows optical anomalies.

Hardness, 5.5 to 6. **Cleavage**, none. Fracture uneven. **Specific gravity**, 4.75 to 4.89.

Diagnostic features. In addition to colour, streak, and hardness, is characterised by penetration twins according to the fluorite law.

Infusible in the blowpipe flame. Powdered loparite fuses with difficulty with soda on charcoal. A solution of the flux in hydrochlor-

ic acid boiled with tin turns violet (reaction of titanium reduction), then light blue (niobium reaction). In the presence of tin, the bead of salt of phosphorus turns yellow in the reducing flame; on cooling turns violet (titanium reaction). Insoluble in acids. Completely decomposed by HF. Readily fuses with $KHSO_4$.

Genesis and occurrence. Loparite is a rock-forming *magmatic* mineral. Occurs as more or less uniformly disseminated crystals in dark aegirite-enriched ($NaFeSi_2O_6$) nepheline-syenites (Lovozero tundra).

Occurs also in many pegmatite dikes as concentrated impregnations or as small crystals in feldspars, eudialyte (zirconium silicate of complex composition), and in other minerals. Common paragenetic associates of loparite are feldspars (microcline, albite), nepheline, aergirite, eudialyte, sphene, and some other minerals. Loparite crystals, especially large ones, often contain inclusions of the surrounding minerals, which indicates that they have formed metasomatically, i.e., are metacrystals.

Uses. Loparite is economically important as a source of niobium, rare earths, titanium, and other elements. Niobium, in the form of ferroniobium has been extensively used lately in making high-grade steels and heat-resistant alloys with aluminium, nickel, and other metals. When added to steels, ferroniobium imparts to them a number of valuable properties: (1) resistance to air hardening; (2) increased elasticity and flexibility; (3) improved welding capacity and resistance to heat and acids. Extra-hard niobium and tantalum alloys are widely used in the manufacture of drills and saws for cutting hard steels, as well as in making springs for watches. Moreover, niobium and tantalum are used for the manufacture of filaments for special-purpose electric lamps. Tantalum is also used as a substitute of platinum, iridium, etc., in powerful electronic tubes. For the uses of rare earths see Monazite.

9. PYROCHLORE GROUP

Included in this group are minerals close to the perovskite group in chemical composition but differing from the latter in chemical formulas. Of the numerous minerals of this group we shall describe pyrochlore, aeschynite, and samarskite.

PYROCHLORE, $(Na, Ca. . .)_2(Nb, Ti. . .)_2O_6$ [F, OH]. Greek *pyros* means fire, *chloros*, green (before the blowpipe certain varieties turn yellowish-green).

Uranium- and thorium-enriched varieties in the metamict state contain much H_2O (7 to 14%), no alkalis, very little calcium oxide (betafite group). Only the external cubic of octahedral crystal forms, sometimes with curved faces, have been retained.

Chemical composition is extremely variable. The content of individual constituents in the pyrochlore-microlite (tantalum analogue) isomorphous series varies as follows (per cent):

Nb_2O_5 ... 63 to 0	Na_2O .... 1 to 6	$(Ce, La)_2O_3$. 2 to 13.3
Ta_2O_5 ... 0 to 77	K_2O ..... 0 to 1.4	$(Y, Er)_2O_3$. 0 to 5.1
TiO_2 .... 2 to 13.5	CaO ..... 4 to 18.1	SnO_2 ..... 0 to 4.0
ThO_2 .... 0 to 5	MnO .... 0 to 7.7	ZrO_2 ..... 0 to 5.7
UO_2 .... 0 to 11.4	FeO ..... 0 to 10	WO_3 ..... 0 to 0.3
UO_3 .... 0 to 15.5	Fe_2O_3 .... 0 to 9.7	H_2O ..... 0 to 6.0

Also present sometimes are small amounts of Sb_2O_5, MgO, PbO (probably as a product of radioactive decay), HfO_2, SiO_2, Al_2O_3, SrO, BeO, CuO, Bi_2O_3, GeO_2, etc.

Thus, the principal variations in the chemical composition of these minerals are expressed in the fluctuations in the content of Nb_2O_5 and Ta_2O_5.

Many minerals, bearing different names, with certain peculiar features of chemical composition and physical properties, are tentatively included in this group, although they have not yet been studied well enough.

System, cubic; symmetry hexoctahedral $3L^44L_6^36L^29PC$. Space group $Fd3m(O_h^7)$. $a_0 = 10.35$. **Crystal structure.** Specimens that have not undergone metamict decay (poor in radioactive elements) have cubic crystal structure. **Habit**, octahedral (Fig. 175). Crystals may be as large as 2 cm across. Octahedral crystals are often truncated by cubic faces. Also massive and colloform. Ordered intergrowths with zircon are observed on (111) planes, the face of the pyrochlore octahedron coinciding with that of the tetragonal zircon {111} dipyramid.

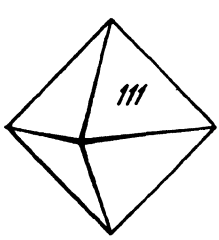


Fig. 175. Pyrochlore crystal.

Colour, dark-brown, reddish-brown, yellowish-green, occasionally brownish-black. Light-yellow rims may develop on the surface (transformation into an optically-anisotropic mineral poorly studied as yet). **Streak**, yellowish-white to light brown or reddish-yellow. **Lustre**, adamantine, greasy, vitreous or resinous (metamict varieties). Semi-transparent or translucent. $n = 2.13$ to 2.27 (for metamict varieties may be as low as 1.96).

Hardness, 5 to 5.5. Brittle. **Cleavage**, practically none. **Specific gravity**, 4.03 to 4.36. Tantalum varieties have higher specific gravity (up to 4.9). **Other properties.** Sometimes strongly radioactive. Altered varieties give a flash on heating (at about 500°).

Diagnostic features. Is characterised by octahedral habit, colour, greasy adamantine lustre. Another characteristic feature is its association with alkaline igneous rocks (nepheline-syenites and syenite-pegmatites). It is very similar to zircon with which it sometimes forms

intergrowths, and to scheelite, from which it differs by hardness and absence of cleavage.

Before the blowpipe fuses with difficulty into a black-brown globule. Certain varieties when heated become yellowish-green. With borax yields a bead which is reddish-yellow in the oxidising and dark-red in the reducing flame. Soluble in strong sulphuric and hydrofluoric acids.

Genesis and occurrence. Occurs in pegmatites of nepheline-syenites, in association with feldspars, mostly with albite, sometimes with zircon, biotite, apatite, ilmenite, sphene, calcite, and other minerals formed at the later pneumatolytic hydrothermal stage of pegmatite formation. Often, when closely intergrown with albite, imparts to the latter a characteristic brownish-yellow coloration.

There are known later transformations of pyrochlore into a secondary product in the form of pseudomorphs after octahedral pyrochlore crystals. It should be noted that the pseudomorphs sometimes have intumescence cracks, in which case the crystals have a somewhat distorted octahedral habit (Fig. 176). This newly formed mineral is optically isotropic. Colour, light-yellow. n about 2.1.



Fig. 176. Octahedral crystal of altered pyrochlore.

Note cracks of intumescence. Black spot in centre of crystal-remnant of primary pyrochlore

Pyrochlore is sometimes found as a neogenetic formation in the ilmenite aggregates deriving probably from endogenous decomposition of ilmenorutile (Ti, Nb, Fe)O_2.

Uses. When found in commercial quantities has economic importance as a source of niobium, tantalum, and uranium. For the uses of niobium see *Loparite*.

AESCHYNITE, (Ce, Ca, Th . . .) $(Ti, Nb)_2O_6$. From the Greek *Aeschyne*, shame (in the past chemists did not know how to decipher its composition). It is a titanoniobate of rare earths. With priorite (tantalum analogue) yields isomorphous mixtures (with rare earths and yttrium). The content of principal constituents varies as follows (per cent):

Ce_2O_3 . . 15.5 to 19.5	TiO_2 . . . 21.2 to 23.9	SnO_2 . . . . . 0 to 0.2
$(Y, Er)_2O_3$. 0.9 to 4.5	Nb_2O_5 . . 23.8 to 32.5	MnO . . . . . 0 to 0.03
CaO . . . . . 2.3 to 2.7	Ta_2O_5 . . . 0 to 6.9	MgO . . . . . 0 to 0.01
FeO . . . . 2.2 to 4.3	ThO_2 . . . 11.2 to 17.5	

System, orthorhombic. Crystals are prismatic, sometimes up to 12 cm long. **Colour**, black, fallow. **Streak**, dark brown, almost black. **Lustre**, adamantine, greasy. The varieties that underwent metamict decay are isotropic. $n = 2.26$.

Hardness, 5 to 6. Fracture conchoidal. **Specific gravity**, 5.16 to 5.23. Infusible but intumescent in the blowpipe flame. Insoluble in acids other than HF.

Occurs in pegmatites of nepheline-syenites in association with nepheline, feldspars, biotite, muscovite, magnetite, zircon, and other minerals. Has been recorded from the mines of the Ilmen Reservation, Hittherö (Norway), and elsewhere.

SAMARSKITE, $(Y, Er...)_4[(Nb, Ta)_2O_7]_3$. **System**, orthorhombic. Named after Samarsky, Chief of Staff of the Corps of Mining Engineers (1842). Chemical composition very complex. The content of principal constituents varies as follows (per cent):

Y_2O_3	6.41 to 14.49	Nb_2O_5	27.77 to 46.44
Er_2O_3	2.72 to 13.37	Ta_2O_5	1.81 to 27.03
Ce_2O_3	0.25 to 3.82	TiO_2	0 to 1.42
La_2O_3	0.37 to 1.07	ZrO_2	0 to 2.29
$(Pr, Nb)_2O_3$	0.74 to 4.17	SnO_2	0 to 0.95
ThO_2	0 to 4.23		
UO_2	4.02 to 16.0		
PbO	0 to 0.98		
CaO	0.2 to 3.79		
FeO	0 to 11.15		

Occurs in prismatic, sometimes lamellar crystals with dull faces which are mostly pinacoids {100}, {010}, and prisms {101}. Also as irregular grains, occasionally massive. Notable are its intergrowths with columbite (Fig. 177). Sometimes columbite crystals are overgrown by a thin samarskite coating which faithfully reproduces the columbite habit.

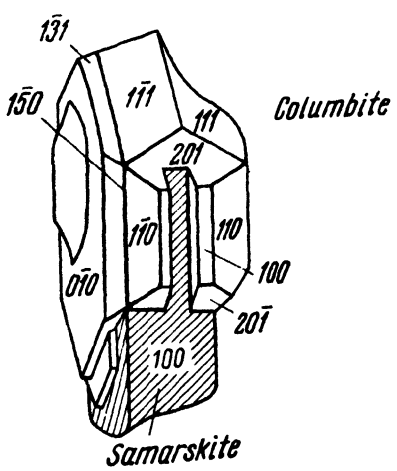


Fig. 177. Oriented intergrowth of samarskite with columbite. Magnified.

Colour, velvet-black, brownish-black. **Streak**, reddish-brown to black. **Lustre**, characteristically strongly resinous. Almost opaque. Thin polished sections, brown in transmitted light. $n = 2.21$ to 2.25 (metamict varieties). Sometimes has strong birefringence. **Hardness**, 5 to 6. Fracture conchoidal. **Specific gravity**, 5.6 to 5.8. Strongly radioactive.

Diagnostic features of samarskite are velvet-black dull crystal faces, conchoidal fracture with strong resinous lustre.

Before the blowpipe fuses slightly at the edges into black glass. In the closed tube decrepitates and becomes incandescent. With salt of phosphorus yields the emerald-green bead of uranium both in

the oxidising and the reducing flames. Fuses with $KHSO_4$. Solution in hydrochloric acid acquires a light-blue coloration (niobium reaction) when boiled with tin or zinc.

Occurs in pegmatite dikes of the Ilmen Reservation in the Urals, where it is associated with feldspars, which are tinted reddish-brown near samarskite (owing to the radioactive decay of samarskite elements), as well as with columbite, aeschynite, monazite, garnets, tourmaline, and other minerals. Outside the Soviet Union, occurs in deposits in North Carolina (with columbite) and Maryland (U.S.A.), on Madagaskar (Antanamalasa), and near Moss (Norway).

10. URANINITE GROUP

The group comprises dioxides of tetravalent metals: U, Th, and Zr. We shall describe only uraninite here.

URANINITE, UO_2. Name derives from composition. The most important source of uranium and radium.

Chemical composition of the naturally occurring crystals does not correspond to its written formula*, being intermediate between UO_2 and UO_3. The presence of U^{6+} in uraninite is possibly due to oxidation. Contains Ra, Ac, Po, and other products of radioactive decay. Radiogenic Pb is always present in uraninites as the end product of U and Th radioactive decay (in the form of Pb^{206}, Pb^{207}, and Pb^{208} isotopes), its content often being as high as 10 to 20 per cent. Uranium ores, however, often contain ordinary lead (as galena inclusion) which, besides the isotopes mentioned above, also contains Pb^{204} in a constant quantity (up to 10 per cent of the total content of isotopes). Some uraninite varieties called *cleveite* and *nivenite* contain rare earths (Ce, La, Er. . .) and also Yt (their total reaching 12 per cent). Coarse-crystalline varieties occurring in pegmatites are notable for the Th content. Occasionally, considerable quantities (up to 7.5 per cent) of Zr may be present. Gases that may be occluded in uraninite are He, Ar, N, Co_2, etc.

Helium is invariably a product of radioactive decay. Almost invariably present is H_2O which enters into the composition of the mineral in the course of alteration.

System, cubic; symmetry hexoctahedral $Fm3m(O_h^5)$. $a_0 = 5.47$.

Crystal structure is of the fluorite type (cf. Fig. 135). **Habit**, cubic with rudimentary octahedral and rhombic dodecahedral face development (Fig. 178). Occurs in octahedral, occasionally in rhombododecahedral crystals. Crystals are usually small (up to 1 cm across), sometimes ingrown in rock. Penetration twins according to the fluorite

* It will be recalled that the compounds formed by uranium with oxygen are UO_2 – black uranium protoxide or dioxide, and UO_3 – yellow amorphous uranium trioxide.

law are rare. **Aggregates.** Mostly as colloform and reniform masses. These varieties are called *pitchblende.* Dull sooty coatings or pulverulent masses are known as *uranium black.*

Colour, black, sometimes with a slight violet tinge. Thin polished sections, viewed in transmitted light, opaque or dark-brown and greenish in strongly altered portions. **Streak,** brownish black, slightly shiny. **Lustre,** submetallic, mostly typically pitchy, waxy or dull for strongly altered varieties.

Hardness, 5 to 6, for strongly altered varieties as low as 3. Brittle. Fracture, uneven, nearly conchoidal. **Specific gravity,** 10.3 to 10.6; lower for strongly altered varieties. Usually ranges from 8 to 10 and

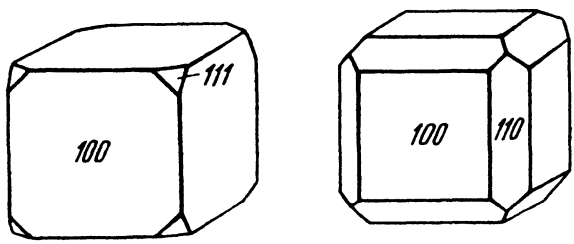


Fig. 178. Uraninite crystals.

may be as low as 6.5 and even 4.5. **Other properties.** Strongly radioactive.

Diagnostic features. Characteristic black colour, strong pitchy lustre on fracture, high specific gravity, and strong radioactivity. For oxidised specimens, a very characteristic feature is association with brightly orange or yellow products of uraninite or pitchblende alteration.

Infusible in the blowpipe flame. Strongly oxidised uraninites rather readily soluble in HNO_3, H_2SO_4 and HF, but very slowly in HCl. The varieties containing rare earths are the most soluble. The borax bead becomes green in the reducing and yellow in the oxidising flame. Neutralised with ammonia, the solution yields a yellow precipitate of ammonium uranate $(NH_4)_2UO_4$.

Genesis and occurrence. The following principal genetic types of uraninite deposits are known:

1. Accumulations of uranium minerals in granite and syenite *pegmatites* where uraninite is comparatively rare and unevenly distributed in paragenesis with the minerals of thorium, rare earths, niobium, tantalum (struverite, fergusonite, monazite, etc.), as well as with tourmaline, zircon, feldspars, micas, sometimes in association with uraniferous carbonaceous compounds (Fig. 179) such as thucholite, carburan, and other minerals of indeterminate composition.*

* Microscopic examinations have shown that "thucholite" and "carburan" are not independent compounds but are mechanical mixtures of carbonate matter with uraninite.

Uraninite formed at high temperatures contains, as a rule, thorium and rare earths.

2. Uranium oxides occur in far greater quantities in *hydrothermal* deposits, where pitchblende is sometimes associated with arsenides of Ni and Co (niccolite, smaltine, rammelsbergite, chloanthite), native bismuth, sometimes bismuthinite, native arsenic, native silver, and argentite. Pitchblende is in some cases associated with hematite, but

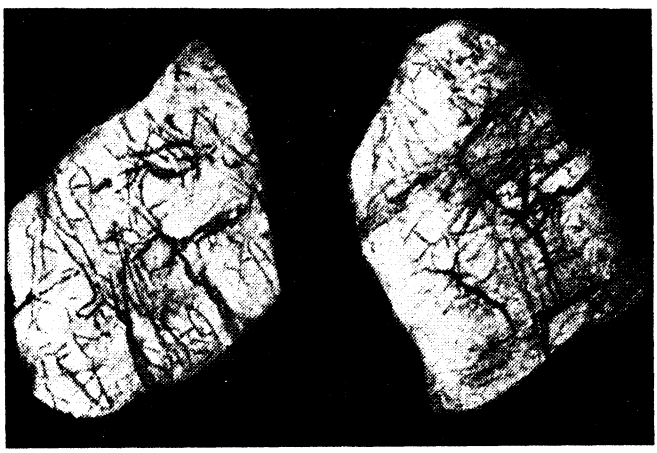


Fig. 179. X-ray photograph of two poilshed specimens of uraninite with black threads of carbonaceous compounds.

more often with calcium and iron carbonates, black decomposed fluorite, and other minerals. However, the bulk of pitchblende occurs independently in carbonaceous veins and stringers in association with rare sulphides, sometimes black fluorite, and other minerals.

At Gilpin, Colorado (U.S.A.), uraninite occurs in quartz-siderite veins as colloform segregations in association with pyrite, chalcopyrite, sphalerite, galena, rare native bismuth, and other minerals. In a gold Guadalupe deposit, at Chihuahua (Mexico) uraninite was found in calcite veins with gold and pyrite.

3. Uranium oxides in the form of uranium black are also formed through *exogenous* weathering of uranium deposits in the lower parts of oxidised zones or in the so-called cementation zone (below the ground-water table) in fissures in ore bodies or the country rocks, and even in the cracks of individual minerals. Uranium black is probably formed by the reduction of water-soluble compounds of hexavalent uranium in an oxygen-deficient environment, compounds being transported by percolating waters to the cementation zone. Uranium suboxides possess very low solubility and, therefore, precipitate from solution. Uranium black occurs as most thin coatings, veinlets, and sooty masses of dark-grey or velvet-black colour, sometimes with a slight brown tinge. Under the same conditions but in wider fissures, more

compact uranium oxides may be deposited in layers forming dull black crusts of colloform texture.

Uranium black is also found in some *sedimentary* rocks deposited under reducing conditions, especially in the presence of organic remains. Its frequent associates are impregnated iron sulphides (pyrite and marcasite), phosphates, and other minerals. Such sedimentary deposits are often enriched with molybdenum and vanadium. It should be noted that, despite their low uranium tenor, the bulk of uranium is contained in such deposits.

Uraninite always suffers some degree of later alteration irrespective of the type and age of deposit. The fact that it always contains higher uranium oxides shows that it is highly oxidisable. In the oxidised zones it decomposes much more readily than in endogenous conditions and is therefore a source of numerous exogenous uranium minerals, which (depending on the weathering conditions, the composition of primary ores and of the surface waters) may be hydroxides, sulphates, carbonates, uranovanadates, uranophosphates, and uranosilicates*. They are all brightly coloured yellow, green, or orange. Their mode of occurrence shows that uranium compounds in the oxidised zone are subject to migration. Although in this process some portions of the zone are depleted and some enriched with uranium, on the whole a considerable part of it is dispersed.

A great deposit of uraninite lies beyond the Arctic Circle at the *Great Bear Lake* (Canada). It was discovered by its bright yellow-orange outcrops of the secondary uranium minerals (the elevated sections of the area have been scoured clean of drift by glaciers). The numerous ore-bearing carbonaceous and quartz veins, lenses and stringers traced over a vast area contain carbonates, hematite, pitchblende, sulphides and arsenides of cobalt and nickel, native bismuth, and more recent native silver, argentite, pyrite, chalcopyrite, galena, sphalerite, etc. The ore minerals very frequently occur as metacolloidal aggregates. The deposit is enclosed in pre-cambrian rocks. Its age determined by different methods is 1,300,000,000 years.

Another rich deposit is located in the *Katanga* province of the Congo. It is variously known as Kasolo, Shinkolobwe and Kalongwe. Mineralisation there is in the form of lenses and veins in dolomite rocks and schists (at a considerable distance from granite masses). The ores and wall rocks contain, besides quartz, occasional tourmaline, monazite, apatite, and also sulphides (pyrite, linneite, chalcopyrite) and selenides of nickel, cobalt, etc. The pitchblende which sometimes occurs as large masses is usually recrystallised into coarse-granular aggregates. Uraninite crystals are also common. Diverse secondary uranium minerals such as janthinite, becquerelite, schoepite, sklodow-

* Amorphous products of uraninite alteration occurring as bright-red, orange, and yellow coatings and crusts are called gummite. It has been established that they are a mixture of orange-red curite (hydrate of lead and uranium) and yellow soddyite (uranium silicate).

skite, kasolite, soddyite, uranospherite, curite, etc., have been observed here in the oxidised zone in considerable amounts. The age of the deposit is about 610,000,000 years.

Uses. It is interesting to note that until radium was discovered by the Curies uraninite ores extracted as a by-product of silver mining were used only in the manufacture of yellow, orange, and black pigments. At the turn of the century uranium ore wastes after the extraction of radium were also used for this purpose. It was only recently that the problem of release and utilisation of the tremendous nuclear energy was solved, that the great value of these ores was discovered. The U.S.S.R. was the first country to harness nuclear energy for peaceful purposes by building the world's first atomic power plant.

The amount of radium present in uraninite is as low as hundred thousandths of one per cent of the total uranium mass. Radium preparations obtained by the treatment of uranium ores have many medical applications such as in the treatment of cancer (in the form of radon, a product of radium decay) for which purpose they are placed in special "guns"; the gamma-radiations of radium is used for detecting flaws in metal castings, reinforced-concrete, etc.

11. QUARTZ GROUP

The members comprising this group have the same very simple composition: SiO_2, and are nothing but a series of polymorphous modifications.

In crystal structure they stand completely apart from other oxides. As will be shown later, they are directly related to silicates in crystal structure. Therefore some authors classify this group of minerals with the silicates. However, since quartz is chemically a typical oxide, according to the classification adopted, we should review it in this section.

The three principal polymorphous modifications of SiO_2 have names of their own: quartz, tridymite, and cristobalite. Their modifications are prefixed by the Greek letters α and β. A hydrated silica or opal, $SiO_2 \cdot nH_2O$, which also exists in nature, will be reviewed separately.

The series of polymorphous transformations of SiO_2 is shown in Fig. 180 as a *TP* graph. The following are the recognised enantiotropic transformations:

$$\alpha\text{-quartz} \underset{573^\circ}{\rightleftarrows} \beta\text{-quartz} \underset{870^\circ}{\rightleftarrows} \beta\text{-tridymite} \underset{1470^\circ}{\rightleftarrows} \beta\text{-cristobalite} \underset{1713^\circ}{\rightleftarrows} \text{melt}$$

Moreover, tridymite and cristobalite undergo enantiotropic transformations in the region of low temperatures in the strongly supercooled state:

$$\alpha\text{-tridymite} \underset{130^\circ}{\rightleftarrows} \beta\text{-tridymite and } \alpha\text{-cristobalite} \underset{180\text{-}270^\circ}{\rightleftarrows} \beta\text{-cristobalite}$$

A characteristic of crystal structure of quartz and of other polymorphous modifications is that the Si^{4+} ion is always surrounded by *four* O^{2-} ions (Fig. 181) which occupy the apexes of a tetrahedron. Each apex of a tetrahedron is also the apex of the adjacent one (Fig. 182). Thus, the crystal structure of these minerals consists essentially of tetrahedra framework with common apexes (Fig. 183). Although the mode of linkage is the same for all the modifications (apex-sharing), they differ in orientation and general symmetry of arrangement.

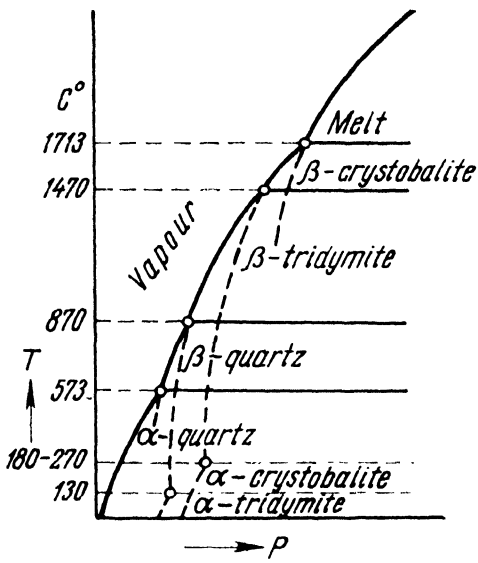


Fig. 180. Single-component SiO_2 system. Vapour-pressure curves for various modifications are shown diagrammatically. At each given temperature the modification characterised by lower vapour pressure (i.e., the one whose curve is closer to the axis of ordinates) will be more stable.

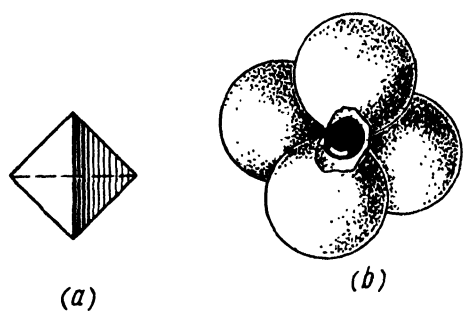


Fig. 181. *a* – tetrahedron placed on edge; its apexes are centers of oxygen ions in the SiO_4 tetrahedral group (*b*), inside of which a Si^{4+} ion is located; *a* and *b* are drawn to the same scale.

Generally speaking, the packing of oxygen ions is not compact, since there are "voids" between the tetrahedra. In the low-temperature modifications they are small and in the high-temperature more "loosely" packed modifications they are larger. This is directly reflected in specific gravity and refractive indices.

Since each oxygen ion is shared by two adjacent SiO_4 tetrahedra, it is located between two silicon ions, whereas each Si^{4+} ion is in fourfold oxygen coordination. Hence the coordination numbers 2 and 4. In each SiO_4 tetrahedron the positive Si^{4+} ion cancels out only half the negative valence of each surrounding O^{2-} ion, but since each oxygen ion is also shared by another tetrahedron, the second half of its valence will be cancelled out as well. Thus, it will be easily seen that on the whole the chemical formula for the compound should be SiO_2.

α-QUARTZ, SiO_2. This modification, stable at low temperatures, is usually called simply quartz; the origin of the name is unknown. Quartz is one of the most widespread and best studied minerals in the earth's crust.

Chemical composition. The written formula probably adequately expresses the composition of colourless transparent varieties. Milk-white and other variously coloured varieties may contain mechanical impurities of gases, liquids, and solids in varying amounts: CO_2, H_2O, hydrocarbons, NaCl, $CaCO_3$, sometimes inclusions of tiny crystals of rutile, actinolite, and other minerals, visible to the naked eye.

System. The higher temperature β-quartz modification crystallises in the hexagonal

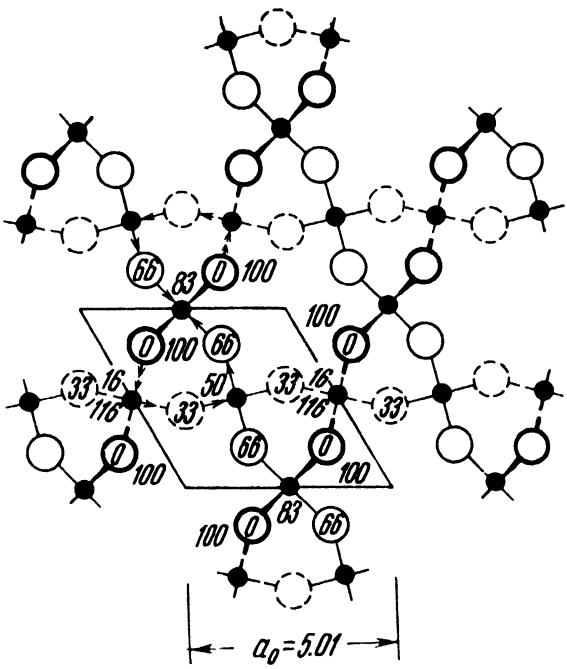


Fig. 182. Crystal structure of the higher-temperature β-quartz modification, projected on (0001).

Figures show relative height of ions above the plane of drawing.

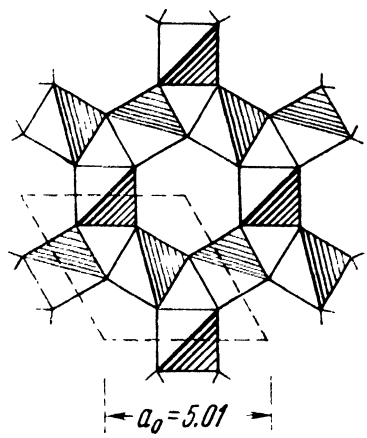


Fig. 183. The same crystal structure as in Fig. 182 but presented as tetrahedra.

Hatchings of varying thickness (on the shaded sides of tetrahedra) show relative position of these tetrahedra above the plane of drawing. Note that tetrahedra adjacent to the internal hexagon are arranged along the spiral axis of the sixth order (as in a double-groove spiral).

system and hexagonal trapezohedral symmetry L^66L^2. The α-quartz modification, more stable at temperatures below 573° (at atmospheric pressure), crystallises in the trigonal system and trigonal trapezohedral symmetry L^33L^3. Space group $C3_12(D_3^4)$. $a_0 = 4.904$; $c_0 = 5.397$. **Crystal structures** are rather simple. In Figs. 182 and 183 the crystal structure of β-quartz and the projections parallel to the c axis on the (0001) plane are given in the same scale. In each SiO_4 tetrahedron two oxygen ions are located somewhat above, and the other two somewhat beneath the silicon ion. The groups of tetrahedra lie in three layers at different heights; their relative positions above the plane of drawing are indicated by lines of different thickness and by figures alongside the circles (Fig. 182). As can be seen in Fig. 183, the tetrahedra are arranged in spirals, all coiling in the same direction. The so-called right- and left-handed quartzes owe their name to the direction in which the spirals coil. Rotation through

60° about the sixfold axis and the transference of the unit cell for one-third of its height along the *c* axis results in coincidence with the former position of the tetrahedra (Fig. 183).

The low-temperature α-quartz modification differs but little from β-quartz in crystal structure. Their relationship is shown in Fig. 184 by projections on the (0001) plane, only the silicon ions being shown. It will be seen that in the

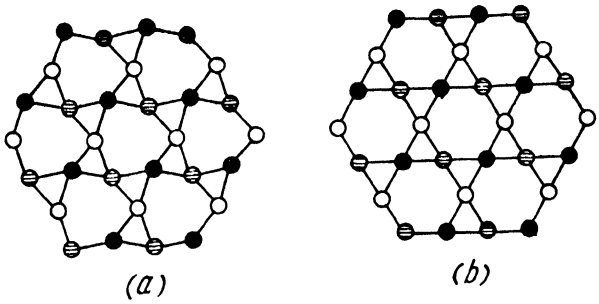


Fig. 184. Relationships in crystal structures of β-quartz (*a*) and α-quartz (*b*).
Only silicon ions are shown, their position in height being indicated by the different shading of circles.

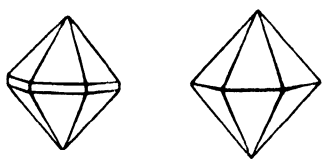


Fig. 185. Crystals of β-quartz. Hexagonal dipyramid (right) in combination with hexagonal prism (left).

polymorphous transformation of high-temperature into low-temperature quartz the centres of the silicon-oxygen tetrahedra are somewhat displaced, the lattice becoming more compact and its symmetry lower: the hexagonal axes become trigonal. The type of bonding between the tetrahedral groups remains the same. Nor does the direction of spiral coiling change (to the left or to the right) in the course of transformation.

Habit. Crystals of β-quartz, or rather the paramorphs of α-quartz after β-quartz occurring in silica-rich effusives (liparites, quartz-porphyrys, etc.) as early magmatic segregations, have the hexagonal dipyramids habit with prismatic faces being greatly shortened or altogether absent (Fig. 185). Though usually very small, in some rocks crystals 1 or even 2 cm across are found. Well-developed crystals of α-quartz occur only in cavities or in loose formations. Individual very large crystals weighing up to 40 tons are known. Although the crystal forms are extremely diverse, they have characteristic prismatic faces *m* $(10\bar{1}0)$, often horizontally striated; rhombohedral faces *r*$(10\bar{1}1)$ and *z*$(01\bar{1}1)$; trigonal dipyramidal faces *s*$(11\bar{2}1)$; trigonal trapezohedral faces *x*(5161), etc. (Fig. 186). Some individuals have equally developed faces of principal rhombohedra, the crystals assuming then the shape of a "hexagonal dipyramid". When etched, the faces of one rhombohedron remain shiny, those of the other become dull. Nor do the etch figures follow the same pattern. The position of the faces of a trigonal trapezohedron $\{51\bar{6}1\}$, and dipyramid $\{11\bar{2}1\}$ distinguishes the right-handed and the left-handed quartz (Fig. 186). These faces are confined to prism edges (120°) and occur at the top and bottom on the opposite sides of the edge.

Besides the phanerocrystalline modifications of α- and β-quartz, there are cryptocrystalline varieties of fibrous texture: *chalcedony* and *quartzine* differing between themselves only in optical properties (e.g., in optic sign).

Twins, according to different laws, are very frequent.

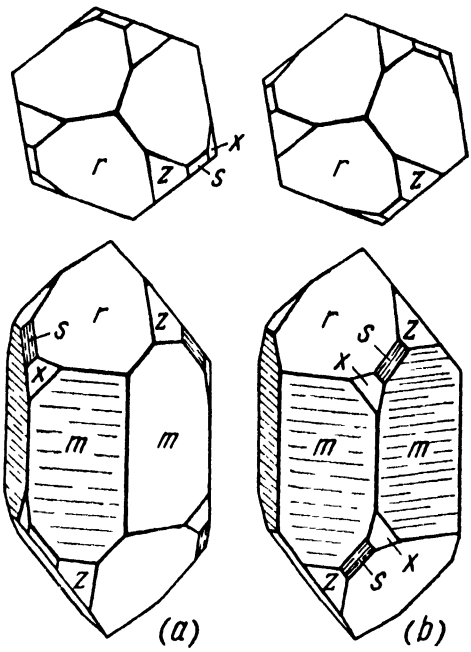


Fig. 186. Left-handed (*a*) and right-handed (*b*) quartz.
m(1010), *r*(1011), *z*(0111), *s*(1121), *x*(5161).

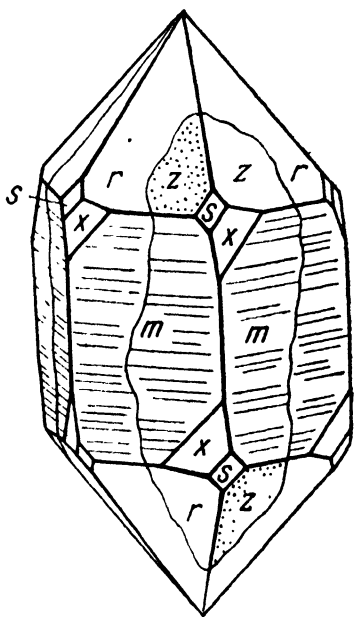


Fig. 187. Dauphiné twin. Sutural line shows the boundary between the two individuals.

1. *Dauphiné* twins (Fig. 187) are so closely intergrown that they look like crystals, with the difference that they have double the number of the *x*-trapezohedron faces (Fig. 188), that develop from each other by rotation through 60° instead of 120° about the vertical axis. The prism faces of both individuals merge together, and the faces of the *r*-rhombohedron coincide with those of the *z*-rhombohedron (Fig. 187). The optical axes of both individuals are parallel and, therefore, the twinning can be revealed only by etching (Fig. 189*a*). The composition faces are sinuous.

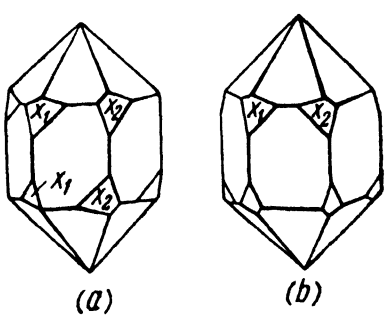


Fig. 188. Dauphiné (*a*) and Brazil (*b*) twins.

2. *Brazilian* twins (Fig. 188) differ from Dauphiné twins in that they have double the number of trapezohedral faces, which are developed in a different way, namely by reflection in a vertical plane. The twinning structure is revealed by etching (Fig. 189*b*). Unlike the Dauphiné structure, the composition faces are straight. Brazilian twins may also be identified optically.

3. *Japanese* twins are arranged parallel to the trigonal dipyramid $\{11\bar{2}2\}$; the individuals are inclined to each other at an angle of 84°34′.

Aggregates. Druses of quartz crystals are very common in cavities (Fig. 41) where they are sometimes intergrown with crystals of other minerals. Massive quartz is composed of granular aggregates. The structure of compact aggregates is readily recognised in thin polished sections under the microscope with crossed nicols. Chalcedony whose

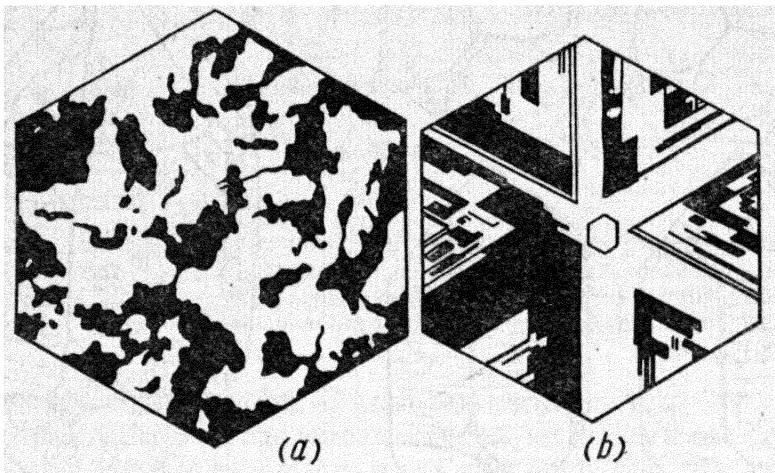


Fig. 189. Etched sections of quartz crystals (perpendicular to the optic axis).
a – Dauphiné twin; boundaries between individuals extremely irregular; *b* – Brazil twin with straight boundaries between individuals.

structure is cryptocristalline (fibrous) often occurs as crusts, reniform masses or spherolites, but mostly in nodules known as flints. Agates (siliceous geodes) have a concentric-banded structure due to alternating of variously coloured layers of chalcedony and sometimes quartz. The centres of the geodes are often composed of crystalline granular quartz (cf. Fig. 42), sometimes in the form of crystal druses.

Colour. Quartz occurs in a wide variety of colours, but most widespread are colourless, milk-white, and grey varieties. Transparent and translucent beautifully coloured varieties have names of their own: (1) *rock crystal*, colourless, water-transparent crystals; (2) *amethyst*, violet varieties; (3) *rauchtopaz*, a smoky transparent quartz tinted grey or brown; (4) *morion*, a black crystalline variety; (5) *citrine*, golden-yellow or lemon-yellow crystals. In addition to the transparent varieties, there exist definitely allochromatic quartz crystals whose colour is due to inclusions of foreign minerals; these also have individual names: *prase*, a greenish variety with inclusions of green acicular actinolite; *aventurine*, a yellowish of brownish-red quartz with a glimmering chatoyancy caused by tiny glistening scales of mica, specularite (Fe_2O_3), etc.

Milk-white quartz masses widespread in hydrothermal deposits sometimes owe their colour to abundant microscopic occlusions of

liquids and gases. The liquid occlusions almost always contain a mobile gas bubble by which one easily recognises the presence of the liquid. Sometimes they even contain NaCl crystals (Fig. 190). On heating to a certain temperature the microcrystals dissolve and the bubbles disappear. On cooling the different phases reappear. In this way it is possible to determine approximately the temperature at which the liquids and gases were trapped in the process of quartz crystallisation. Quartz may also be milk-white due to intense fracturing caused by dynamic factors (just as transparent ice turns milk-white when struck with a hammer).

Chalcedony, more often than crystalline quartz, has different colours and tints: milk-grey, bluish-black (sapphirine), yellow, red, orange (carnelian), brown (sard), green (plasma), apple-green due to the presence of nickel compounds (chrysoprase), and green containing scattered red

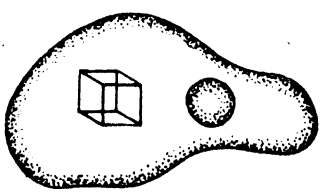


Fig. 190. Gas bubble and small halite crystal in drop of liquid occluded in quartz. Magnified.



Fig. 191. Agate partly with horizontal and partly with concentrical varicoloured bands.

spots (heliotrope), etc. *Agates* or *onyxes* often composed of the thin, variously coloured, concentric or parallel bands of chalcedony (Fig. 191) sometimes show most diverse combinations of tints: black with white, brown with white (sardonyx), red with white (carneolonyx), etc.

Lustre, vitreous; for chalcedony, waxy to dull. **Optical constants.** Uniaxial, positive. $n_x = 1.553$ and $n_y = 1.544$. Capable of rotating the polarisation plane, the direction of rotation depending on the type of quartz, i.e., right-handed, or left-handed.

Hardness, 7. **Cleavage**, either absent or imperfect rhombohedral. Fracture, conchoidal. **Specific gravity**, 2.5 to 2.8, for pure varieties 2.65; β-quartz, with less close packing, has a somewhat lower specific gravity. **Other properties.** Transmits ultraviolet rays. Piezoelectrical,

i. e., develops electric charges when subjected to pressure. The twofold axes are the electrical ones, the end of each twofold axis terminating at the edge truncated by trapezohedral faces, developing a negative charge, and the opposite a positive charge. Melting point 1713°. A product of solidification of molten quartz is quartz glass (amorphous quartz) which has a number of special properties such as acid-resistance, low expansion coefficient, transparency to ultraviolet rays, etc.

Diagnostic features. Quartz crystals are readily identifiable by their characteristic form. In compact aggregates quartz is recognised by high hardness, conchoidal fracture, and absence of cleavage.

Chalcedony differs from similar minerals (opal, smithsonite $ZnCO_3$, cryptocrystalline fluorite, etc.) mostly by hardness. Is also readily distinguishable by optical properties.

Infusible in the blowpipe flame. Insoluble in acids except HF with which it forms SiF_4, a volatile compound. Soluble by alkalis; chalcedony is strongly attacked by KOH.

Genesis and occurrence. Being widespread in nature, quartz enters into the composition of rocks and ore deposits of most diverse genesis.

1. It is an essential constituent of many intrusive and effusive acid *igneous* rocks, along with feldspars and micas (granites, gneisses, quartz rocks, etc.). Porphyry quartz crystals in acid effusive rocks have a crystalline-banded texture and often contain inclusions of volcanic glass.

2. Large crystals (rauchtopaz, morion, amethyst, etc.) occur in cavities in *pegmatites* and also in association with feldspars, muscovite, topaz, beryl, tourmaline, and other minerals. Intergrowths are often observed with large individuals of potassium feldspars — orthoclase and microcline, whose polished specimens display patterns resembling Hebrew characters. It is characteristic that all quartz inclusions in each feldspar crystal have a uniform optical orientation.

3. Being a constant mineral of veins, in which it occurs in large masses, quartz is common in *hydrothermal* deposits extremely numerous throughout the world, in which it occurs in association with most diverse minerals: cassiterite, wolframite, gold, molybdenite, pyrite, chalcopyrite, tourmaline, calcite, chlorites, etc. Quartz practically always contains microinclusions of gases, liquids, and mineral solids.

Agates and onyxes as amygdules (secretions) of most diverse forms and sizes are widespread in many effusive rocks—melaphyres, bazalts, andesites, etc. (altered blister lavas). The formation of these varieties was due to the migration of concentrated colloidal silica solutions into the above rocks at the latest stage of hydrothermal processes.

4. In the course of *exogenous* processes, quartz and chalcedony, in the form of fine-granular aggregates, derive from the dehydration and crystallisation of silica gels. Sometimes, quartz crystals are formed in cavities, e.g., in the fissures of exogenously silicified limestones, serpentinites, and other rocks.

The formation of chalcedony in these conditions is much more extensive since it is due not only to the dehydration of silica gel, but also takes place independently. It has been deposited, for example, after opal in the voids between colloform segregations of the latter. Chalcedony occurs most widely as flints in limestones, and as nodules in the crust of weathering, resembling the amygdules and geodes of homogeneous chalcedony of hydrothermal origin found in effusive igneous rocks.

5. In the course of *metamorphism*, large masses of quartz are formed by dehydration of opal-bearing sedimentary rocks which gives rise to the so-called jaspers and laminated hornfels (very close-grained quartz and quartz-chalcedony rocks).

Most interesting, however, both from the mineralogical and the practical standpoints are veins of the "Alpine-cleft" type in lenticular fissures developing in the course of metamorphic and schist-forming processes (p. 133). In large cavities and fissures, the walls may be lined with well-formed, often large, crystals of quartz accompanied by chlorites, feldspar, rutile, brookite, etc. These veins and crystals have many specific features. The rock crystal individuals have most diverse orientation in respect of the walls of the cavities. It has been found that their orientation depends on that of the quartz grains exposed in the wall rock which served as the initiators for the large crystals that have grown in the cavity. Undeformed rock crystals are piezoelectric.

Being resistant to weathering and chemically inert, quartz accumulates as detrital grains in placers and sedimentary rocks (sandstones, quartzites).

Quartz pseudomorphs have been found after most diverse minerals: calcite, barite, gypsum, feldspars, olivine, etc., and also after animal and vegetal remains.

Since quartz deposits are very numerous, we shall limit ourselves to the most important localities.

The following deposits in the U.S.S.R. are highly interesting mineralogically: old pegmatite mines at *Murzinka*, *Lipovka*, and *Shaytansk* (north-east of Sverdlovsk) where druses of excellent rock crystals, smoky quartz, and amethyst occur associated with feldspars, tourmaline, lepidolite, etc. Pegmatite dikes containing morion and amethyst are widespread in the *Adun-Chilon* ridge (Trans-Baikal country), *Volhynia* (the Ukraine), etc. Quartz veins with rock crystal are also found along the *Aldan* River and in the *Pamirs*.

Sealing-wax-red banded jaspers used as ornamental stones are widespread in the Magnitogorsk area (the Urals). Well-known is the uniformly greenish-grey kalgan jasper, and also the jaspers occurring in the Orsk district (the Southern Urals), which display a wide variety of patterns.

Deposits of the so-called industrial agate occur at *Akhaltsykh* and elsewhere in Transcaucasia. They are genetically associated with sheets of effusive rocks.

Notable foreign localities for noble quartz varieties are (Minas Geraes *Brazil*) and *Uruguay* (mostly amethyst), *Madagascar* (rock crystal), the *Swiss Alps*, etc. All these deposits are in the main associated with pegmatite dikes and quartz veins of the Alpine-cleft type. The best agates are found in India, Brazil, Uruguay, Germany (Oberstein, Rhineland, etc.).

Uses. Quartz and chalcedony have a great many applications.

1. Transparent and beautifully-coloured varieties are used as gemstones.
2. Colourless rock crystal is used in the manufacture of optical instruments.
3. In precision mechanics some varieties of these minerals (especially industrial agate) are used as fulcrums and step bearings, watch jewels, etc.
4. In electronics, for the manufacture of piezoelectric crystal plates for frequency stabilisation, piezoelectric resonators, etc. Only untwinned and perfectly homogeneous crystals (rock crystal, smoky quartz, morion) with a minimum distance of 3.5 cm between the opposite prismatic faces, may be used for these purposes.
5. Quartz is used in making highly refractory and acid-resistant laboratory utensils, and in the manufacture of quartz lamps used in medicine as a source of ultraviolet radiation, since quartz is one of the few minerals transparent to ultraviolet rays.
6. In glass and porcelain making use is made of pure quartz sands with a maximum iron content of 0.002 per cent.
7. Another use of quartz is in the preparation of silicon carbide or carborundum (SiC), a high-grade abrasive, which is harder than corundum.
8. Fine-grained quartz sands are used in sandblasters for polishing metal and stone articles, for cutting certain rocks, and for other purposes.
9. Sandstones composed of cemented rounded quartz grains, as well as their metamorphosed varieties (quartzite rocks) are used as a building material.

TRYDIMITE, SiO_2. *Trydimos* is the Greek for triple; so named because of its frequent occurrence as trillings. The high-temperature modification, β-trydimite, which crystallises in the hexagonal system, in the unstable range readily changes to low-temperature α-trydimite which, though similar in crystal structure, crystallises in the orthorhombic system. Under atmospheric pressure α-trydimite with time may gradually change into the more stable α-quartz. The transformation of β-trydimite into β-quartz, i.e., into a modification of the same hexagonal system but entirely different in crystal structure, is a much slower process involving considerable changes in volume and specific gravity (specific gravity of β-quartz is 2.51, that of β-trydimite 2.26).

The crystals of α-trydimite, which is more stable at low temperatures, occur as pseudohexagonal plates (Fig. 192) or more often as trillings (Fig. 193) with an angle of 35°18′ between the plates. There occur also imbricate and rosette-like aggregates. The colour of α-trydimite is white, greyish-white; sometimes colourless. **Lustre**, vitreous $n_x = 1.473$, $n_y = 1.470$, and $n_z = 1.469$. **Hardness**, 6 to 7. **Cleavage**, imperfect. **Specific gravity**, 2.30.

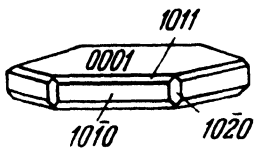


Fig. 192. Tridymite crystal.

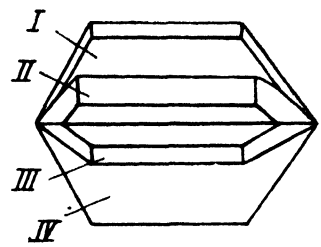


Fig. 193. Tridymite trilling.

Occurs mostly in the cavities of acid effusive rocks: trachytes at Siegengebirge (Germany), andesites at San Cristobal (Mexico), volcanic products of Mt. Vesuvius, etc.

CRISTOBALITE, SiO_2. Named after the place of occurrence San Cristobal (Mexico). Polymorphous modifications: high-temperature β-cristobalite in the cubic system and low-temperature α-cristobalite. The latter crystallises in the tetragonal system, but is at the same time pseudocubic.

Crystals of β-cristobalite are octahedral in habit (Fig. 194), more seldom cubic or skeletal. Twins on (111) are known. **Colour**, milk-white. **Lustre**, vitreous. $n_y = 1.49$. **Hardness**, 7. **Specific gravity**, 2.27.

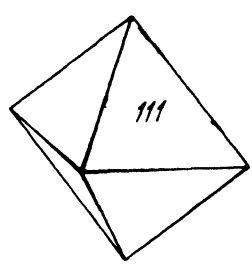


Fig. 194. Cristobalite crystal.

The mineral is readily obtained during the making of quartz glass, and also crystallises during the firing of silica brick. Is found in rapidly-cooled effusive rocks, often together with α-trydimite: in the andesites of San Cristobal (Mexico), the lavas of Main in Rhineland (Germany), Yellowstone Park (U.S.A.) — as globules (spherolites) up to 1 mm in diameter in obsidian (volcanic glass), and also in cavities sometimes with trydimite plates growing over small cristobalite crystals.

Other ways of formation of β-cristobalite are known as well, e.g., through the action of basaltic magma on quartz-bearing sedimentary rocks (sandstones). Cristobalite is in this case formed out of quartz at high temperatures. Such formations have been recorded from upper Tertiary clayey sandstones in Western Georgia (U.S.S.R.).

OPAL, $SiO_2 \cdot nH_2O$. Typical solid hydrogel. The origin of the name is unknown. Varieties differing in physical properties are (1) *precious opal*, opalescent; *hydrophane*, light and very porous, clouded when dry and transparent in water; (3) *hyalite*, stalactitic or globular.

Chemical composition extremely variable. Water content from 1 to 5 per cent, rarely up to 34 per cent. All opals lose some water in a desiccator. This process is especially rapid in the first few days (Fig. 195). On heating some opals lose most of their water at temperatures below 100°, and others at higher temperatures (between 100 and 250°). The causes of this difference in the strength of the water bond is as yet obscure.

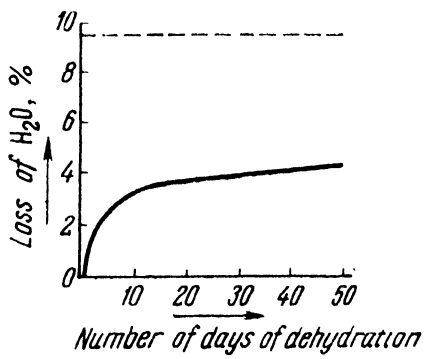


Fig. 195. Dehydration curve for opal (over H_2SO_4).

Morphological features. Usually occurs in compact glassy of sinter-like masses. It is the principal constituent of organisms making up shells of diatoms, siliceous spicules of sponges, the skeletons of radiolaria, partly of some foraminifera and bryozoan feeding on colloidal silica solutions (sols). Owing to the presence of silica, the skeletons of these organisms are well preserved as fossils even in most ancient sediments. Silica hydroxides also enter into the composition of the stalks of cereals, hard nodules of equisetaceous plants, especially of bamboo and other plants that absorb silica sols from the soil through their roots. Silica sols are capable of impregnating dead trunks of trees and completely replacing the wood with opal so that the woody structure is faithfully retained (wood opal).

Colour. Pure opal is colourless, but owing to impurities, especially iron and other chromophores, it occurs in a variety of tinges: yellow, brown, red, green, and black. **Lustre**, vitreous; for porous varieties waxy and earthy. Translucent varieties opalescent (the term itself derives from the name of the mineral). $n = 1.40$ to 1.46.

Hardness, 5 to 5.5 (for varieties with low water content up to 6). Brittle. **Specific gravity**, 1.9 to 2.5 (depending on the content of water and absorbed heavy matter).

Diagnostic features. Compact opals are characterised by glassy appearance and sinter-like shapes. Opal strongly resembles chalcedony externally, differing from it by lower hardness and water content.

Infusible in the blowpipe flame, but often decrepitates violently. Yields water in the closed tube. Insoluble in acids. Rather easily soluble in KOH and HF. Dehydrated opal dissolves in soda with effervescence (due to evolution of CO_2).

Genesis and occurrence. Opal is frequently deposited from *hydrothermal* springs and geysers in volcanic regions as sinters (siliceous tuff, **geyserite**) and of white translucent botryoidal masses with a pearly

lustre. Also occurs in cavities and fissures in effusive rocks, sometimes as amygdules and geodes.

The bulk of opal is formed, however, through exogenous decomposition of silicates as a result of the *weathering* of rocks of most diverse composition, but most frequently ultrabasic. The silica liberated in the disintegration of the crystal structures of silicates first changes into a sol, upon the coagulation of which it is precipitated as sinter-like nodules in the eluvial zone, or is deposited metasomatically, often together with hydroxides of iron, aluminium, and other elements on various bedrocks.

Large opal beds are formed by *sedimentation* through the coagulation of silica sols brought by river waters to near-shore zones of marine basins. These formations include the so-called gaizes, tripolis, diatomites, kieselgur (mountain meal), etc., that are loose or finely porous, sometimes more or less hard rocks, often altered at the surface into chalk-like masses by the mechanical action of freezing water they are saturated with.

Finally, mention should be made of the fossilising role of silica colloids in the metasomatosis of plant remains such as the trunks of trees. Whatever its mode of formation, opal gradually changes into chalcedony or quartz.

Table 8

The Principal Properties of SiO_2 Modifications

Modification	System	Specific gravity	Refractive indices		
			n_x	n_y	n_z
Quartz glass	—	2.204	—	1.460	—
β-cristobalite	Cubic	2.21	—	—	—
α-cristobalite	Tetragonal	2.27	—	1.487	1.484
β-tridymite	Hexagonal	2.26	—	—	—
α-tridymite	Rhombic	2.30	1.473	1.470	1.469
β-quartz	Hexagonal	2.51	—	—	—
α-quartz	Trigonal	2.655	1.553	1.544	—
Opal	—	1.9-2.5	—	1.44	—

Sedimentary opal-bearing rocks (gaizes, tripolis, and diatomites) are especially widespread in Tertiary shallow-water deposits in Ulyanovsk, Saratov and other regions of the European part of the U.S.S.R., along the eastern slope of the Urals; in the Trans-Caspian and the Trans-Caucasian regions and elsewhere. Outside the Soviet Union, the

most important localities are Bohemia, Italy, and Tripoli (hence the name of tripoli). Deposits of precious opals are known on the southern slope of the Carpathians, at Kosice (in cavities in andesite), in New South Wales and Queensland (Australia) in sandstones occupying an enormous territory, and elsewhere.

Uses. Precious opals are ornamental stones. Tripoli is used for polishing metals and stones, and other purposes; kieselgur for the manufacture of filters, ceramics, light-weight bricks, etc.

Summary. Thus all the natural modifications, except opal and lechatelierite (amorphous quartz glass), are characterised by crystal structures comprised of silicon-oxygen tetrahedral networks which share corners, i.e., each silicon ion is surrounded by four oxygen ions, and each oxygen ion by two silicon ions. The structures differ in the spatial orientation of the tetrahedra. As shown in Table 8, the features of crystal structures determine the physical properties of these minerals.

CLASS 2.

HYDROXIDES OF HYDROXYL-CONTAINING OXIDES

The most important minerals in this class are the so-called hydrates or hydroxides, i.e., compounds of metals with the hydroxyl OH radical, completely or partly replacing the oxygen ions in oxides. Thus, $Mg(OH)_2$ corresponds to magnesium oxide—MgO; 2AlO(OH) or 2Al $(OH)_3$ correspond to aluminium oxide—Al_2O_3, etc.

Most of these compounds crystallise in layered structures with the hexagonal or hexagonal-type closest packing of $[OH]^{1-}$ ions. This feature explains many common physical properties of these minerals. The optimal cations of the compounds with layered structure are Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+} and Cr^{3+}.

1. BRUCITE GROUP

The group includes hydrates of divalent metals, such as Mg, Fe, and Mn crystallising in the trigonal or hexagonal system. Only brucite will be discussed here.

BRUCITE, $Mg[OH]_2$. **Chemical composition.** MgO 69%, H_2O 31%. May contain isomorphous admixtures of Fe (ferrobrucite) and Mn (manganobrucite).

System, trigonal; symmetry ditrigonal scalenohedral $L_6^3 3L^2 3PC$. Space group $C\bar{3}m(D_{3d}^5)$. $a_0 = 3.125$; $c_0 = 4.72$. **Crystal structure,** typically laminated. The anion of this structure is a dipole hydroxyl group $[OH^{1-}]$. In the crystal structure these groups follow the pattern of the closest hexagonal packing (Fig. 196). Each layer consists of two flat sheets of hydroxyl ions parallel to the (0001) plane. Sandwiched

between these sheets is a sheet of Mg^{2+} cations that occupy all the *octahedral* sites between the two OH sheets, i.e., each Mg ion is surrounded by six hydroxyl anions, viz., three $[OH]^{-1}$ ions of one sheet and three $[OH]^{-1}$ ions of the other sheet. The perfect cleavage is parallel to the planes between these treble layers which are linked by weak residual forces. **Habit,** thick-tabular. Commonly as foliated talc-like aggregates. Sinter-like metacolloidal formations also occur sometimes.

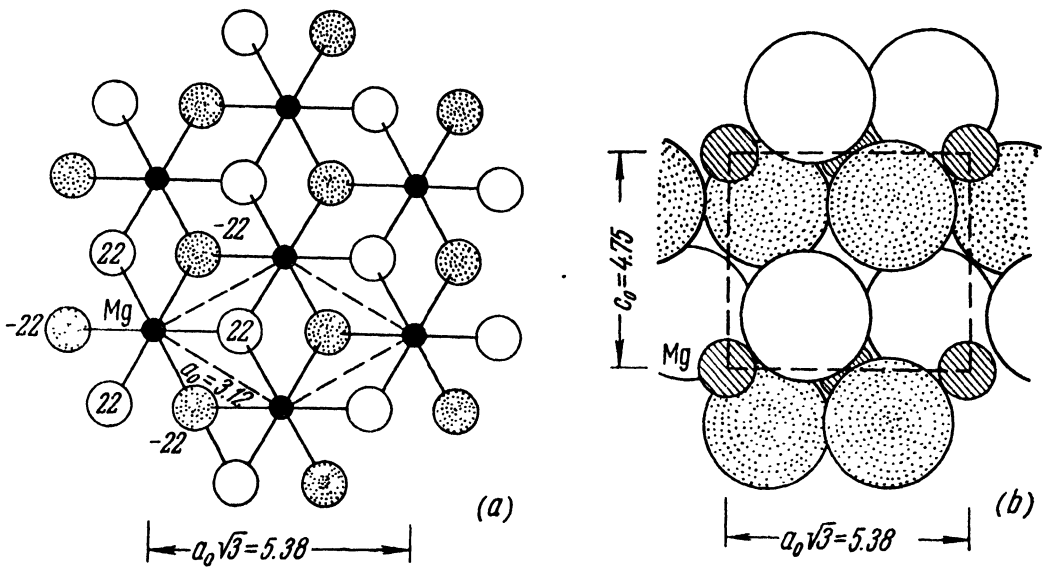


Fig. 196. Crystal structure of brucite.

a – structure projected on (001). White circles (OH) are above, and dotted circles beneath the sheet of Mg^{2+} cations; *b* – a view of two layers saturated with valences, each consisting of two hydroxyl ion sheets and a sheet of magnesium ions in between.

Colour, white, rarely greenish or colourless. **Lustre,** vitreous on fracture and pearly on cleavage surfaces. $n_x = 1.580$ and $n_y = 1.559$.

Hardness, 2.5. **Cleavage,** {0001} excellent. Thin, easily separated foliae flexible. **Specific gravity,** 2.3 to 2.4.

Diagnostic features. Brucite is similar to talc – $Mg_3(OH)_2Si_4O_{10}$, pyrophyllite – $Al_2(OH)_2Si_4O_{10}$, and hydrargillite $Al(OH)_3$. Differs from them sharply by ready solubility in hydrochloric acid.

Infusible, but glows, before the blowpipe flame. Dissolves readily in acids without effervescence. Gives off water in the closed tube.

Genesis. Is formed through hydrolysis of dissolved magnesium compounds in a strongly alkaline environment. Often occurs as thin veinlets and selvages in fissures in serpentinites, these being the product of hydrothermal alteration of magnesia-rich ultrabasic igneous rocks (dunites and peridotites). Associates are serpentine, magnesium hydrocarbonates, aragonite, etc. Sometimes found in dolomitised limestones with calcite, hydromagnesite, and periclase, often as pseudomorphs after periclase, probably of hydrothermal origin. Has also been recorded from strongly alkaline soils.

In a more acidic environment at the surface, brucite readily carbonatises.

Uses. When found in commercial quantity, brucite is a source for metallic magnesium.

In the U.S.S.R., occurs in all unweathered serpentinite masses in the Urals, the Caucasus, and in Siberia. A fibrous asbestos-like variety, nemalite, occurs at the Bazhenovskoye asbestos deposit (town of Asbest, east of Sverdlovsk).

2. HYDRARGILLITE GROUP

This group comprises the so-called trihydrates of certain trivalent metals. The most widespread in nature is $Al(OH)_3$. Ferric hydroxide, $Fe(OH)_3$, which forms first in the hydrolysis of iron salts, is unstable and rapidly dehydrates. Fe^{3+} ions in small quantities may be admixed to $Al(OH)_3$ only isomorphously. Aluminium hydrates also contain Ga^{3+} ions as an isomorphous admixture in quantities much higher than its clark indicates.

HYDRARGILLITE, $Al(OH)_3$. The name derives from the Greek *hydor*—water and *argillos*—white clay. First established in the last century in the Urals. Synonym: gibbsite.

Chemical composition. Al_2O_3 65.4%, H_2O 34.6%. May contain isomorphous admixtures of Fe_2O_3 (up to 2%) and Ga_2O_3 (up to 0.006%). Chemical analyses often show almost complete correspondence of its composition to the formula.

System, monoclinic; symmetry prismatic L^2PC. Space group $P2_1/n$ (C_{2h}^2). $a_0 = 8.624$; $b_0 = 5.060$; $c_0 = 9.700$; $\beta = 94°34'$. **Crystal structure** layered, close to the distorted structure of brucite. Its specific features are explained by the fact that the aluminium ion has a greater charge and smaller radius than the magnesium ion. In hydrargillite, as in brucite, each layer consists of two closely packed sheets of hydroxyl ions with a sheet of Al^{3+} cations in between (Fig. 197). Since the aluminium ion carries a greater charge than the magnesium ion, less Al^{3+} cations will be required to cancel out the negative charge of the hydroxyl ions. Therefore Al^{3+} cations do not occupy all the octahedral sites between the OH sheets, as in the structure of brucite, but only two-thirds of them. As a result, the Al^{3+} ions are arranged not as centred hexagons, as in the brucite structure, but as simple hexagons (cf. distribution of black circles in Figs. 196 and 197). If such a hexagon is outlined, it will be easily seen that in the brucite lattice it would include six hydroxyl ions and three complete Mg^{2+} ions (one central ion and six peripheral ones, each having 2/6 of the valence), i.e., the hexagon will be expressed by the formula $Mg_3(OH)_6$. On the other hand, in the hydrargillite structure, which has the same number of hydroxyl ions, the formula of the hexagon will have only two Al^{3+} ions, i.e., will be $Al_2(OH)_6$. Another difference lies in the manner of linkage of the

treble layers: while in the brucite structure each $(OH)^{1-}$ ion is located against the centre between the three $(OH)^{1-}$ ions of the adjacent layer, in the hydrargillite structure each $(OH)^{1-}$ ion of one layer lies opposite to each $(OH)^{1-}$ ion of the next layer (see the right-hand drawings of Figs. 196 and 197).

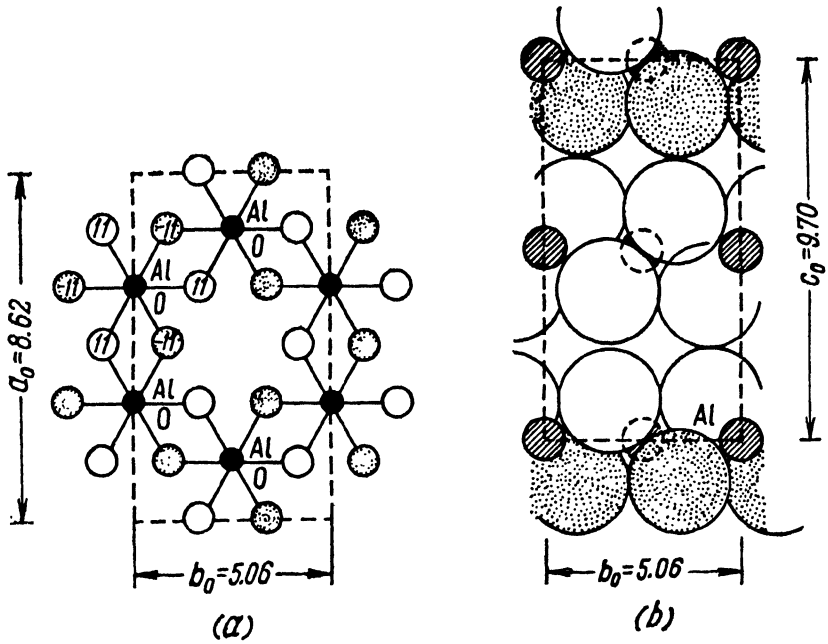


Fig. 197. Crystal structure of hydrargyllite.

Habit, hexagonal-tabular (Fig. 198). Occurs in complex twins according to several laws, usually along (100) and (110). More often as radial-foliated aggregates, sometimes as sinters or pisolitic and globular concretions. The bulk of hydrargillite at the earth's surface occurs as thin-scaly or cryptocrystalline masses.

Colour, white or slightly greyish, greenish, and reddish. **Lustre,** vitreous, pearly on cleavage surfaces. $n_x = 1.587$, $n_y = 1.566$, and $n_z = 1.566$.

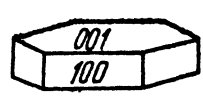


Fig. 198. Hydrargyllite crystal.

Hardness, 2.5 to 3.5. **Cleavage,** parallel to the basal pinacoid {001} excellent. **Specific gravity,** 2.43. **Other properties.** On heating changes to boehmite, AlOOH, and on ignition up to 950° to γ-Al_2O_3 (with a spinel-type cubic structure).

Diagnostic features. Characteristic features of hydrargillite are excellent cleavage, vitreous lustre, and low specific gravity. Differs from similar diaspore by hardness (6 to 7 for diaspore), from mica by specific gravity and optical properties (micas are optically negative).

Infusible in the blowpipe flame, but yields OH, and becomes white and opaque. The hydroxyl is lost in two stages: (1) at a temperature of 202-196° (conversion to boehmite) and (2) at a temperature of

510° (further dehydration). Ignited hydrargillite becomes bright-blue when moistened with Co solution. Like hydrates of other metals, dissolves in dilute hydrochloric acid.

Genesis and occurrence. Derives from the decomposition and hydrolysis of aluminium-bearing silicates, partly in the course of *hydrothermal* processes (at a comparatively low temperature), but chiefly from *surface weathering*, mainly under tropical and subtropical climatic conditions.

Hydrargillite of hydrothermal origin occurs rather rarely and in negligible amounts. It has been observed in certain endogenous deposits as one of the last minerals to crystallise from low-temperature hydrothermal solutions.

In the process of weathering in tropical countries aluminium hydroxides, including hydrargillite, are usually formed together with iron hydroxides. Hydrargillite is present in far greater amounts in the so-called *laterites**, i.e., products of weathering widespread in modern tropical countries as a mantle over bedrock, and comprised mainly of hydroxides containing Fe_2O_3 and, to a smaller extent, Al_2O_3 and SiO_2. It is also found in *bauxites* which are essentially aluminium hydroxides and are also formed by *sedimentation* in bodies of water, apparently as a result of weathering and denudation of aluminium-bearing rocks.

The formation of bauxites in certain deposits is also attributed to decomposition of limestones and dolomites under exogenous conditions, the assumption being that the clayey residues were further decomposed in alkaline environment and the silica thus liberated carried away.

In the course of regional metamorphism hydrargillite loses its water changing to diaspore, and to corundum (emery) at greater depths, or in the presence of SiO_2 to alumosilicates.

In the Soviet Union, hydrargillite occurs as an accessory of diaspore in bauxite deposits in the *Tikhvin* district, Leningrad Region, and elsewhere. Hydrargillite crystals up to 5 cm across, and hence of mineralogical value, have been recorded from hydrothermal formations of the *Shishim* and *Nazyam* mountains in the Zlatoust district (Southern Urals) in metamorphic schists, and also as the alteration product of nepheline in the pegmatites of Vishneviye mountains (Middle Urals).

Uses. Hydrargillite, like such constituents of bauxite as diaspore and boehmite, is a source of alumina, for making aluminium. Bauxites used for this purpose should not contain more than 10 to 15 per cent of silica.

The chemical industry uses slightly ferruginous (light-coloured) bauxites to obtain aluminium salts, mostly sulphates. Bauxites of lower grades are used for the manufacture of abrasives (alundum and

* "Later" is the Latin for brick (the weathering products have the colour of well-fired brick).

aloxite) and refractories for high-temperature furnaces (with a melting point above 2000°). Increasing use is made of special grades of bauxites as adsorbents in refining of mineral and vegetable oils, in the manufacture of paints, as catalysts, etc.

SASSOLITE, $B(OH)_3$. System, triclinic; symmetry, pinacoidal. Occurs in fine-scaly, hexagonal-tabular colourless or slightly coloured crystals. Lustre, vitreous; pearly on cleavage surfaces. Optically negative. $n_x = 1.459$, $n_y = 1.456$, and $n_z = 1.340$.

Hardness, 1. Cleavage {001}, excellent. Specific gravity, 1.48. Readily fusible. Colours the flame green. Poorly soluble in cold water.

Occurs as white efflorescences—products of fumarole activity in volcanic areas: in large amounts on Volcano Island (the Lipari Archipelago, north-east of Sicily), in cracks of Avacha Volcano on Kamchatka, and elsewhere. Was first found at Sasso in Tuscany (Italy). Dissolved boron hydroxide is often recognised in oil reservoir waters and in the products of mud volcanoes (on the Kerch Peninsula and along the Caucasian coast of the Caspian Sea).

3. LEPIDOCROCITE-GOETHITE GROUP

Included in this group are the so-called monohydrates of trivalent metals: Al, Fe, Mn, and Co. The compounds are dimorphous and crystallise in the orthorhombic system.

The lepidocrocite subgroup (FeOOH) includes its aluminium analogue—boehmite (AlOOH), while the goethite ($HFeO_2$) subgroup includes diaspore ($HAlO_2$). Manganite the empiric formula of which is similar to the above compounds will also be described here, although otherwise it has little in common with them.

BOEHMITE, AlOOH. Named after Boehm who established the presence of this mineral in bauxite by X-ray studies; the mineral resembles lepidocrocite (FeOOH) in crystal structure.

Chemical composition, the same as of diaspore. Al_2O_3 84.97% (according to formula). Contains also SiO_2, Fe_2O_3 (probably as a mechanical admixture of opal and iron hydroxides), and also Ga_2O_3.

System, orthorhombic; symmetry rhombic dipyramidal. Space group *Amam* (D_{2h}^{18}). $a_0 = 3.78$; $b_0 = 11.8$; $c_0 = 2.85$. **Crystal structure**, analogous to that of lepidocrocite and is described below. **Habit.** Occurs in cracks and pores in bauxite and also in the decomposition products of nepheline as very small lamellar or lenticular crystals (Fig. 199) usually in combinations: (010), (111), (113), {110}, etc. Characteristically, the faces {010} are lustrous, whereas the faces of other forms are dull. Usually occurs as cryptocrystalline masses or as colloform aggregates (in bauxites).

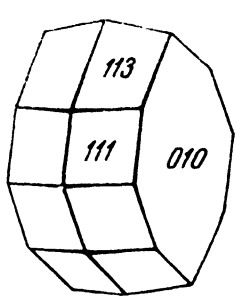


Fig. 199. Boehmite crystal from Vishneviye mountains.

Colour. Colourless or white with a yellowish tinge. The average refractive index for cryptocrystalline varieties is 1.640-1.645.

Hardness, 3.5. **Cleavage,** {010} perfect. **Specific gravity,** 3.01 to 3.06. On ignition changes to γ-Al_2O_3 (cubic modification crystallising in the spinel structure).

Diagnostic features. In view of the extremely small size of crystals, a debyegram is the most reliable means of identification. Differs from diaspore by lower refractive index and lower hardness.

Before the blowpipe does not fuse, but turns white, and splits along cleavage planes. Gives off water in the glass tube. Insoluble in acids.

Genesis and occurrence. Until recently boehmite has been found only in *exogenous* bauxite deposits (cf. hydrargillite). Lately it was discovered in the ancient crust of weathering of the Yakovlevskoye deposit (Kursk Magnetic Anomaly) in association with kaolinite overlying metamorphic schists of ferrous-magneso-aluminous composition. Still more recently, it was found as a low-temperature hydrothermal mineral in small crystals (Fig. 199) in cavities in pegmatites of alkaline rocks of the *Vishneviye mountains* (Middle Urals) associated with water-transparent hydrargillite on acicular zeolite (natrolite) crystals. It has probably formed through hydrothermal alteration of nepheline.

LEPIDOCROCITE, FeOOH. *Lepidos* is the Greek for plate, *crocos*, saffron. Synonym: rubinglimmer.

Chemical composition, similar to that of goethite. According to the chemical analyses data, contains far less impurities than goethite. As the latter has varieties containing adsorbed water (in finely crystalline colloform masses) called *hydrolepidocrocite*, $FeOOH \cdot nH_2O$.

System, orthorhombic; symmetry, rhombic dipyramidal. Space group *Amam* (D_{2h}^{17}). $a_0 = 3.87$; $b_0 = 12.51$; $c_0 = 3.06$. **Crystal structure.** As shown in Fig. 200, the Fe^{3+} cations are surrounded by six oxygen ions (the front and the rear anions have been left out) which occupy the apexes of distorted octahedra arranged in chains parallel to the *a* axis. The chains are laterally (through octahedral edges) linked with each other into continuous double sheets parallel to (010), i.e., perpendicular to the plane of the drawing (in the vertical direction). Figure 200 shows the double sheets connected to each other by weak hydrogen bonds in the form of continuous zigzag strings: $-O-H-$ $-O-H-O-$. Each O^{2-} anion adjacent to the H ions, is linked on one side with two Fe^{3+} cations and receives one half of valence from each of them; on the other side, it is bonded with two H cations, its valence being thus fully saturated. As for the O^{2-} anions within the double sheets (Fig. 200), their valences are also fully saturated by the shares of valences supplied by Fe^{3+} cations (each O anion is surrounded by four Fe cations). Thus, two types of oxygen ions take part in the structure of lepidocrocite, and, therefore, the formula of this mineral must be written as FeOOH. Hydroxyl ions as such are absent. In the

goethite ($HFeO_2$) structure, however, all the oxygen ions are chemically equivalent. The less close packing of ions in the lepidocrocite structure is reflected in its lower specific gravity. **Habit.** Occurs in fine crystals, platy along (010), in cavities (Fig. 201), but mostly in fine-scaly or fibrous aggregates. Sometimes in reniform aggregates on the walls of geodes.

Colour, dark-red to reddish-black, sometimes shows a golden tinge (in scaly masses). **Streak**, orange or brick-red. **Lustre**, adamantine. Thin polished sections transparent. $n_x = 2.51$, $n_y = 2.20$, and $n_z = 1.94$.

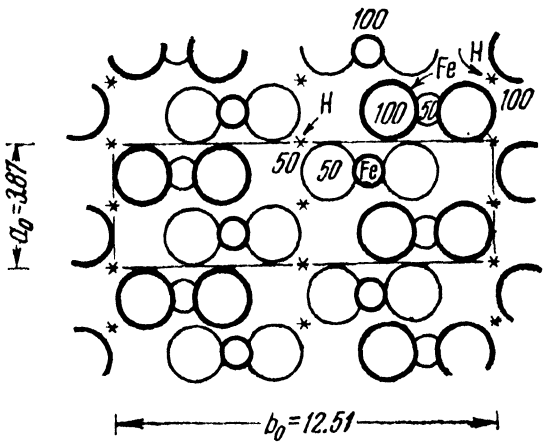


Fig. 200. Crystal structure of lepidocrocite, FeOOH. Large circles – oxygen ions, small circles – Fe^{3+} ions. Possible positions of H^{1+} ions shown by asterisks.

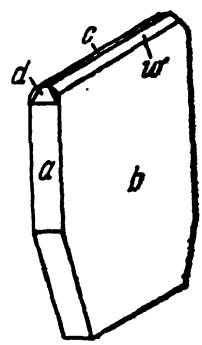


Fig. 201. Lepidocrocite crystal *a* {100}, *b* {010}, *c*{001}, *d*{201}, *w*{031}.

Hardness, 4. **Cleavage**, {010} excellent and {001} perfect. **Specific gravity**, 4.09 to 4.10.

Diagnostic features. Often mistaken for hematite, especially in massive aggregates. Separate laminae are readily identifiable by crystal form, red colour in transmitted light, orange- or brick-red streak, and low specific gravity (as different from hematite).

Infusible in the blowpipe flame; at high temperatures becomes black and magnetic. Gives off water in the closed tube. Soluble in hydrochloric acid.

Genesis and occurrence. Lepidocrocite in platy crystals (ruby mica) occurs occasionally as one of the last-formed minerals in *hydrothermal* deposits, e.g., at *Siegen*, Westphalia (Germany), and in iron-ore vein deposits (in the cavities of quartz stringers) in the Angara-Ilim region (U.S.S.R.) and elsewhere. Much more often, lepidocrocite occurs in concentric layers of scaly aggregates in brown ironstone sinters or on the walls of geodes of *surface* origin: at the Poletayevskoye deposits (south-west of Chelyabinsk), near Lipetsk, and elsewhere.

Microscopic and X-ray examination of the products formed on prolonged heating shows that lepidocrocite is capable of altering to goethite. The conditions under which these transformations occur and

under which various modifications of iron monohydroxide are formed have not yet been fully established. Possibly, the acidity of the environment (pH) in which iron hydroxides are formed plays an important part in this process.

DIASPORE, $HAlO_2$. *Diaspore* is the Greek for dispersal (some specimens, when heated, crack and disintegrate into small particles). First established in the last century in the Urals.

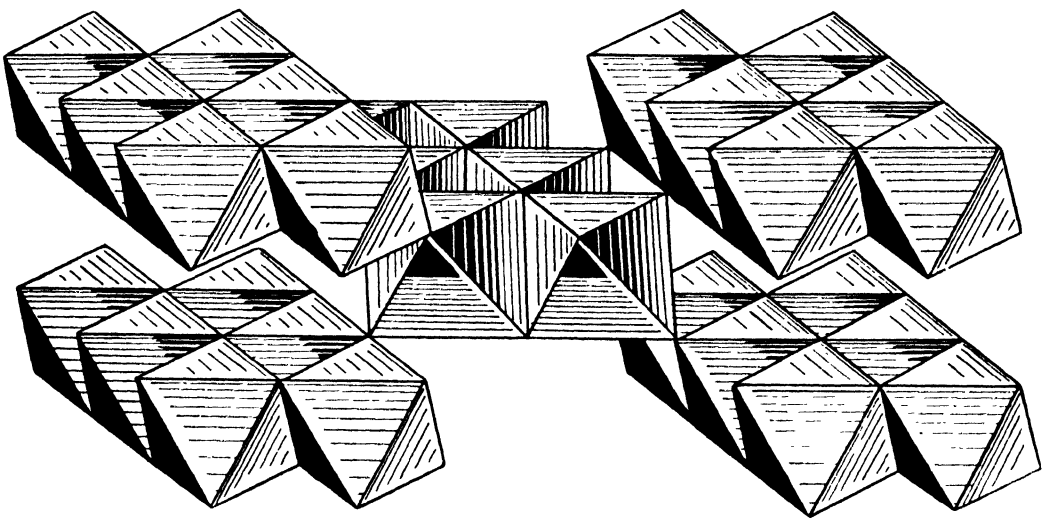


Fig. 202. Crystal structure of diaspore presented as Pauling octahedra.

Chemical composition. Al_2O_3 85%, H_2O 15%. Certain varieties contain as isomorphous admixtures Fe_2O_3 (up to 7%), Mn_2O_3 (mangandiaspore), Cr_2O_3 (up to 5%), and SiO_2 (up to 4%). May also contain up to several hundredths of per cent of Ga_2O_3.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Pbnm(D_{2h}^{16})$. $a_0 = 4.40$; $b_0 = 9.36$; $c_0 = 2.84$. **Crystal structure** is shown in Fig. 202. It is characterised by the close hexagonal packing of O^{2-} ions, with the Al^{3+} ions occupying the octahedral voids, i.e., between six oxygen ions. Each oxygen ion is linked with three Al ions, i.e., the coordination numbers for Al and O are the same as in the crystal structure of rutile (6 and 3). The H^{1+} protons are probably located between the pairs of oxygen ions (Fig. 202), and owing to their infinitesimal size, do not need any space of their own within the crystal structure. Thus, the structure of diaspore is practically composed of Al and O ions in the 1 : 2 ratio (as in rutile). Its similarity to rutile, as demonstrated by N.V. Belov, is also structural with the difference that in diaspore (goethite), instead of single columns, there are pairs of closest-packed columns parallel to the *c* axis. Hence the platy habit, cleavage, and geniculate twins at an angle of about 122°.

Habit, platy, sometimes tabular (010) (Fig. 203), and frequently columnar parallel to the *c* axis. Faces striated vertically. Usually occurs in foliated or scaly aggregates.

Colour, yellowish-brown, white, light-violet, greenish-grey. **Lustre**, vitreous; pearly on cleavage surfaces. **Streak**, white. $n_x = 1.750$, $n_y = 1.722$, and $n_z = 1.702$.

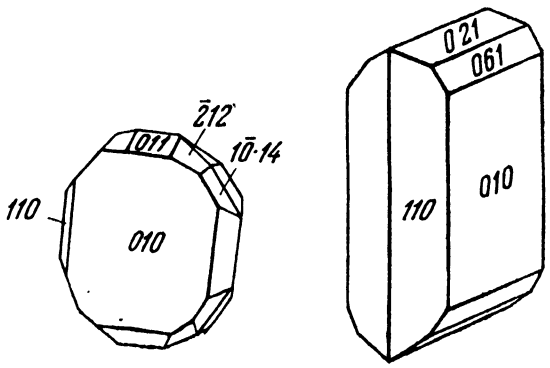


Fig. 203. Diaspore crystals. The second axis in left-hand figure faces the viewer.

Hardness, 6 to 7. Very brittle. **Cleavage**, {010} distinct. **Specific gravity**, 3.3 to 3.5. On ignition changes to α-Al_2O_3 (corundum).

Diagnostic features. Foliated aggregates, high hardness (as compared with hydrargillite, micas, etc.). May be mistaken only for certain varieties of chloritoid (alumosilicate of Fe and Al), a mineral sometimes associated with diaspore and corundum in metamorphic rocks from which it is almost indistinguishable by external features. In contrast to chloritoid, diaspore is not soluble in sulphuric acid, and has somewhat different optical properties.

Infusible in the blowpipe flame. Insoluble in acids and KOH. Becomes soluble in sulphuric acid only after strong ignition. On heating in a test tube disintegrates into small white scales.

Genesis and occurrence. Occurs rarely in *contact-metasomatic* and *hydrothermal* deposits in marbled limestones in association with corundum, muscovite, hematite, rutile, etc.

Large masses and scaly aggregates occur in *exogenous* bauxite deposits in association with hydrargillite, boehmite, etc.

Often found in *metamorphic* rocks with corundum, chloritoid, and other minerals (in emery deposits, probably as a product of bauxite metamorphism), sometimes in crystalline schists as a rock-forming mineral, accompanied by disthene and other minerals.

In the U.S.S.R., occurs associated with corundum and alumosilicates, in emery rock deposits in the Urals such as Kossoy Brod (Sverdlovsk district), in marbled limestones along the Borzovka River (Kyshtym district), and also at Aktash (Uzbekistan) in association with dumortierite, pyrophyllite, alunite, corundum, etc.

Large plates and crystals occur in the emery mines of Chester, Massachusetts (U.S.A.) and on the Island of Naxos (Greece).

For uses of bauxites see *Hydrargillite.*

GOETHITE, $HFeO_2$ and **LIMONITE** (hydrogoethite), $HFeO_2 \cdot nH_2O$. Named after Goethe (1749-1832). At first the mineral was called onegite, after the place of discovery (Lake Onega), but since its properties were not described, the name has not survived in mineralogical literature. Synonym: acicular iron ore (in German literature).

The name of limonite derives from the Greek *lemon* for meadow (allusion to meadow and bog ores).

Chemical composition. Fe_2O_3 89.9%, H_2O 10.1%. The water content is often in excess of that given by the formula and may be as high as 12 to 14% for limonite. For this reason several mineral species were formerly distinguished according to water content and certain physical properties. X-ray data show that there is actually only one compound with a ratio of $Fe_2O_3 : H_2O = 1 : 1$, possessing a definite crystal structure. All the iron hydroxides richer in water are actually hydrogels containing varying amounts of adsorbed water, depending on the degree of dehydration.

The so-called *turgite*, according to X-ray and thermal analyses, is a mixture of goethite with hydrohematite and, therefore, not a mineral in its own right.

The accumulations of natural iron hydroxides are mostly mixtures of goethite with limonite, and also with silica hydroxides, argillaceous matter, etc. These mixtures are usually called *brown iron ores.*

System, orthorhombic; symmetry, rhombic dipyramidal. Space group *Pbnm*. $a_0 = 4.64$; $b_0 = 10.0$; $c_0 = 3.03$. **Crystal structure**, analogous to that of diaspore. **Habit and aggregates.** Rare acicular or columnar crystals (Fig. 204). Occasional twins similar to geniculate twins of rutile along (011). Usually in sinter-like, reniform, or stalactitic forms (Fig. 45) of thin radial- or parallel-fibrous texture on fracture (needle iron ore) or in porous, spongy, slagy or pulverulent masses. Pseudomorphs after crystals of pyrite and other iron sulphides are quite frequent. Also occurs in the forms of oölites, pisolites, concretions, and geodes.

Colour of limonite and goethite is dark-brown to black. Pulverulent or ochrous limonite which often derives from the physical weathering of compact black limonite and iron silicates is rather light yellow-brown in colour. From comparative chemical and X-ray evidence this ochrous variety does not differ materially from compact limonite. **Streak** of goethite is brown with a reddish tinge. That of limonite is mostly light-brown or yellow-brown. **Lustre** of goethite adamantine to submetallic. Goethite is often found on the surface of reniform or stalactitic limonites as thin lustrous pitch-black crusts. $n_y = 2.35$ to 2.39.

Hardness, 4.5 to 5.5 for goethite and 4 to 1 for limonite, depending on physical condition. **Cleavage** of goethite {010} perfect. **Specific gravity**, 4.0 to 4.4 for goethite and 3.3 to 4.0 for limonite.

Diagnostic features. Goethite and limonite are rather easily identifiable by colloform formations, brown streak and yellow-brown ochrous selvages.

Fusible in the blowpipe flame; upon prolonged heating become strongly magnetic. In the glass tube give off water, and turn red, altering to anhydrous Fe_2O_3. Slowly dissolve in hydrochloric acid.

Genesis and occurrence. In small acicular or columnar crystals goethite very rarely occurs as an *endogenous mineral*: in cavities of melaphyres, in amethyst geodes on Volk-Ostrov (an island on Lake Onega); sometimes in hydrothermal deposits as one of the most low-temperature minerals in cavities, e.g., at Přibram (Czechoslovakia) in association with earlier sphalerite and pyrite untouched by weathering.

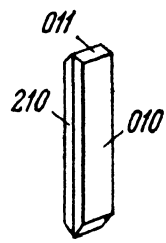


Fig. 204. Goethite crystal.

In the main, however, goethite and limonite are widespread as *exogenous* minerals and almost exclusively as colloform or metacolloidal masses. They are formed for the most part through the hydrolysis of salts deriving from the oxidation and decomposition of iron-bearing minerals: sulphides, carbonates, silicates, etc., in which iron is in divalent form. The formation of iron hydroxides on the earth's surface is observed literally everywhere and in most diverse forms.

Large masses of brown iron ores are found in the oxidised zones of sulphide deposits. These are the so-called *iron hats* (gossans)—loose, lumpy, or compact masses chiefly composed of limonite, goethite, sometimes lepidocrocite, etc.

Large masses of iron hydroxides accumulate in sedimentary deposits of young (Tertiary) brown iron ores accumulated in marine and lacustrine basins. The precipitation of iron hydroxides as well as of other hydroxides in the near-shore zones of these basins is evidently due to the coagulation of colloidal solutions brought by surface waters in marine waters through the action of electrolytes, and in freshwater lakes through the life activity of ferrobacteria. In addition to that, in certain sedimentary deposits iron hydroxides are formed as a result of recent oxidation of the carbonate and silicate iron ore facies in the oxidised zone.

Thus, limonite and goethite are formed almost exclusively at the very surface of the earth in the conditions of free access of oxygen and moisture.

In the course of regional metamorphism iron hydrates lose their water and are converted to anhydrous oxides (hematite and magnetite).

Deposits of brown iron ores of diverse origin are very widespread. The U.S.S.R. has many huge deposits.

Uses. Brown iron ores, as well as hematites and magnetites, are a very important source of iron and steel. In the blast-furnace, the ores are completely dehydrated and converted into very finely-porous

masses. Since the rate of ore reduction greatly depends on the specific surface of the mass, these ores are more economical than magnetite and hematite ores. Therefore, their permissible minimum iron content is 35-40% (instead of 50 to 60% for compact magnetite and hematite ores).

MANGANITE, $Mn^{\cdot\cdot}Mn^{\cdot\cdot\cdot\cdot}O_2(OH)_2$, or $MnO_2 \cdot Mn(OH)_2$. The presence of di- or tetravalent (not trivalent) manganese was established through the study of the magnetic anisotropy of the ions.

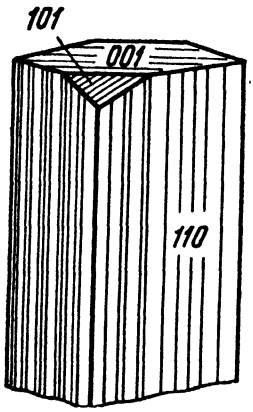


Fig. 205. Manganite crystal.

Chemical composition. MnO 40.4%, MnO_2 49.4%, H_2O 10.2%. Impurities: SiO_2(up to a few per cent), Fe_2O_3 (up to 1 per cent), negligible quantities of Al_2O_3, CaO, etc. The H_2O content in cryptocrystalline and oölitic masses of manganite, as well as in goethite, may be in excess of the limit indicated by the formula (hydromanganite). Dehydration curves show that the excess water is adsorbed.

System, monoclinic; symmetry, prismatic. Space group $B2_1/d(C_{2h}^5)$. $a_0 = 8.86$; $b_0 = 5.24$; $c_0 = 5.70$; $\beta = 90°$. **Crystal structure** materially differs from that of goethite and still awaits deciphering. **Habit**, prismatic (Fig. 205), columnar parallel to the *c* axis. Faces {110} are deeply striated vertically. **Aggregates.** In cavities of hydrothermal deposits manganite occurs often in druses of columnar crystals. In sedimentary deposits occurs widely as finely-crystalline aggregates, also as oölites, and rarely as sinters.

Colour, black. **Streak**, brown. **Lustre**, submetallic. $n_x = 2.53$, $n_y = 2.24$ and $n_z = 2.24$.

Hardness, 3 to 4. Brittle. **Cleavage**, {010} perfect. **Specific gravity**, 4.2 to 4.33.

Diagnostic features. Crystals readily identifiable by columnar habit, characteristic striation of prism faces, and also by brown streak. The distinguishing feature of colloform water-abundant variety is brown colour of both the mineral and the streak. Positive identification requires X-ray photography.

Infusible in the blowpipe flame. In the closed glass tube gives off abundant water. Borax and salt of phosphorus beads in the reducing flame are violet (presence of manganese). Dissolves in concentrated hydrochloric acid with evolution of chlorine.

Genesis and occurrence. Manganite generally forms under conditions of oxygen deficiency. Occurs as druses of crystals in certain *hydrothermal* manganese deposits, being one of the last minerals to be formed in paragenesis with barite and calcite.

Occurs in quantity in *sedimentary* deposits as oölites or massive occupying an intermediate place between the facies of psilomelane-

pyrolusite ores (compounds of tetravalent manganese), and of carbonate ores containing divalent manganese located farther from the coastline.

Sometimes is found as globules of radially fibrous texture in clays.

Unstable in the oxidised zone, changing readily to cryptocrystalline, almost anhydrous MnO_2, i.e., all the manganese is oxidised to tetravalent manganese. Therefore, manganese hats comparatively rarely contain manganite.

Huge masses of manganite are found at *Chiatury* as brown oölitic ores. As black globular concretions it is widespread at the *Nikopol* deposit (the Ukraine).

Crystals, sometimes large, have been recorded from the hydrothermal deposits of *Ilfeld*, Hartz; *Ilmenau*, Thuringia (Germany), and elsewhere.

Uses. Along with psilomelane pyrolusite-ores, manganite is an important material for ferromanganese and other ferrous alloys (spiegel and silicospiegel) used in steel making.

4. PSILOMELANE GROUP

This group comprises diverse manganese hydroxides of complex and variable composition, occurring as cryptocrystalline and colloform masses. Earlier they were all classified with amorphous substances. Subsequently, however, on the basis of X-ray studies, many were found to be crystalline. In crystal structure they differ sharply not only from the oxides and hydroxides of manganese, reviewed heretofore, but also from one another. The differences, according to V.I. Mikheyev's incomplete X-ray studies, depend on the cations in their composition.

The chemical composition of many of these hydroxides is still obscure. They are complex hydrates, the simplest of which is the "monohydrate" of manganese dioxide, $MnO_2 \cdot H_2O$. This, in V.I. Vernadsky's opinion, corresponds to natural metamanganous acid, H_2MnO_3, which can be easily obtained in the laboratory in the form of a chocolate-brown gel.

More complex compounds include, besides the MnO_2 and MnO manganese oxides, the following oxides: K_2O, BaO, CaO, sometimes PbO, ZnO, CoO, NiO, CuO, occasionally Li_2O, WO_3, P_2O_5, As_2O_5, etc. There also have been recognised colloidal mixtures of hydroxides of manganese with those of SiO_2, Fe_2O_3, Al_2O_3, and with organic substances. These compounds have many different names depending on metal oxides entering into their composition. But in field practice these mineral species are known under the general name of "psilomelane".

The mineral species can be identified positively by means of debyegraphs and chemical analyses. Thermographs are unfortunately almost useless in the diagnostics of these minerals.

The soft pulverulent brown or black varieties of psilomelane were formerly known as "wad". Today this term has lost its meaning, since detailed investigation of the varieties with the aid of X-rays and chemical analyses has shown that this form includes many minerals of the most diverse composition: mineral species of the psilomelane group, and also manganite, vernadite, etc.

PSILOMELANE, $m\mathrm{MnO}\cdot\mathrm{MnO_2}\cdot n\mathrm{H_2O}$. The precise formula has not been established as yet. *Psilos* is the Greek for bald *melas*—black. In the United States it has been suggested that the term be used for the variety in which barium predominates, called by other authors romanechite. The reason for this is that the first specimens which were given the name of psilomelane proved to be rich in barium. However, the most widespread variety of the psilomelane group is poor in barium.

Chemical composition is variable. The $\mathrm{MnO} : \mathrm{MnO_2}$ ratio varies greatly according to the degree of oxidation of the manganese protoxide. The $\mathrm{MnO_2}$ content is usually 60 to 80 per cent, whereas that of MnO only 8 to 25 per cent, and $\mathrm{H_2O}$ from 4 to 6 per cent (most of it evaporates at temperatures over 110°). Small amounts of BaO (up to a few per cent) are often present, sometimes alkalis, CaO, CoO, MgO, ZnO, and also $\mathrm{SiO_2}$, $\mathrm{Fe_2O_3}$, $\mathrm{Al_2O_3}$ as foreign admixtures. $\mathrm{WO_3}$ (up to 1 per cent, occasionally 5 to 8 per cent) is sometimes present, in which case the variety is called *tungomelane.*

System, orthorhombic (?). Usually occurs in sinter masses with a concentric banded structure or as fine crystalline aggregates. Often as dendritic coatings (cf. Fig. 47).

Colour, black, sometimes brownish-black. **Streak**, usually black. **Lustre**, submetallic, for friable varieties dull.

Hardness, 4 to 6 (for compact varieties), varies depending on water content and physical state. Brittle. **Specific gravity**, 4.4 to 4.7.

Diagnostic features. As a member of the psilomelane group identifiable by sinter aggregates, black streak, and characteristic manganese reaction. Positive identification, however, is possible only by means of chemical analysis.

Infusible in the blowpipe flame. Dissolves in hydrochloric acid with evolution of chlorine. In the closed tube gives off water and oxygen. Gives a violet bead with borax and salt of phosphorus in the reducing flame.

Genesis and occurrence. As other minerals of the group, is formed mostly exogenously in the *oxidised zones* of manganese ore deposits and in deposits of *sedimentary* origin. Is also found as a minor mineral in the manganese ores of *hydrothermal* origin.

In the oxidised zone it is mostly a secondary mineral derived from braunite, hausmannite, sometimes from manganous silicates and carbonates (together with vernadite), but occasionally directly through the coagulation of manganese hydroxides—as sinters in cavities or massive.

In sedimentary deposits of manganese psilomelane occurs as compact intercalations or as oölites and globular concretions with a concentric-conchoidal structure.

In the course of weathering psilomelane is oxidised and dehydrated, being converted into pyrolusite, mostly on the surface of cavities and pores, often as a black sooty mass. Among the biggest sedimentary manganese deposits containing psilomelane are those at *Chiatury* (Transcaucasia) and *Nikopol* (the Ukraine).

Uses. Together with pyrolusite and other manganese oxide minerals, it is the principal ore for ferromanganese. The low-manganese ores are added to blast-furnace charges.

General. In this last section devoted to inorganic minerals we shall consider complex compounds which, from the chemical standpoint, are salts of various oxygen acids. This class includes nearly two-thirds of all the known minerals. Hence their importance in mineralogy.

Silicates are the most predominant among these components. Also very numerous are sulphates and phosphates. All of them occur in the earth's crust only in the solid state and are a product of chemical reactions proceeding under most diverse geological conditions.

We shall not dwell on the general chemical characteristics of the oxysalts, since they are thoroughly discussed in chemical textbooks.

However, it should be remembered that salts are generally divided into *anhydrous* and *hydrous* (containing H_2O molecules), and further subdivided as follows.

1. *Acid salts* (e.g., nahcolite or acid sodium carbonate, $NaHCO_3$) containing an H^{+1} proton instead of one metallic cation. These salts are comparatively rare in nature.

2. *Normal* or *medium* salts, such as calcite (calc-spar), $CaCO_3$, and gypsum, $CaSO_4 \cdot 2H_2O$, which are the most widespread in nature.

3. *Basic* salts containing $[OH]^{1-}$ hydroxyl ions that neutralise the surplus positive charge of the cations. They are very common in nature, e.g., malachite, $Cu_2[CO_3][OH]_2$, and aluminite, $Al_2[SO_4][OH]_4 \cdot 7H_2O$.

In the basic salts, the $[OH]^{1-}$ anion, as has been confirmed in many instances, may be partly or completely replaced by other anions, mostly by the equidimensional F^{1-} anion, sometimes by O^{2-} and Cl^{1-} anions (the structure remaining unchanged). All such salts, including those containing OH, we shall term as *salts with additional anions.*

Binary and more complex salts, as compounds of definite composition, differ from simple salts in that either cations or anions, or both, are represented by different ions which do not or almost do not replace one another isomorphously. Examples: dolomite, $CaMg[CO_3]_2$, tychite, $Na_6Mg_2[CO_3]_4[SO_4]$.

Salts of *variable composition* reveal both isovalent and heterovalent isomorphism. In the latter case, positive and negative charges are always in equilibrium. Examples: ferrorhodochrosite, (Mn, Fe) Co_3; chillagite, $Pb[MoO_4, WO_4]$; and wilkeite, $Ca_5[PO_4, SiO_4, SO_4]_3[F, OH]$.

Crystallochemical features of compounds. The characteristic feature of the crystallochemistry of the oxysalts is the presence in their crystal structures of *anionic groups*: $[NO_3]^{1-}$, $[CO_3]^{2-}$, $[SO_4]^{2-}$, $[PO_4]^{3-}$, etc. The cations located in the centres of these groups have small ionic radii, high charges (Fig. 206) and are linked with the oxygen ions by the covalent type of bonding.

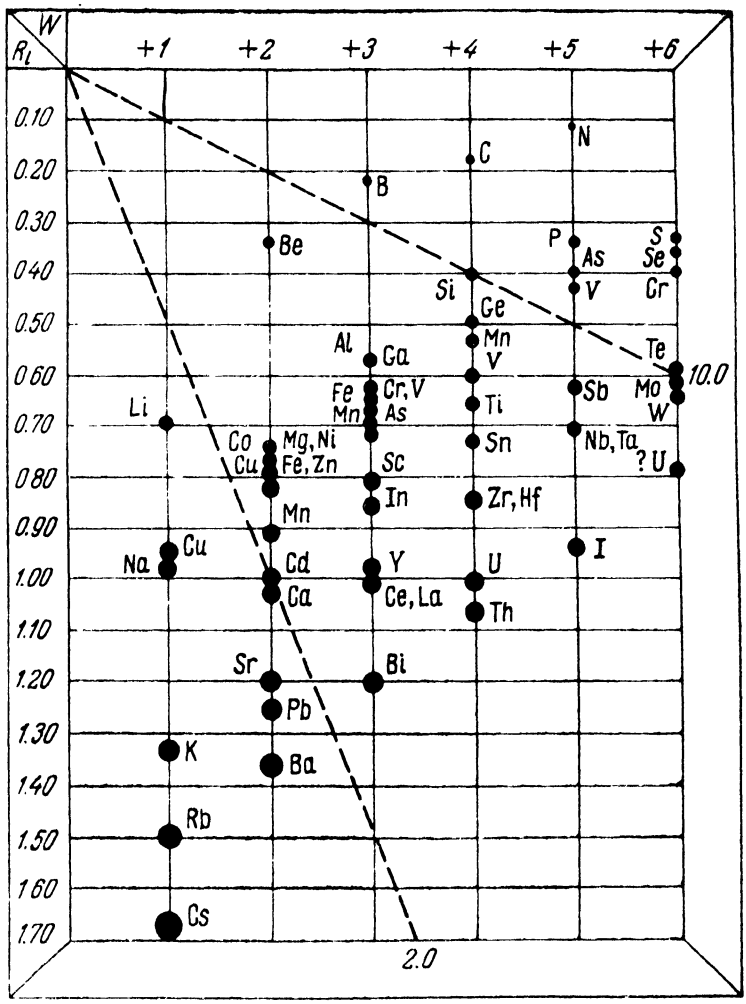


Fig. 206. Chart of principal cations widespread in natural compounds.

It should be emphasised that the bonding of the oxygen ions with the central cation is very strong and depends on the so-called electrostatic valence, i.e., the share of the cationic charge taken by each surrounding oxygen ion. Thus, in the $[NO_3]^{1-}$ anionic group, which consists of one N^{5+} and three surrounding O^{2-} ions, each oxygen ion shares the charge in the ratio of 5 : 3; in the $[CO_3]^{2-}$ anionic group this ratio is 4 : 3, in $[SO_4]^{2-}$ 6 : 4; in $[PO_4]^{3-}$ 5 : 4, etc.

This ratio everywhere exceeds unity (i.e., more than half of oxygen valence is spent for the bonding with the central cation), and only for $[BO_3]^{3-}$ and $[SiO_4]^{4-}$ it is unity. This means that the oxygen ions are more strongly bonded with the smaller cations within the group than with the cations in the crystal structure outside the group. It is in this that the oxysalts differ materially from complex oxides for which the values of electrostatic valences of bonds between the cations and the surrounding oxygen ions are always less than unity.

Thus, anionic groups constitute very strongly bonded compact radicals participating in crystal structures as *independent* structural units. Their independent nature is also stressed by the fact that they do not disintegrate upon the dissolution of the salts. They differ materially from simple anions in shape and, naturally, in size. The XO_4-type anions have tetrahedral coordination and closely resemble isometric bodies in shape. The XO_3-type anions are flat triangles (CO_3 and BO_3), more seldom obtuse pyramids (AsO_3, etc.), in which the O ions are at the corners of the triangles, while the bonding cation is located over the centre of the triangle.

Apart from the anionic groups of simple configuration, there exist, as will be shown later, more complex radicals. It is noteworthy that they are found in borates and silicates, i.e., salts of the weakest acids.

The salts of stronger acids have crystal structures in which the type of bonding is typically ionic, as in halides, with the only difference that anionic groups take the place of simple anions. No wonder, therefore, that in a number of physical properties these salts closely resemble the minerals belonging to the class of chlorides and fluorides.

The principal anionic groups of simple structure, which occur in natural oxysalts, are listed in Table 9 in the order of increasing electrostatic valences of ionic potentials. The table also gives the anionic sizes or ionic "radii" (according to A. Y. Fersman). It should be noted that the concept of radii of anionic groups is a purely fictional one. The values cited were obtained by A. Y. Fersman by purely theoretical calculations and are all approximate. These tentative values are useful, however, for general consideration of the properties of minerals, especially when it is remembered that properties depending on the energy of the crystal lattice such as hardness, fusibility, volatility, relative solubility, etc., are estimated in practice by very rough scales.

The same data are shown graphically in Fig. 207. For the sake of comparison, the graph also shows as white circles the univalent simple anions of the halides, and divalent simple anions entering into the composition of oxides, sulphides, selenides, and tellurides.

Since the vast majority of oxysalts are typically ionic compounds, the stability of the crystal structures should largely depend on the ratio of sizes of the cations and anions as structural units. For the oxysalts, these ratios cannot be expressed in any numerical values

since the size of anionic groups cannot be expressed in the terms of radii, their configuration differing materially from the spherical shape which is conventionally attributed to simple ions.

However, there is no doubt that such isometric complex anions as $[SO_4]^{2-}$, $[PO_4]^{3-}$, and $[SiO_4]^{4-}$ should be far larger than simple anions (e.g., O^{2-}). It is natural, therefore, that the anions in simple compounds of AX-type (where X is a complex anion) should give *the most stable* crystal structures only in combination with *large* cations. Such compounds indeed have low solubility, low fusibility, and low volatility. Here are some examples.

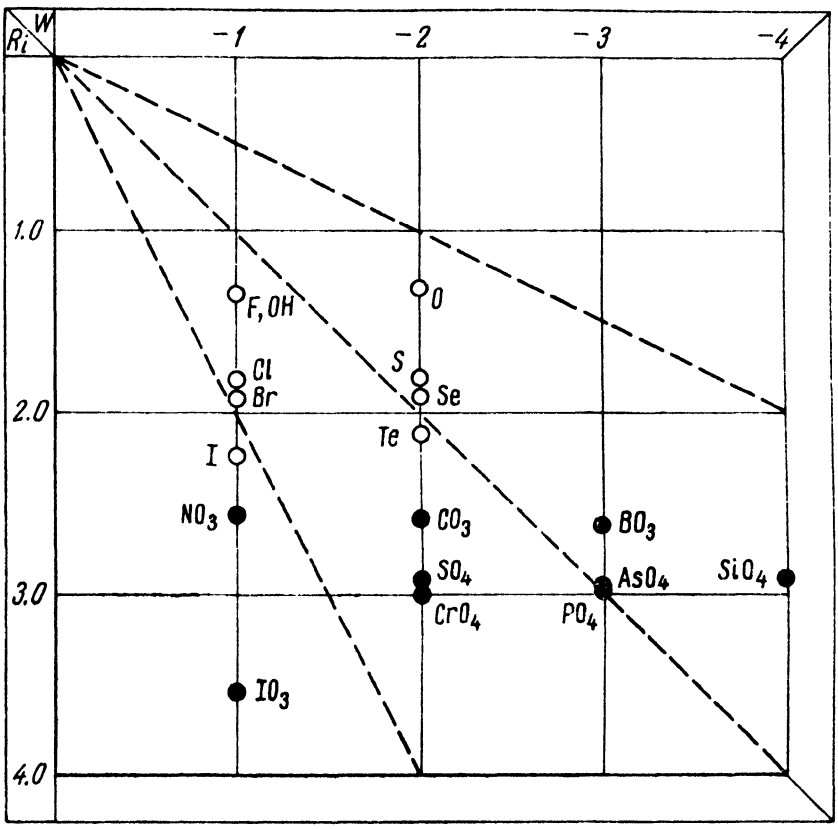


Fig. 207. Approximate dimensions of complex anions (black circles) compared with those of simple anions occurring in natural compounds.

In compounds of the AX-type (i.e., with anion-to-cation ratio of 1 : 1) the divalent $[SO_4]^{2-}$ anion gives the following most stable compounds (sulphates): barite, $BaSO_4$, and anglesite, $PbSO_4$, i.e., in combination with the *largest* divalent cations (see column of divalent cations in Fig. 206). This also explains the isomorphous admixture of Ra^{2+} in Ba^{2+} sometimes found in barites (the ionic radius of Ra^{2+} is somewhat larger than that of Ba^{2+}). No wonder, that in the oxidised zones of uranium deposits, which contain sulphides subjected to the

action of sulphate waters, the concentration of radium in relation to uranium is higher than in the zones of primary ores (the compounds of hexavalent uranium are much more soluble under these circumstances than those of radium sulphate).

As to the divalent cations with *small* ionic radii in nature they are capable of forming only *hydrous sulphates* crystallising at low temperatures and at the last stages of crystallisation of solutions. In most instances, hydrous salts contain 2, 4, 6 and 7 molecules of H_2O. X-ray studies of the $NiSO_4 \cdot 6H_2O$ compound show that the Ni^{2+} cation in the crystal structure is surrounded by 6 electrically neutral (not compensating for the cationic charge) water molecules. Therefore, the volume of such hydrated cations is artificially increased, as it were, which makes possible a crystal structure containing such large anions as $[SO_4]^{2-}$. From the crystallochemical standpoint, the formula of this compound should be more correctly written as $[Ni(H_2O)_6]SO_4$. Such hydrous salts have definitely increased or high solubility and are easily dehydrated, their crystal structures undergoing rearrangement or complete destruction.

It should be noted that the medium-sized Ca^{2+} cation (Fig. 206), which under certain conditions forms the $CaSO_4$ anhydrous sulphate (anhydrite), in the presence of water alters to the more stable hydrous $CaSO_4 \cdot 2H_2O$ compound (gypsum)*. Gypsum, according to X-ray studies, has a layered structure in which the H_2O molecules are located between the sheets of Ca^{2+} and $[SO_4]^{2-}$ ions. Hence highly perfect cleavage of gypsum crystals in this direction.

The $[PO_4]^{3-}$ trivalent anion reveals a picture similar to that of sulphates. The largest trivalent cations (Fig. 206), which are capable of combining with this anion into stable crystal structures, are the rare earths (Ce . . .) and La. Indeed, widespread in nature is a very stable rare-earth phosphate—(Ce, La . . .) PO_4 (monazite). In the process of weathering, monazite being a chemically inert mineral passes into placers. It is not accidental that the most important rare-earth concentrations are associated with this mineral. Another, less stable, phosphate, YPO_4 (xenotime) occurs less frequently. Phosphates with smaller trivalent cations (Al, Fe^{3+}, Mn^{3+}) occur in nature as hydrous salts.

A significant fact is that the $[SiO_4]^{4-}$ anion forms the most stable compounds with large tetravalent cations (Zr^{4+}, and Th^{4+}, often with an isomorphous admixture of U^{4+} uranium): zircon, $ZrSiO_4$, and thorite, $(Th,U)SiO_4$.

The crystal structures of thorite and its varieties are destroyed only through radioactive decay. Zircon, which does not contain radioactive elements, is a very stable mineral and therefore is widespread in the form of rolled grains in placers and sediments of most different ages. The bulk of zirconium in the earth's crust is concentrated in this

* Containing fewer H_2O molecules than in the previous case.

mineral. Only in silica-poor and alkali-rich magmas is it capable of forming other minerals.

Classification. It is customary to classify salts according to their acid radicals or, which is the same thing, according to complex anions. The order in which they are placed may be the same as that of electrostatic valences or ionic potentials (Table 9). It would be logical to begin the discussion of oxysalts, which immediately follow such oxides as the quartz group minerals, with silicates and borates crystallochemically closest to them and to finish it with the iodates, in the order of diminishing anionic potentials. However, for easier presentation, the reversed, simple-to-complex pattern seems more convenient, the carbonates coming under discussion before the sulphates.

Table 9

Complex Anions of Principal Natural Oxysalts

Anions	"R_t"	Electrostatic valency	Ionic potential	Shape of anion
$[NO_3]^{1-}$	2.57	0.19	0.39	Triangle
$[CrO_4]^{2-}$	3.00	0.34	0.67	Tetrahedron
$[SO_4]^{2-}$	2.95	0.34	0.68	Ditto
$[CO_3]^{2-}$	2.57	0.39	0.78	Triangle
$[PO_4]^{3-}$	3.00	0.50	1.00	Tetrahedron
$[AsO_4]^{3-}$	2.95	0.51	1.02	Ditto
$[BO_3]^{3-}$	2.68	0.56	1.12	Triangle
$[SiO_4]^{4-}$	2.90	0.69	1.38	Tetrahedron

The minerals corresponding to oxysalts fall into the following classes:

1. Nitrates.
2. Carbonates.
3. Sulphates.
4. Chromates.
5. Molybdates and tungstates.
6. Phosphates, arsenates, and vanadates.
7. Borates.
8. Silicates.

CLASS 1.

NITRATES

General. In the earth's crust, nitrogen occurs exclusively in the form of complex anions such as $[NO_3]^{1-}$ and $[NH_4]^{1+}$, and in the form of gas in the atmosphere.

The nitrates as salts of strong nitric acid, HNO_3, easily soluble in water are confined almost exclusively to recent formations in hot

desert countries. They derive their nitrogen from the atmosphere. The oxidation reactions of the element are predominantly biogenic, i.e., associated with bacterial activity in soils or possibly with atmospheric electricity discharges (on high plateaus).

The most important are the nitrates of alkalis – K and Na. Less important are nitrates of alkali earths – Mg, Ca and Ba. In the oxidised zones of copper deposits, in the conditions of desert weathering, rare Cu nitrates of complex composition sometimes occur. Compounds of nitrates with hydrates and salts of other acids are also known.

SODA NITRE, $NaNO_3$. Synonym: Chile saltpetre.

Chemical composition. Na_2O 36.5%, N_2O_5 63.5%.

System, trigonal; symmetry, ditrigonal scalenohedral $L_6^3 3L^2 3PC$. Space group $R\bar{3}c(D_{3d}^6)$. $a_0 = 5.07$; $c_0 = 16.81$. Isostructural with calcite. Crystallises in rhombohedra which, in polar angle, are very close to the rhombohedra of calcite. Characteristically resembles calcite in a number of other properties as well. Twins are along $(01\bar{1}2)$ and also along (0001), $(02\bar{2}1)$ $(10\bar{1}1)$. Generally as granular crusts and efflorescence.

Colour, white, grey, reddish brown, and lemon-yellow. **Lustre**, vitreous. $n_y = 1.585$.

Hardness, 1.5 to 2. Brittle. **Cleavage**, rhombohedral $(10\bar{1}1)$, perfect. **Specific gravity**, 2.24 to 2.29.

Diagnostic features. Gives a flash in the blowpipe flame on charcoal; fuses readily, colouring the flame yellow (Na). Readily soluble in water. Taste, slightly saline, cool.

Genesis. Formed in hot arid regions, devoid of vegetation, through biochemical decomposition (oxidation) of nitrogen-bearing organic matter (guano and other droppings of birds and animals) as well as of algae, nitrobacteria, etc. The rare atmospheric precipitations wash down newly formed nitre into hollows and ravines where soda nitre settles forming saltierras or even massive deposits.

Minerals occurring in paragenetic association with soda nitre are gypsum, mirabilite (sodium hydrosulphate), halite, occasionally iodates, etc.

The greatest deposits of soda nitre are located on a high plateau in *Chile*, at the foot of the Andes. For millions of years, beginning with the Upper Cretaceous period, the region was a very hot and arid desert (rain once in 4 or 5 years).

In the U.S.S.R., deposits of saltpetre, mainly potassium nitrate, are fairly widespread in the form of saltierra formations on hills and in ravines.

Uses: (1) saltpetre is the best of mineral fertilisers; (2) as a strong oxidiser it is used in the treatment of nickel ores; (3) as decoloriser in the glass industry; (4) as a preserving agent for canned fish, meat, etc.; (5) as a component of gunpowder and various explosives.

With the advent of industrial catalytic synthesis of nitrogen compounds (ammonia and nitric acid) from atmospheric nitrogen, the world output of natural soda nitre declined sharply. However, the soda nitre deposits have retained their importance for the local industries.

POTASSIUM NITRATE, KNO_3. Synonym: saltpetre.

System, orthorhombic; symmetry, orthorhombic dipyramidal. Space group *Pnma*. $a_0 = 5.42$; $b_0 = 9.17$; $c_0 = 6.45$. Occurs as friable white crusts and efflorescences similar to those of soda nitre. $n_y = 1.505$. **Hardness**, 2. **Cleavage**, {011} perfect. **Specific gravity**, 1.99. Behaviour before the blowpipe is similar to that of soda nitre.

Potassium nitrate is more widespread than soda nitre. In the past India was an important producer (the deposits are now depleted). As crusts and efflorescences it is widespread mostly in the same localities as soda nitre.

CLASS 2.

CARBONATES

General. This class includes numerous mineral species some of which are relatively widespread in nature. This is especially true of $CaCO_3$ which often forms enormous sedimentary series of marine origin. Carbonates are often accessories of metalliferous ore deposits and sometimes are a source of important metals, e.g., manganese (rhodochrosite), and iron (siderite).

The $[CO_3]^{2-}$ anion can form more or less stable compounds with cations of divalent metals with medium or large ionic radii. Such metals are few in number, the most important being Mg, Fe, Zn, Mn, Ca, Sr, Pb, Ba, and also Cu, Zn, Pb, etc., with additional $[OH]^{1-}$ and Cl^{1-} anions.

Univalent cations (Na, K, and NH_4), which very closely approach these metal cations in size, may form anhydrous carbonates, provided, however, that the crystal structure contains an H^{1+} cation, i.e., in the form of acid salts. Hydrocarbonates are also characteristic of the Mg^{2+} cation, which is in general prone to hydration in aqueous environments.

Carbonates of trivalent metals are known for rare earths with an additional F^{1-} anion. Of the smaller trivalent cations, the carbonates occasionally contain only Al^{3+}, and then always as binary and hydrous salts of divalent metals (Cu and Pb).

There are no carbonates of tetra- or pentavalent metals. Hexavalent uranium forms a rare anhydrous carbonate with an additional O^2 anion, $UO_2(CO_3)$ (rutherfordite). All the other known carbonates of uranium are hydrous.

The carbonates possess certain specific physical properties. The hardness of anhydrous carbonates is never high, usually ranging from

3 to 5. They are well soluble in water. This is especially true of carbonates of alkalis and bicarbonates of those elements whose cations have relatively small ionic radii, e.g., Mg^{2+}, Co^{2+}, or on the contrary those, whose ionic radii are very large, e.g., Ba^{2+}. The Cu^{2+} carbonate occurs exclusively in the form of basic salts, which probably depends on the structure of the cation itself. This is also probably the cause of the intense green and blue colours of copper carbonates. All the other carbonates are either colourless or of pale colours. Optically the carbonates are characterised by comparatively high birefringence (n_x-n_z) due to the flat shape of the CO_3 anion.

Anhydrous and *hydrous* carbonates constitute the primary subdivisions of the class, each being further divided into groups of isostructural chemical compounds. The remaining carbonates occur in nature as isolated mineral species and will be grouped according to their cations.

Anhydrous Carbonates

1. CALCITE GROUP

This group comprises a great number of mineral species that are carbonates of the following divalent metals (in the order of increasing ionic radii): Mg, Zn, Fe^{2+}, Mn^{2+}, Ca, Sr, Pb, and Ba. It should be noted that ions with radii smaller than that of Ca yield extensive isomorphous series of minerals crystallising in the trigonal system, whereas ions with radii longer than that of Ca form carbonates in the orthorhombic system. The carbonate of calcium itself is dimorphous, i.e., it can crystallise in either system.

Carbonates	Mg	Zn	Fe^{2+}	Mn^{2+}	Ca			
trigonal system	0.74	0.83	0.80	0.91	1.04			
					Ca	Sr	Po	Ba
orthorhombic system ..					1.04	1.20	1.26	1.38

The crystal structure of the trigonal modification of $CaCO_3$ is shown in Figs. 208 and 209.

If the cubic structure of NaCl is compressed along the threefold axis so that the interfacial angles become 101° 55′, the result will be the rhombohedral face-centred structure of calcite (Fig. 209), in which the Ca ions will take the sites of Na, while the $[CO_3]$ groups—the sites of Cl. Thus the packing of ions in calcite corresponds to a somewhat distorted closest *cubical* packing of the structural units.

The crystal structure of aragonite, the orthorhombic $CaCO_3$ modification, differs from that of calcite in that the Ca^{2+} and $[CO_3]^{2-}$ ions are arranged in the closest *hexagonal* packing (Fig. 210). Hence the pseudohexagonal symmetry of crystal trillings (interfacial prism angles in some of the crystals are very close to 60 and 120°). Both in the calcite and aragonite structures each $[CO_3]^{2-}$ ion is surrounded by

six calcium ions. Judging by the difference in specific gravity, the crystal structure of aragonite is more compact than that of calcite.

Another important characteristic of the calcite minerals is the tendency to form isomorphous mixtures and binary salts. In the calcite

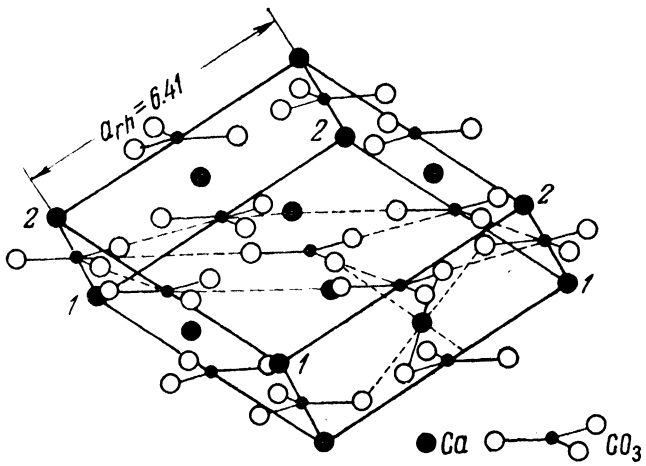


Fig. 208. Arrangement of ions in unit cell of a cleavage rhombohedron $\{10\bar{1}1\}$. Both types of ions arranged as in face-centred structures.

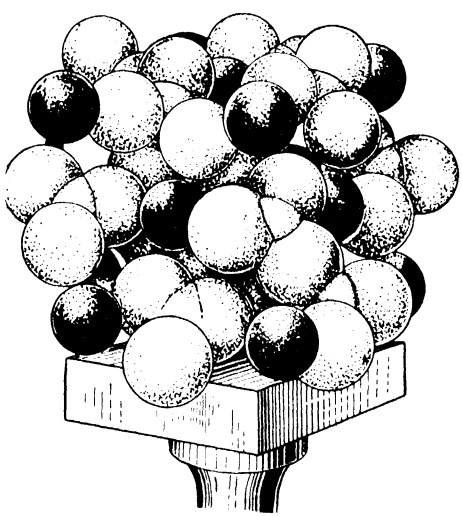


Fig. 209. Model of calcite crystal structure.

Black spheres – calcium cations; light-coloured triangles – CO_3 anions.

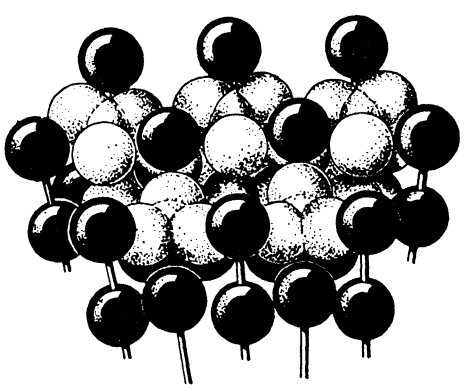


Fig. 210. Model of aragonite crystal structure.

series, Mg, Zn, and Fe^{2+} extensively replace each other as it should have been expected in view of the relationship between the ionic radii of the cations.

The carbonates of Fe^{2+} and Mn^{2+} similarly form a continuous series of isomorphous mixtures. As for Ca, whose ionic radius differs

materially from those of the above cations (except Mn^{2+}), it is capable of forming only binary salts with them. Calcium and magnesium ions (or other small cations) alternate in crystal structures parallel to the threefold axis. As a result, the symmetry of binary salts of the calcite series is of a somewhat lower order: instead of the ditrigonal scalenohedral class ($L_6^3 3L^2 3PC$) we have a rhombohedral class ($L_6^3 C$), i.e., there are no twofold axes passing through the central carbon ion or the oxygen ions surrounding the latter.

CALCITE, $CaCO_3$. Synonym: calcareous spar. It is a member of a very extensive isomorphous group. *Iceland spar*, a colourless and transparent variety (Fig. 19) has remarkable optical properties.

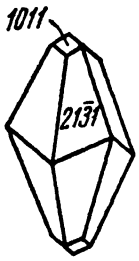


Fig. 211. Scalenohedral calcite crystal.

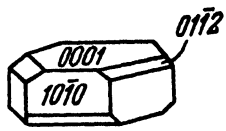


Fig. 212. Tabular calcite crystal.

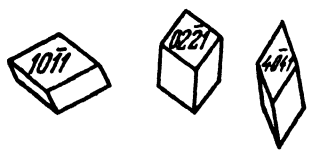


Fig. 213. Rhombohedral calcite crystals.

Chemical composition. CaO 56%, CO_2 44%. Impurities: Mg, Fe, Mn (up to 8%), much more rarely Zn (up to 2%), Sr (strontian calcite), etc.

System, trigonal; symmetry, ditrigonal scalenohedral $L^2 L_6^3 3PC$. Space group $\bar{R}3c(D_{3d}^6)$. $a_0 = 4.98$; $c_0 = 17.02$. **Crystal structure** is typical of the group (see description above). **Habit** of crystals occurring exclusively in cavities is extremely diverse. The most common are scalenohedral crystals (Fig. 211), more seldom tabular (Fig. 212) or platy, prismatic or columnar; rhombohedrous, more frequently acute than obtuse (Fig. 213). The known simple forms of crystals number several hundreds. The most common faces are prismatic $\{10\bar{1}0\}$; rhombohedral $\{10\bar{1}1\}$ (cleavage rhombohedron), $\{01\bar{1}2\}$, $\{02\bar{2}1\}$, $\{40\bar{4}1\}$; scalenohedral $\{21\bar{3}1\}$; pinacoidal $\{0001\}$, etc. The twinning plane is usually (0001) of a pinacoid (Fig. 214) or the $(01\bar{1}2)$ face of an obtuse rhombohedron, parallel to which polysynthetic twins are often formed in marbles and crumpled limestones (such twinning may be obtained artificially by exerting pressure with a knife edge on the cleavage edge of a calcite fragment). More rarely the twinning plane is the face of the cleavage rhombohedron $(10\bar{1}1)$ (Fig. 215), etc.

Aggregates. As stated earlier, druses of calcite crystals together with other minerals occur in cavities. Coarse-granular aggregates of transparent or translucent calcite, with individual granules possessing perfect cleavage occur fairly often. A rare occurrence is veined asbestos-like calcite with silky lustre (satin spar), the fibres of which run perpendicular to the walls of fissures in rocks. Well known are

deposits of calcite in the form of stalactites and stalagmites in caverns in limestones. Large compact masses of calcite are known as *marbles*. Compact cryptocrystalline varieties of calcitic rocks often stratified and rich in fossil fauna, are called *limestones*. Friable limestones containing minute shells of foraminifera are known as chalk. There is also oölitic limestone sometimes also called roestone (Fig. 44). The terms "calcareous tufa" and "travertine" are applied to the porous calcium-carbonate formations around cold and hot lime-saturated mineral springs (calcite in such cases forms through the recrystallisation of de-

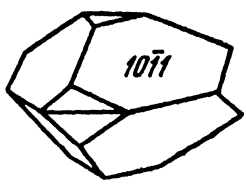


Fig. 214. Calcite twin on (0001).

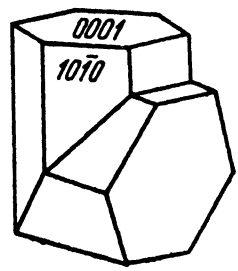


Fig. 215. Calcite twin on $(10\bar{1}1)$.

posited $CaCO_3$ colloids, or aragonite). Sometimes, carbonate of lime depositing from hot springs produces thinly banded translucent compact varieties of a remarkable pattern, known as "onyx marble".

Colour. Predominantly colourless or milk-white, but when impure may have different (usually light) shades of grey, yellow, pink, red, brown, and black. **Lustre**, vitreous. $n_y = 1.658$ and $n_z = 1.486$.

Hardness, 3. Brittle. **Cleavage**, {1011} perfect. **Specific gravity**, 2.6 to 2.8, and for chemically pure crystals 2.72 at 23°. **Other properties.** When compressed, yields twins and becomes electrically charged. Specimens from some deposits display luminescence, the cause of which is not clear yet.

Diagnostic features. Coarse-crystalline varieties readily identifiable by rhombohedral cleavage, rather low hardness (can be scratched easily with a knife point or a needle), and by vigorous effervescence when the mineral or its powder is moistened with a drop of hydrochloric acid.

Decrepitates before the blowpipe flame with evolution of CO_2, i.e., dissociates into CaO and CO_2. The resultant CaO glows brightly and colours the flame orange. Dissolves well with effervescence in dilute hydrochloric acid (even cold) (evolution of CO_2).

Genesis. Calcite is one of the most widely distributed minerals in the earth's crust and may form whole massifs (limestone mountains). Its formation takes place in the course of most diverse geological processes.

1. Very widespread are crystalline formations of *hydrothermal* origin. It is formed in large masses in contact-metasomatic deposits through re-deposition or recrystallisation of limestones. In pegmatites it is one of the last-formed minerals of the hydrothermal stage. Charac-

teristically in numerous metalliferous, mostly sulphide vein deposits, calcite is, as a rule, among the last minerals to crystallise.

To the same class also belongs calcite amygdules and geodes in effusive igneous rocks, as well as aragonite and calcite deposited from certain mineral springs in the form of "calcareous tufa" (as a result of the vigorous evolution of CO_2 from the spring water due to abrupt decline of external pressure).

2. Although *weathering* processes do not give rise to large accumulations of calcite, some new formations are observed fairly frequently in fissures and cavities within oxidised zones of ore deposits and rocks. In this case the source of calcite are atmospheric carbon dioxide and calcareous minerals decomposing in the weathering crust. It should be noted that in general, in the course of weathering of rocks large masses of lime pass into solution as calcium bicarbonate and may be transported by running waters over large distances, sometimes right to the sea, provided it does not meet on the way the conditions which cause it to precipitate as crystalline or colloidal $CaCO_3$ carbonate.

The stalactites in limestone caves result from the deposition of calcium carbonate from saturated solutions which seep slowly into the caves. Calcium carbonate is deposited when a hanging drop of the solution begins to evaporate, becomes strongly supersaturated, giving up a colloidal or finely-dispersed sinter-like precipitate which gradually solidifies and crystallises with further dehydration.

3. Enormous masses of $CaCO_3$ are formed by *sedimentation*, especially in marine basins, first as calcareous silts, dead marine plants and invertebrates with calcareous skeletons. With time all this material is converted to limestone. Oölitic limestone is most probably formed through coagulation of colloidal solutions of calcium carbonates around minute sand grains and gas bubbles suspended in turbulent water. Recent formation of oölites in marine basins is confined to shallow near-shore zones of tropical and subtropical seas. At first the oölites are composed of aragonite which later on is converted to calcite.

Irrespective of its mode of formation, calcite is a relatively unstable mineral in the weathering crust. In the eluvial zone, and especially in oxidised zones of sulphide-ore deposits, calcite is leached out because of its high solubility in acids. In the course of exchange decomposition reactions calcite is often replaced by other minerals (gypsum, dolomite, smithsonite, malachite, etc.) as shown below:

$$H_2SO_4 + CaCO_3 + H_2O = CaSO_4 \cdot 2H_2O + CO_2$$
$$ZnSO_4 + CaCO_3 + 2H_2O = ZnCO_3 + CaSO_4 \cdot 2H_2O, \text{ etc.}$$

Not only are coagulates of iron hydroxides, colloidal silica, etc., often observed on the surface of limestones in the zone where the ground water is saturated with calcium carbonate, but often the limestones themselves are completely replaced by the coagulates.

Large crystals of transparent calcite (Iceland spar) in the U.S.S.R. have been recorded from deposits along the *Nizhnaya Tunguska River*

ni effusive rocks — traps and mandelstones; here calcite occurs as veins and pockets containing gigantic monocrystal individuals. Numerous small deposits of Iceland spar are widespread in *Central Asia*, in the Zeravshan-Gissar, Pskem-Ugam, and other districts.

Notable foreign localities for Iceland spar are in *Iceland*, where it is found in effusive igneous rocks.

Chalk, as a rock, is widely distributed in thick series of Cretaceous carbonate rocks on the Russian platform and elsewhere in the Soviet Union. It is quarried on a large scale (to be used chiefly in chemical and cement industries) in the *Belgorod* district, in the vicinity of *Slavyansk*, *Kramatorsk* (Donets Coal Basin), and elsewhere.

Marbles of beautiful patterns are quarried in the Urals in the *Ufaley*, *Zlatoust* and other districts; in *Karelia*, the *Trans-Baikal area*, the *Crimea*, and elsewhere. Deposits of yellowish and greenish onyx marbles are known in Transcaucasia (Armenia and Georgia).

Famous foreign localities of excellent marbles are at *Carrara* on the eastern coast of the Gulf of Genoa (Italy) and in *Greece*; the wonderful antique statues were made of these marbles.

Uses. Calcite, especially calcite rocks, has many uses.

1. Iceland spar, owing to its high birefringence, is used in the manufacture of different polarising optical instruments, mainly for nicol prisms for microscopes, polarimeters, colorimeters, etc. For this purpose, colourless and perfectly transparent untwinned crystals or fragments thereof are selected, which must have no cracks and be at least 1.5 to 2 cm in size.

2. Asbestos-like satin spar and onyx marble are used as ornamental stones and gem materials.

3. Limestones, depending on their composition or physical and mechanical properties are used: (a) in chemical industry (pure limestones) for the manufacture of fertilisers, in the production of sugar, soda, caustic soda, chloride of lime, etc. (liquid or solid carbon dioxide is obtained simultaneously as a by-product of calcining); (b) in metallurgy (low-phosphorus and low-sulphur limestones) as flux in blast-furnace process; (c) in making slaked lime, Portland, Roman, and other cements; (d) in the printing industry as lithographic stones (compact cryptomerous limestone with a conchoidal fracture, readily splitting into thin slabs).

4. Polished marbles for facing the internal walls of buildings, for statuary, and also in electrical engineering (switchboards, etc.).

5. Chalk is used for crayons and also in whiting, and polishing preparations as well as for the production of cement, paints, toothpowder, rubber (filler), etc.

ARAGONITE, $CaCO_3$. Named after the place of discovery (Aragon, Spain).

Chemical composition, the same as that of calcite: CaCO 56.0%, CO_2 44.0%. Often contains impurities: Sr (up to 5.6%), Mg, Fe, and Zn.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group, $Pmcn$ (D_{2h}^{16}). $a_0 = 4.94$; $b_0 = 7.94$; $c_0 = 5.72$. **Crystal structure** has been described earlier. **Habit**, prismatic, often pseudohexagonal, acicular. Crystals may have chisel-like terminations (Fig.216). Principal forms: prism {110}, pinacoids {010} and {001}. The pinacoid may be striated parallel to the *a* axis. Other forms: prism

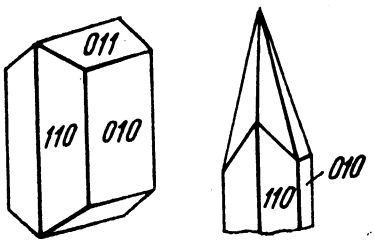


Fig. 216. Prismatic and acicular aragonite crystals.

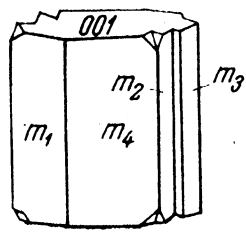


Fig. 217. Aragonite. Penetration trilling on (110).

{011} giving the crystal a chisel-like termination, dipyramid {111}, sometimes very acute dipyramids combined with prisms, making the crystals spear-shaped (Fig. 216). Twins on (110) are frequent as also are trillings of pseudohexagonal habit (Figs. 217 and 218), fourlings and complex polysynthetic twins. Therefore, groove-like reentrant angles between prism faces are quite common. Untwinned crystals are extremely rare. **Aggregates** often occur as rod-like (Fig. 219), radiated, and stellate intergrowths. Also observed as

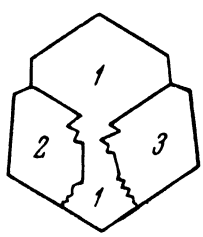


Fig. 218. Penetration boundaries in cross section.

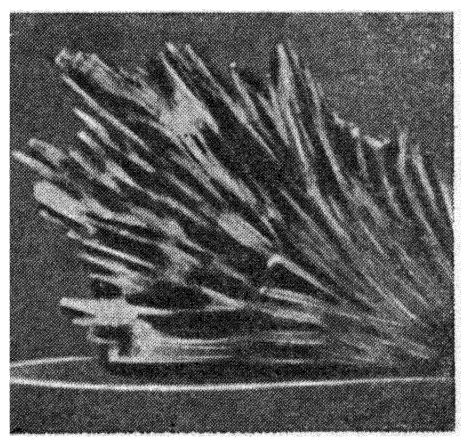


Fig. 219. Aggregate of rod-like aragonite crystals.

crystalline crusts, sinters, globular forms and oölitic masses (pisolitas or roestone). Very striking are occasional "iron flowers" — interlaced and branching "stems" of snow-white colour. And finally, the mother of pearl lining of most shells of molluscs is composed of very thin aragonite plates arranged parallel to the contours of the shell surface. As known, sand particles or any other foreign bodies penetrating inside the shell are coated with layers of calcium carbonate with some organic admixtures producing pearls.

Colour of aragonite is white, yellowish white, sometimes light-green, violet, or grey. Some crystals are transparent and colourless. **Lustre**, vitreous, greasy on fracture. In cathode rays shows weak pale-violet or orange luminescence $n_x = 1.686$, $n_y = 1.681$, and $n_z = 1.530$.

Hardness, 3.5 to 4. Brittle. **Cleavage**, {010} distinct, {110} and {011} very indistinct. Fracture, often conchoidal. **Specific gravity**, 2.9 to 3.0 (higher than that of calcite, an evidence of closer packing of atoms). **Other properties.** Unstable at ordinary temperatures; in the presence of a solvent gradually changes to calcite, and therefore does not occur in older deposits. At 400° the change to calcite is very rapid. Curiously enough, those aragonite modifications that have not been polymorphously converted to calcite contain larger (up to several per cent) ions of strontium, which in the opinion of N. V. Belov, apparently has a stabilising effect on this modification. Aragonite is more soluble in water than calcite.

Diagnostic features. Aragonite is very similar to calcite in colour and behaviour in hydrochloric acid but differs from it by the absence of rhombohedral cleavage, by the crystal habit with its characteristic, sometimes very fine, grooves on prism faces, and by higher hardness. Zeolites (hydrated silicates of Na, Ca, etc.) that appear to be similar to aragonite, do not evolve carbon dioxide in hydrochloric acid. Witherite and strontianite have a higher specific gravity and fuse before the blowpipe.

Before the blowpipe aragonite behaves like calcite. It is decomposed in acids with vigorous evolution of carbon dioxide. Powdered aragonite (as well as powdered strontianite and witherite) when boiled in a cobalt nitrate solution turns violet (Meigen's test), whereas powdered calcite suffers almost no change of colour, or turns bluish or greenish, and that only upon prolonged boiling.

Genesis and occurrence. Aragonite is much less widely distributed in nature than calcite. Being one of the lowest-temperature minerals, it is fairly frequently formed toward the end of *hydrothermal* processes. Such is the origin, for instance, of aragonite found in fissures in serpentinised ultrabasic rocks where surface processes could have had no effect. To the same type of formation belong the small acicular aragonite crystals in the cavities of undecomposed basalts, occasionally in marbles, volcanic lavas, deposits from hot springs supersaturated with $CaCO_3$ in the form of calcareous tufa or oölites (pisolites of Karlovy Vary, Czechoslovakia), etc.

The bulk of aragonite is formed, however, by diverse *exogenous* processes, often with the participation of dissolved magnesial salts. As radial-fibrous formations and sinters which are quite often large, it is widely distributed in the weathering crust of ultrabasic magnesial igneous rocks in association with dolomite, gypsum, argillaceous matter, and other exogenous minerals. It also occurs in vugs in red iron ores as a crusty growths of small crystals and "iron flowers", as,

for instance, in the Bakal deposit (Southern Urals), in gypsum-bearing strata, in native sulphur deposits, etc.

MAGNESITE, $MgCO_3$. Magnesia is a region in Thessaly (Greece). The mineral is known from ancient times. Synonym: magnesium carbonate.

Chemical composition. MgO 47.6%, CO_2 52.4%. The most common isomorphous admixtures are Fe, sometimes Mn, Ca.

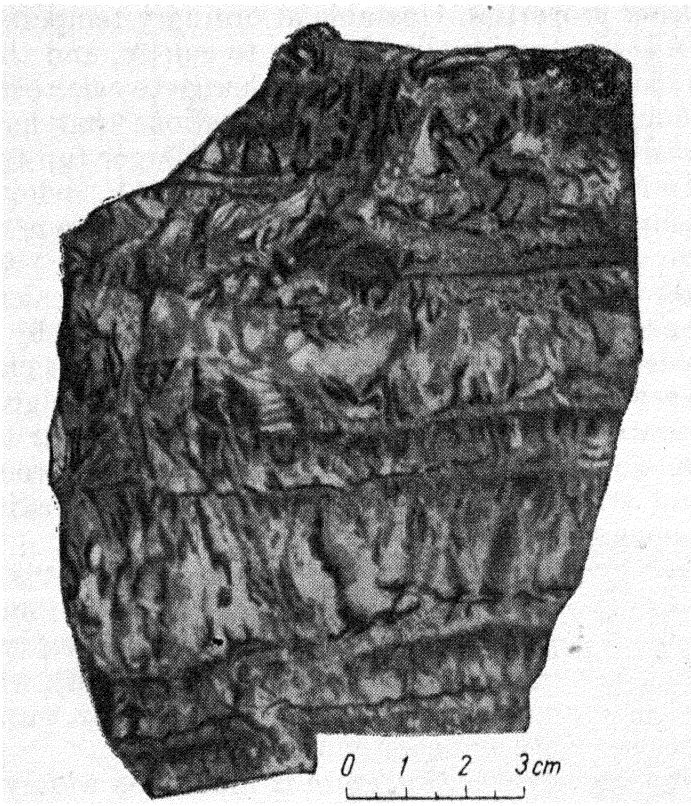


Fig. 220. Banded coarse-grained magnesite aggregates.

System, trigonal; symmetry, ditrigonal scalenohedral $L_6^3L^23PC$. Space group, the same as that of calcite. $a_0 = 4.584$; $c_0 = 14.92$. **Crystal structure**, analogous to that of calcite. **Habit**, generally rhombohedral. Occurs mostly as coarse-granular aggregates (Fig. 220). Porcelain-like metacolloidal masses, at times resembling cauliflower in shape, are very characteristic of deposits derived from weathering.

Colour. white with a yellowish or greyish tinge, sometimes snow-white. **Lustre**, vitreous. $n_y = 1.700$ and $n_z = 1.509$.

Hardness, 4 to 4.5. Brittle. **Cleavage**, rhombohedral on {1011} perfect. The fracture of metacolloidal porcelain-like formations is conchoidal. **Specific gravity**, 2.9 to 3.1.

Diagnostic features. Crystalline varieties, like all carbonates of the calcite series, differs from other minerals by rhombohedral cleav-

2. Siderite occurs in typically *sedimentary* deposits formed in marine lagoons and bays. Their formation was evidently due to the reducing conditions prevailing in the deeper parts of near-shore zones characterised by oxygen deficiency and by the decomposition of organic remains with the evolution of carbon dioxide and hydrogen sulphide from protein matter. Such sedimentary siderite ores sometimes have a typically oölitic texture.

Some of the ores of the great *Kerch* sedimentary deposit are composed of siderite. It is possible that brown iron ore is partly the product of oxidation of these ores. Outside the Soviet Union, notable are the rather large deposits of compact argillaceous spherosiderite, coloured dark due to admixed carbonaceous matter found in extensive coal beds in *Scotland* and *South Wales* (Britain).

In the oxidised zone siderite is unstable readily forming iron hats composed of limonite, goethite, sometimes hydrohematite and occurring both as loose, generally earthy masses and as geodes, which are often hollow inside.

Uses. When siderite occurs in large masses with little undesirable impurities (phosphorus, sulphur, etc.), it is an ore of iron. Prior to smelting, siderite ores are calcined.

RHODOCHROSITE, $MnCO_3$. "Rhodon" is the Greek for rose; "chros", colour. The name is descriptive of its colour. Synonym: dialogite.

Chemical composition. MnO 61.7% (Mn 47.8%), CO_2 38.3%. The most frequent isomorphous admixtures are Fe, Mg, Ca, occasionally Zn and Co.

System, trigonal; symmetry, ditrigonal scalenohedral $L_6^3 3L^2 3PC$. Space group $R\bar{3}c(D_{3d}^6)$. $a_0 = 4.73$; $c_0 = 15.51$. Crystal structure analogous to that of calcite. Well-formed crystals are rare and occur only in cavities. Common forms: $\{10\bar{1}1\}$ and $\{01\bar{1}2\}$, sometimes $\{0001\}$ and $\{11\bar{2}0\}$. Faces are often saddle-shaped or lenticularly curved. **Aggregates** are commonly crystalline-granular, reniform and globular with a radiated or spherulitic texture. Occurs also in rod-like aggregates (Fig. 222) and earthy masses.

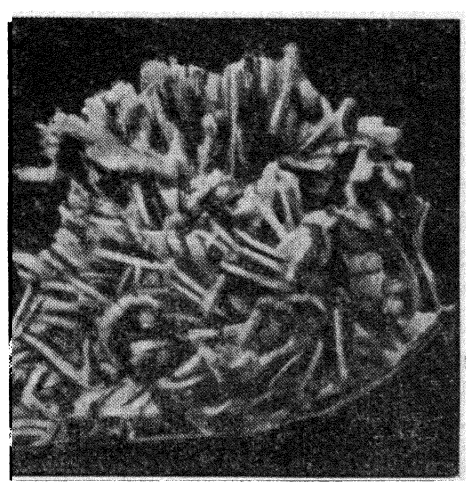


Fig. 222. Aggregate of rod-like rhodochrosite crystals.

Colour of crystals pink or raspberry-red. With increasing calcium content colouring pales. On exposure to air gradually turns brown (oxidisation). Fine-granular and earthy masses have a white colour with a very slight pink tinge. **Streak**, white. **Lustre**, vitreous. $n_y = 1.817$ and $n_z = 1.597$.

Hardness, 3.5 to 4.5. Brittle. **Cleavage**, rhombohedral parallel $\{10\bar{1}1\}$. **Specific gravity**, 3.6 to 3.7.

Diagnostic features. In crystalline masses rhodochrosite is readily identifiable by rhombohedral cleavage, pink colour, and low hardness (is scratched with a knife blade). White cryptocrystalline and earthy aggregates may be identified positively only by chemical and spectral analyses.

Infusible in the blowpipe flame but decrepitates, and successively turns greenish grey and black (owing to oxidation). With borax and salt of phosphorus gives the manganese reaction (in the oxidising flame gives a violet bead, a colourless one in the reducing flame. Dissolves slowly in cold hydrochloric acid, but when heated the dissolution proceeds rapidly with effervescent evolution of carbon dioxide.

Genesis and occurrence. Judging by the composition of the iron-manganese carbonates, $MnCO_3$ and $FeCO_3$ give a continuous series of isomorphous mixtures. The clark of manganese in the earth's crust is about 50 times lower than that of iron. Nevertheless, in nature rhodochrosite forms deposits of its own.

In rare *hydrothermal* vein or metasomatic deposits of manganese, rhodochrosite is formed in association with sulphides and silicates of manganous oxide, crystallising after braunite, quartz, barite, etc. Rhodochrosite of hydrothermal origin in association with pyrite, chlorites, and other minerals is found in the U.S.S.R., in the *Sapalsk* deposit in marbled limestones near Nizhny Tagil. In certain tungsten deposits, rhodochrosite may occur as veins genetically associated with quartz veins containing hübnerite ($MnWO_4$) and other minerals.

In much greater masses rhodochrosite occurs in *sedimentary* deposits of manganese ores. According to the data of geological research, opal-rhodochrosite sediments have formed at some distance from the coastline in the deeper parts of the basins where the decomposition of organic remains in the conditions of oxygen deficiency evidently produced reducing conditions. In such deposits, rhodochrosite commonly contains isomorphous admixtures of Ca, Fe, and Mg and is associated with iron sulphides, manganocalcite, opal, etc. As a rule, sedimentary carbonate manganese ores are also enriched in phosphorus. Considerable masses of rhodochrosite ores are known in the sedimentary deposits of *Chiatury* (Transcaucasia), *Polunochny* (the Northern Urals), and elsewhere.

Uses. Low-phosphorus hydrothermal rhodochrosite ores are an important material for ferromanganese. Sedimentary carbonate ores may be used as an addition to blast-furnace charges and also by the chemical industry.

SMITHSONITE, $ZnCO_3$. Synonym: zinc spar.

Chemical composition. ZnO 64.8% (Zn 52%), CO_2 35.2%. Commonly contains isomorphous admixture of Fe, Mn, Mg, sometimes Co, rarely Cd, In, etc.

System, trigonal; symmetry, ditrigonal scalenohedral $L_6^3 3L^2 3PC$. Space group $R\bar{3}c(D_{3d}^6)$. $a_0 = 4.65$; $c_0 = 14.95$. **Crystal structure,** the same as of calcite. Rare crystals have both rhombohedral and scalenohedral habit. The most frequent forms: rhombohedral $\{10\bar{1}1\}$ and $\{40\bar{1}1\}$; scalenohedral $\{2\bar{1}31\}$; more seldom pinacoidal $\{0001\}$; rhombohedral $\{01\bar{1}2\}$, $\{02\bar{2}1\}$; and prismatic $\{1\bar{1}20\}$. Faces are often curved and rough. **Aggregates.** Usually in earthy or compact cryptocrystalline aggregates, often as sinters and crusts as well as conchoidal (Fig. 223), cellular, and porous masses.

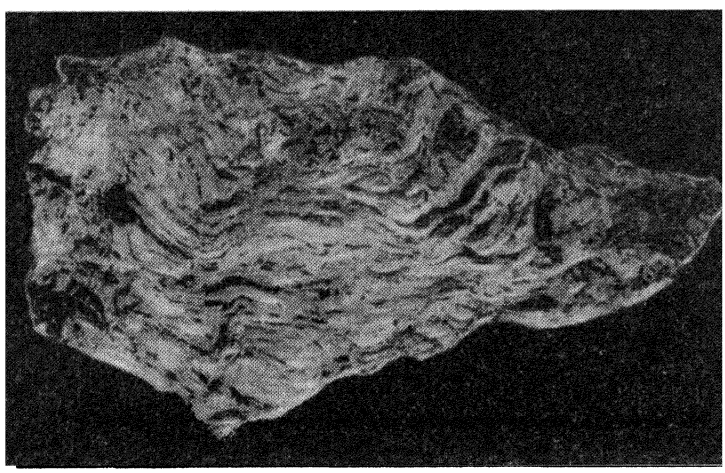


Fig. 223. Laminated-conchoidal structure of a smithsonite mass. ¾ natural size.

Colour, white with greenish, brownish, and greyish tinges. Intensely green varieties contain malachite admixtures. Brown varieties owe their colour to iron hydroxides. **Lustre**, vitreous. $n_y = 1.849$ and $n_z = 1.621$. In cathode rays shows a faint pink luminescence.

Hardness, 5 (the highest for the calcite group minerals). **Cleavage**, rhombohedral, noticeable only in crystalline aggregates. **Specific gravity**, 4.1 to 4.5.

Diagnostic features. When in crusts, sinters and cryptocrystalline masses, is distinguished with difficulty from its paragenetic associates such as opal, zinc silicates (calamine, willemite), etc. Being rather light in colour, it is inconspicuous among limestones. Identification always requires blowpipe and chemical analysis. Other less important characteristics of smithsonite are its high specific gravity and hardness (5).

Infusible in the blowpipe flame and, like all the carbonates, decrepitates, and on charcoal gives a white coating of ZnO. Ferruginous varieties become brown. Rather readily soluble in acids, sometimes with effervescence (especially the earthy varieties). Upon ignition moistened in a $Co[NO_3]_2$ solution and ignited once more in the oxidising flame, becomes green.

Genesis and occurrence. Smithsonite is a typical mineral of the lower horizons of the oxidised zones of lead-zinc sulphide *deposits in limestones*. Sometimes it forms large masses, mostly in the foot walls of ore bodies (Fig. 224). When the primary ores contain much calcite, smithsonite is also found in the upper parts of oxidised zones, associated with zinc silicates, galena, and sometimes with remains of sphalerite. It is formed metasomatically through the exchange-decomposition reaction of well-soluble zinc sulphate with calcite:

$$ZnSO_4 + CaCO_3 + 2H_2O = ZnCO_3 + CaSO_4 \cdot 2H_2O$$

This reaction probably occurs after the neutralisation of the excess of sulphuric acid in solution through reaction with the same calcite. If *ferrous* oxide sulphate is present in the solution, which may happen only in the deeper horizons of the oxidised zone, smithsonite contains isomorphous admixture of $FeCO_3$, sometimes in large amounts (monheimite). Ferruginous smithsonite decomposes under oxidising conditions with separation of iron hydroxides. In this case the zinc in the form of smithsonite which has already been stripped of iron, may be re-deposited elsewhere. Smithsonite masses intensely pigmented with iron hydroxides differ little from porous or cavernous masses of limonite, and are therefore frequently overlooked. The smithsonite may be recognised by blowpipe analysis or in polished sections under the microscope.

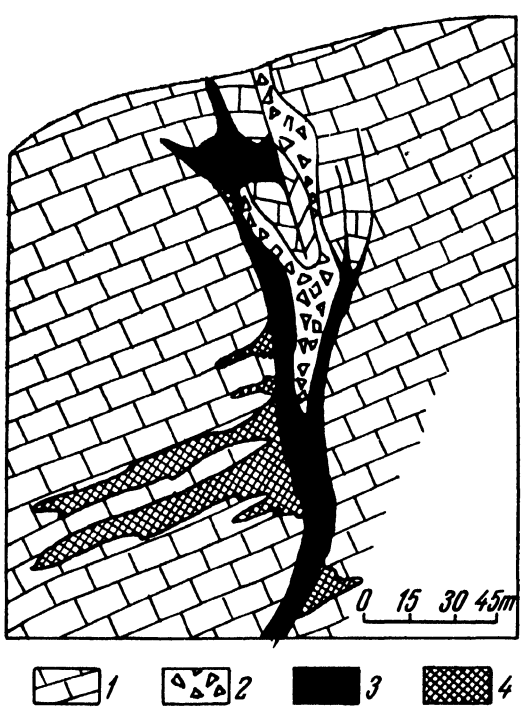


Fig. 224. Oxidised lead and zinc ores.

1 – limestone; *2* – subsidence breccia; *3* – oxidised lead ores; *4* – secondary zinc ores formed through replacement of limestone.

In the U.S.S.R., smithsonite in large masses occurred at *Turlan* (Achisai); in the Kara-Tau Ridge (Southern Kazakhstan), which was for a long time thought to be a purely lead deposit, until rich oxidised zinc ores were discovered beyond the principal ore body (Fig. 224); in numerous lead-zinc deposits of the Eastern Trans-Baikal area (Nerchinsk district), and elsewhere.

Outside the U.S.S.R., there are numerous deposits, among which the most important is at *Leadville*, Colorado (U.S.A.). At first, it was worked in the oxidation zone only for its lead; only 30 years later rich smithsonite ores were found here (so inconspicuous they were in limestones and other rocks).

Uses. Smithsonite ores, if found in quantity, may be an important source of zinc. Their zinc content is often 2 to 3 times higher than in primary sulphide ores. Thus, in the lower parts of oxidised zones of lead-zinc sulphide ores in limestones or dolomites, not only zinc is separated from lead but the metasomatically deposited exogenous products are also enriched in zinc.

CERUSSITE, $PbCO_3$. "Cerussa" is the Latin for white paint. Synonym: white lead ore.

Chemical composition. PbO 83.5% (Pb 77.5%), CO_2 16.5%. May contain as mechanical impurities dispersed residual PbS and Ag_3S, colouring the mineral black, occasionally $ZnCO_2$.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Pmcn$ (D_{2h}^{16}). $a_0 = 5.173$; $b_0 = 8.480$; $c_0 = 6.130$. **Crystal structure**, analogous to that of aragonite. **Habit** may be diverse, viz., pseudohexagonal dipyramidal (Fig. 225) with dipyramid faces {111} and prism faces {021}; tabular or platy (Fig. 226) with predominant pinacoidal development {001} or {010}, sometimes {100}; rod-like, etc.

Twins and trillings are frequent; the most common twinning plane {110}. **Aggregates.** Usually granular massive. Less often sinter-like, cryptocrystalline and earthy masses. Also occurs in snow-white fibrous varieties.

Colour, commonly white with greyish, yellowish, or brownish tinges. Ferruginised masses are brown and therefore often overlooked. Occasionally grains are black due to microscopic inclusions of residual sulphides. Individual crystals are often colourless or transparent. **Lustre**, adamantine, sometimes vitreous (depending on orientation).

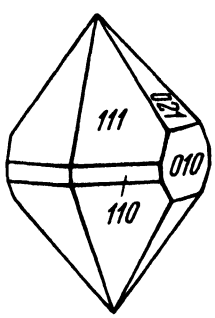


Fig. 225. Pseudohexagonal dipyramidal cerussite crystal.

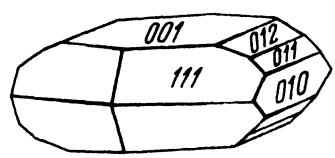


Fig. 226. Tabular cerussite crystal.

Fracture, often uneven, conchoidal. In cathode rays shows bright greenish-blue fluorescence. $n_x = 2.078$, $n_y = 2.076$, and $n_z = 1.804$.

Hardness, 3 to 3.5. Very brittle. **Cleavage**, sometimes observed on {110} and {021} distinct. **Specific gravity**, 6.4 to 6.6.

Diagnostic features. Unlike the other carbonates, cerussite has high specific gravity and adamantine lustre. Often observed in association with anglesite and galena.

Decrepitates strongly before the blowpipe, turns yellow (PbO), on charcoal is reduced readily to metallic lead. Dissolves in dilute nitric acid with brisk evolution of carbon dioxide. Also soluble in KOH.

It is interesting to note that cerussite masses coloured with iron hydroxides are externally indistinguishable from other limonitised materials containing no cerussite. However, when broken, a piece of such cerussite emits a characteristic crackle or squeak. Miners working the cerussite portions of the oxidised zones of ore deposits rely on this property to distinguish cerussite.

Genesis and occurrence. Cerussite is confined almost exclusively to oxidised zones of lead-zinc sulphide deposits. Usually occurs as an alteration product of anglesite which, in turn, is formed through the oxidation of galena. Being almost insoluble in water and stable in air, cerussite protects galena from further decomposition.

Well-formed, and often large, crystals of cerussite occur on the walls of leaching cavities in the oxidised zones. The formation of these crystal druses implies that there has been some transportation of soluble lead compounds. However a possibility of formation of cerussite at the low-temperature stage of hydrothermal processes is not excluded.

Pseudomorphs of cerussite after other minerals (galena, anglesite, calcite, fluorite, etc., are comparatively rare. Large masses of cerussite were mined in the U.S.S.R. in the *Turlan* deposit, Kara-Tau Ridge (Southern Kazakhstan), and elsewhere. Extremely well-formed cerussite crystals occurred at the Tayninskoye and Kadainskoye deposits in the *Nerchinsk* district, Trans-Baikal area, and in the *Altai mountains* (Ridder, Zyryanovskoye and Nikolayevskoye).

Uses. An important lead ore, especially in extensive oxidised zones of lead-zinc deposits.

STRONTIANITE, $SrCO_3$. First discovered at Strontian (Western Scotland).

Chemical composition. SrO 70.2%, CO_2 29.8%. Practically always contains CaO. The variety known as *calciostrontianite* contains up to 13% of CaO_3. Less often contains BaO, PbO, etc.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^33PC$. Space group *Pmcn* (D_{2h}^{16}). $a_0 = 1.118$; $b_0 = 8.404$; $c_0 = 6.082$. At a temperature of 700° (according to other data, at 929°), changes to a hexagonal modification which never occurs in nature. **Crystal structure**, analogous to that of aragonite. Crystals are rare, mostly as thin needles or barrel-shaped prismatic forms (Fig. 227). Twins are common along (110). **Aggregates.** Usually massive granular, often thin rod-like or fibrous.

Colour. Colourless or greenish, yellowish, and greyish. **Lustre**, vitreous; on fracture, greasy. In cathode rays gives very faint bluish fluorescence. $n_x = 1.668$, $n_y = 1.667$, and $n_z = 1.520$.

Hardness, 3.5 to 4. Brittle. **Cleavage**, {110} distinct and {021} indistinct. **Specific gravity**, 3.6 to 3.8.

Diagnostic features. Externally, hard to distinguish from aragonite. Behaviour before the blowpipe and reactions with acids are highly characteristic.

Before the blowpipe, when intensely heated, swells into cauliflower shapes. Incandesces strongly and colours the flame intense carmine-red (Sr), readily soluble in acids with effervescence. When its solution in hydrochloric acid is evaporated and some alcohol poured on the residue a bright-red flame (Sr) flares up.

Genesis and occurrence. Occurs mostly in *hydrothermal* formations in association with celestite, barite, calcite, sulphides, and other minerals, also in sedimentary rocks (limestones and marls), although frequently in the form of more recent veinlets in cavities and cracks.

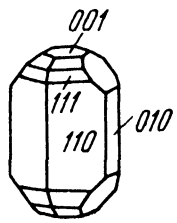


Fig. 227. Strontianite crystal.

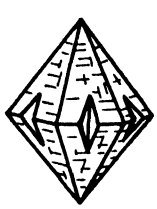
In the U.S.S.R., strontianite deposits occur in the Crimea. Outside the Soviet Union, large deposits of strontianite were worked at *Hamm*, Westphalia (Germany) where they occur as veinlets and veins in Cretaceous marls. The cavities there contained very well developed crystals. As an accessory mineral, strontianite occurs in many hydrothermal deposits, mostly in barite veins accompanied by sulphides.

Uses. A secondary source of strontium. For other uses see "Celestite".

WITHERITE, $BaCO_3$. **Chemical composition.** BaO 77.7%, CO_2 22.3%. Sometimes contains strontium.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Pmcn(D_{2h}^{16})$. $a_0 = 5.252$; $b_0 = 8.828$; $c_0 = 6.544$. **Crystal structure**, analogous to that of aragonite. Crystals occur as pseudo-hexagonal dipyramids. Trillings are common on (110) (Fig. 228). **Aggregates.** Also occurs in globular and reniform shapes, sometimes in veined, fibrous, and foliated aggregates.

Colour. Colourless or white, but usually coloured greyish or yellowish. **Lustre**, vitreous; fracture, greasy. In cathode rays, shows yellow fluorescence. $n_x = 1.677$; $n_y = 1.676$, and $n_z = 1.529$.


Fig. 228. Witherite. Penetration trilling.

Hardness, 3 to 3.5. Brittle. **Cleavage**, {010} distinct and {110} indistinct. **Specific gravity**, 4.2 to 4.3. **Other properties.** Witherite dust is toxic to man. Therefore, the wet method is used in drilling blastholes in witherite-bearing ores and rocks.

Diagnostic features. High specific gravity distinguishes witherite from otherwise similar aragonite and strontianite. Also characteristic are its blowpipe behaviour and reactions with acids.

Before the blowpipe fuses readily into transparent bead which looks like enamel on cooling. This feature places it apart from all other carbonates. The flame is coloured characteristically yellow greenish. Soluble with effervescence in dilute nitric and hydrochloric acids. On addition of a few drops of sulphuric acid, an abundant precipitate of $BaSO_4$ falls out.

Genesis and occurrence. Usually occurs in *hydrothermal* deposits in paragenesis with calcite, dolomite, sulphides of Pb, Zn, Fe, and often with barite which is sometimes deposited after witherite. May occur as an exogenous mineral. Occurs in pseudomorphs after barite, formed apparently, through the action of carbonate solutions. Replacement of witherite by barite has also been observed.

Large accumulations of witherite are extremely rare. The one at *Settlingstone* in Northumberland (Britain) is actually the only specific witherite deposit. Witherite there is accompanied by calcite, sulphides, and later-formed barite (in thin cracks and in the spaces between witherite crystals). In the Soviet Union, barite-witherite deposits occur as a series of veins in the Karakal district (Turkmenia) where they are confined to the fissures of a large tectonic fractured zone in Cretaceous sedimentary rocks.

Uses. Witherite is a secondary source of barium compounds for the reason that it occurs in nature much more rarely than barite. The uses of barium-bearing minerals are described under "Barite" (p. 372).

PARISITE, $Ca(Ce, La...)_2[CO_3]_3F_2$. Contains up to 50% of $(Ce, La)_2O_3$. A very rare mineral.

System, hexagonal. Usually occurs in compact granular masses. Colour, reddish brown, brownish yellow. Lustre, vitreous. $n_x = 1.757$ and $n_y = 1.676$. Hardness, 4 to 4.5. Cleavage or parting, {0001} distinct. Specific gravity, 4.35. Infusible in the blowpipe flame. Decomposes slowly in hydrochloric acid. When heated with sulphuric acid, HF is evolved.

Occurs in pegmatites. Finds have been recorded from emerald mines in Muso, Columbia (South America), and elsewhere.

Summary. Thus, the calcite-group minerals have many physical properties in common. It will be seen from the general table of main properties of the principal calcite minerals (Table 10), that only the carbonates of heavy metals such as Mn, Fe, and Zn are somewhat different from the rest, especially to the carbonate of lead—cerussite.

The greatest differences are in the solubility of the metals in water saturated with carbon dioxide. The carbonate of Mg is highly soluble; carbonates of Ba and Ca come next, and the carbonate of Pb is the least soluble of all.

Table 10

Basic Properties of Calcite Minerals

Mineral	System	Specific gravity	Hardness	Refractive index			Solubility (at 180° and CO_2 pressure of 1 atm), mg per litre	Dissociation temperature at CO_2 pressure of 1 atm, °C
				n_x	n_y	n_z		
Calcite, $CaCO_3$	Trigonal	2.7	3	—	1.658	1.486	1,100	900
Dolomite, $CaMg[CO_3]_2$	Ditto	2.9	3.5-4	—	1.681	1.500	—	—
Magnesite, $MgCO_3$	Ditto	3.0	4 -4.5	—	1.700	1.509	25,800	600
Rhodochrosite, $MnCO_3$	Ditto	3.7	3.5-4.5	—	1.817	1.597	400	500
Siderite, $FeCO_3$	Ditto	3.9	3.5-4.5	—	1.875	1.633	720	500
Smithsonite, $ZnCO_3$	Ditto	4.4	5	—	1.849	1.621	700	400
Aragonite, $CaCO_3$	Orthorhombic	3.0	3.5-4	1.686	1.681	1.530	—	900
Witherite, $BaCO_3$	Ditto	4.3	3 -3.5	1.677	1.676	1.529	2,700	800
Strontianite, $SrCO_3$	Ditto	3.7	3.5-4	1.667	1.667	1.520	1,250	800
Cerussite, $PbCO_3$	Ditto	6.5	3 -3.5	2.078	2.076	1.804	140	—

which make up isomorphous series, not given in the table, their properties vary depending on the ratio between their constituents. The same applies to binary salts. The thermal dissociation of the latter proceeds in two stages.

2. MALACHITE GROUP

Included in the group are basic anhydrous copper carbonates—malachite and azurite.

MALACHITE, $Cu_2[CO]_3[OH]_2$ or $CuCO_3 \cdot Cu[OH]_2$. "Malache" is the Greek for hollyhock. Apparently derives its name from the likeness of its colour to that of the plant.

Chemical composition. CuO 71.9% (Cu 57.4%), CO_2 19.9%, H_2O 8.2%. May contain very small amounts of CaO, Fe_2O_3, SiO_2, etc., apparently as adsorbed or mechanical foreign admixtures.

System, monoclinic; symmetry, prismatic. Space group $P2_1/a(C_{2h}^5)$. $a_0 = 9.49$; $b_0 = 12.00$; $c_0 = 3.24$; $\beta = 98°42'$. Extremely rare crystals are of prismatic habit.

Aggregates. Usually in rounded masses (Fig. 229) with a radial-fibrous structure. Large reniform masses have a characteristic concentric banded structure, most striking in polished specimens (Fig.230). Also occurs in earthy varieties (copper green).

Colour, green. **Streak**, pale-green. **Lustre**, vitreous to adamantine, and for fibrous varieties, silky. $n_x = 1.909, n_y = 1.875$, and $n_z = 1.655$.

Hardness, 3.5 to 4. Brittle. **Cleavage**, $\{\bar{2}01\}$ perfect and $\{010\}$ distinct. **Specific gravity**, 3.9 to 4.0.

Diagnostic features. Readily identifiable by green colour, frequent sinter forms, and radially fibrous structure. Differs from similar chrysocolla (copper hydrosilicate), phosphorohalcite (copper phosphate), and other green copper minerals by its behaviour in hydrochloric acid (evolves carbon dioxide).

Fuses in the reducing blowpipe flame and gives a copper globule. When moistened with hydrochloric acid, colours the flame light-blue. Gives water in the closed tube and turns black. Soluble with effervescence in hydrochloric acid. The solution turns blue when ammonia is added.

Genesis and occurrence. Malachite forms exclusively in the oxidised zones of copper sulphide deposits, especially in limestones or when the primary ores contain much carbonates. The most common copper mineral in oxidised copper ores, malachite develops either through the replacement of carbonates or by filling cavities as typical colloform (sinter) forms. Since at the surface of limestones or Ca and Mg carbonates solutions become definitely alkaline, the copper sulphate solutions on reaching this environment are hydrolised by reacting with bicarbonate solutions.

Moreover, copper carbonates may probably derive from the slow reaction of a copper sulphate or hydrate with a solution saturated with atmospheric carbon dioxide.

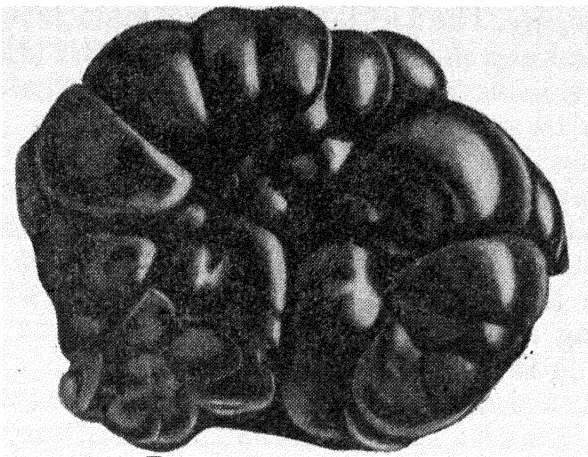


Fig. 229. Reniform malachite.

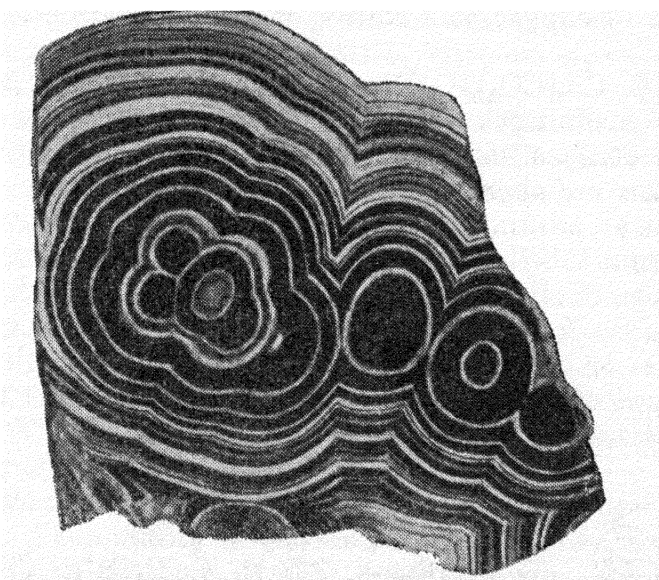


Fig. 230. Concentrically-banded structure of malachite (polished surface).

Malachite occurs frequently as pseudomorphs after azurite, cuprite, native copper and also after such minerals as atacamite, calcite, chalcopyrite, etc. As inclusions and salvages of copper green frequently occurs in the oxidised zones of copper deposits. However, large accumulations, especially those of ornamental grade, have now become a rarity.

In the U.S.S.R. *Mednorudyanskoye* and *Gumeshevskoye* deposits were of world renown.

The Mednorudyanskoye was the only deposit in the world that supplied malachite of rich and beautiful patterns. It is from there that came the facings of the columns of St. Isaac's Cathedral (Leningrad), of the Malachite Hall of the Winter Palace, the malachite table tops of the Hermitage, etc. The first large block of malachite weighing about 50 tons was found at a depth of 70 m together with other oxygen compounds of copper, in strongly ferruginised and decomposed rocks at the contact between skarns and limestone.

The Gumeshevskoye deposit was discovered in the late 18th century. It had supplied an enormous quantity of excellent ornamental-grade malachite, specimens of which were displayed in many museums. The large sinter masses at that deposit occurred in red clays. It is from here that came the enormous block of malachite, of most beautiful pattern, weighing almost 1.5 tons, displayed at the museum of the Leningrad Mining Institute.

Uses. Compact sinter varieties of malachite, sometimes occurring in large masses, are used for facings and mosaics, vases, trinket-boxes and other ornamental objects. Malachite fines are used in the manufacture of pigments. Disseminated earthy malachite, along with other oxidised ores of copper, is a source of metallic copper.

AZURITE, $Cu_3[CO_3]_2[OH]_2$ or $2CuCO_3 \cdot Cu[OH]_2$. The name comes from "azure" meaning sky-blue. Synonyms: azure copper ore, chessylite.

Chemical composition. CuO 69.2% (Cu 55.3%), CO_2 25.6%, H_2O 5.2%. Crystals are chemically rather pure. A rare case of mechanical impurity was an admixture of specks of secondary native gold in some specimens from the Berezovskoye deposit in the Urals.

System, monoclinic; symmetry, prismatic L^2PC. Space group $P2_1/c(C^5_{2h})$. $a_0 = 4.96$; $b_0 = 5.83$; $c_0 = 10.27$. **Habit.** Crystals occur as short columns or prisms and also as thick tablets or plates (Fig. 231). Often in druses of fine crystals, continuous granular masses, sometimes in radial and earthy aggregates ("blue malachite").

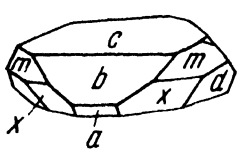


Fig. 231. Azurite crystal: *c* {001}, *b* {102}, *a* {100}, *m* {110}, *x* {112}, and *d* {123}.

Colour, dark blue, in earthy masses, azure. **Streak**, light blue. **Lustre**, vitreous. $n_x = 1.838$, $n_y = 1.758$, and $n_z = 1.730$.

Hardness, 3.5 to 4. Brittle. **Cleavage**, {001} perfect and {100} indistinct. **Specific gravity**, 3.7 to 3.9.

Diagnostic features. Readily identifiable by characteristic blue colour and association with malachite and other oxygen copper compounds.

Readily fusible in the blowpipe flame; in the reducing flame gives a copper globule. Soluble in acids with effervescence. Also dissolves in ammonia, colouring the solution light blue.

Genesis. In small amounts, occurs practically always in paragenesis with malachite, frequently being deposited after it. Conditions often

arise under which azurite is less stable than malachite and hence is replaced by the latter. Malachite pseudomorphs after fine azurite crystals are known. Characteristically, such malachite occurs as continuous cryptocrystalline masses instead of having a radial-fibrous structure.

Uses. With other oxygen copper compounds goes into the smelts. Pure azurite, when found in quantity, is used for the manufacture of blue pigment.

Hydrous Carbonates

The most common of the carbonates containing H_2O molecules, the hydrous carbonates of Na, Mg, U, etc. Only decahydrocarbonate of sodium will be discussed here.

SODA, $Na_2CO_3 \cdot 10H_2O$. The name "soda" was used already in the 17th century, though its origin is unknown. Synonyms: natrite, natron.

Chemical composition. Na_2O 21.6%, CO_2 15.4%, H_2O 63.0%. Mechanical impurities may consist of other well-soluble sodium salts.

System, monoclinic; symmetry, prismatic L^2PC. Crystals are rhombohedral tabular. Usually occurs in granular aggregates.

Colour, white, grey or colourless. **Lustre**, vitreous. $n_x = 1.440$, $n_y = 1.425$, and $n_z = 1.405$.

Hardness, 1 to 1.5. **Cleavage**, {100} perfect. **Specific gravity**, 1.42 to 1.47. Precipitates from pure saturated solutions of Na_2CO_3 under atmospheric pressure, in the range of temperatures between -2 and $+32°$.

Diagnostic features. Readily soluble in water. When treated with hydrochloric acid vigorously evolves carbon dioxide. On exposure to air, rapidly loses water and turns white. When slightly heated, melts or rather dissolves in its own crystallisation water, like many other water-abundant crystallohydrates, with separation of thermonatrite ($Na_2CO_3 \cdot H_2O$). When the precipitate is fused in a platinum loop, the flame becomes intense yellow (sodium).

Genesis. Is formed in quantity in certain saline sodium-rich lakes, with excess CO_2. Presumably the soda derives from the exchange decomposition reaction between Na_2SO_4 and inflowing calcium bicarbonate, $Ca[HCO_3]_2$. It may also be formed biochemically through the reduction of sulphates by microorganisms and subsequent action of carbon dioxide with evolution of H_2S, according to the reactions:

$$Na_2SO_4 \rightarrow Na_2S + O_4$$

$$Na_2S + H_2O + CO_2 \rightarrow Na_2CO_3 + H_2S$$

As snow-white efflorescences and coatings, soda appears on the surface of loose rocks and soils in countries with an arid and hot climate.

In the Soviet Union, all the large soda lakes are situated in the Asiatic part of the country: the Petukhovskoye and Mikhailovskoye lakes

in the *Kulunda Steppe*, south of the Kulunda railway station (Northern Kazakhstan). The deposition of soda begins in autumn with decreasing temperature and it is recovered from the bottom in winter. Thus, in the *Doroninskoye* soda lake (Eastern Siberia) the brine is pumped onto the ice in a layer up to 6 cm deep. The soda from the freezing brine precipitates on the ice of the lake. Upon the evaporation of the water of the frozen brine by strong winds, the soda is raked into heaps and delivered to the factory for treatment.

Numerous large soda lakes are known in Tripoli, Egypt, Iran, Tibet, south-eastern California, and elsewhere.

Uses. Soda is used in diverse industries such as soap-making, glass-manufacture, dyeing, and also in metallurgy and chemistry. In countries where there are few soda lakes, soda is made artificially, chiefly from mirabilite and halite.

CLASS 3.

SULPHATES

General. The geochemistry of sulphur, it will be recalled, has a number of specific features. This element capable of forming not only neutral 8-atom S_8 molecules (see "Native sulphur"), but also differently charged positive and negative ions. It will also be remembered that there exist negatively charged S^{2-} ions (analogous to O^{2-}) and $[S_2]^{2-}$ ions — as the products of electrolytic dissociation of H_2S. The formation of sulphides is associated with these anions. In an oxidising environment, sulphur may form an SO_2 molecular compound (sulphurous gas) and, in solutions — $[SO_3]^{2-}$ complex anions and in a still more oxidising environment — $[SO_4]^{2-}$ groups containing S^{4+} and S^{6+} cations. Crystalline formations constituting the compounds of metals with these anions are known as sulphites (never occur in nature) and sulphates (widely occur in nature).

Thus, the formation of metal sulphates occurs only under conditions of increased oxygen concentration, i.e., at increased partial oxygen pressure in the environment, and at relatively low temperatures. In the earth's crust such conditions occur near the surface where the vast majority of these compounds, both endogenous and exogenous, are found.

Although the minerals of this class include a wide variety of compounds, the number of stable and widely occurring minerals is rather limited.

So large a complex anion as the $[SO_4]^{2-}$ may form stable crystalline structures only in combination with large divalent cations. Indeed, as will be shown later, the most stable are the sulphates of Ba, Sr, and Pb. Cations with smaller ionic radii enter into the composition of sulphates only in a hydrated state, i.e., when clad in an H_2O molecular "jacket". The smaller the cation the greater is the number

of H_2O molecules that can be attached to it. In the case of water-rich sulphates, the amount of H_2O in the same type of compound may vary depending on the H_2O vapour pressure in the environment. Thus, for the sulphate of ferrous oxide there exist salts with seven, six, five, and one H_2O molecules. All these salts differ from one another in crystal lattice.

Univalent cations of alkali metals naturally enter into the composition of simple sulphates either in double numbers or in association with H^{1+}. They form loose crystal structures and are easily soluble in water (as are sulphates with smaller divalent cations).

Sulphates of trivalent metals, mainly of Al^{3+}, and Fe^{3+} occur exclusively as hydrous compounds.

Very widespread are binary and more complex salts of uni-, di-, and trivalent metals. Very frequent are sulphates with additional anions such as $[OH]^{1-}$, occasionally with Cl^{1-}, $[CO_3]^{2-}$, $[PO_4]^{3-}$, etc., especially when they contain trivalent metals or strongly polarising Cu^{2+} cations.

In conclusion we shall note certain physical properties common to all the minerals of this class, the most striking of which is their low hardness. There are no sulphates with a hardness over 3.5 and for water-abundant varieties it is as low as 2. Comparing the optical properties of the sulphates with those of the earlier reviewed salts, we find that their birefringence (n_x-n_y) is much lower. Some sulphates are even optically isotropic, which is explained by the fact that as different from the flat CO_3 and NO_3 groups, the tetrahedral SO_4 groups are isometric structural units. Most characteristically sulphates containing additional $[CO_3]^{2-}$ anions have considerably higher birefringence (e.g., caledonite, $Pb_5Cu_2[SO_4]_3[CO_3][OH]_6$.

In this description the minerals will be divided into groups, as usual, according to chemical composition and crystal structures. However, few such groups are known for anhydrous minerals. Other, rather numerous minerals of diverse composition, are best grouped according to cationic valency, and therefore hydrous and anhydrous sulphates will be discussed together.

1. BARITE GROUP

The group includes those sulphurous compounds of Sr, Ba and Pb which do not occur in nature as hydrosulphates. Anhydrous sulphate of calcium (anhydrite) although crystallising in the orthorhombic system, as the above sulphates, differs from the both in crystal structure and crystal form, since the Ca^{2+} ion has a smaller radius. Since anhydrite is genetically very closely associated with hydrous calcium sulphate (gypsum), it will be discussed in detail together with gypsum.

BARITE, $BaSO_4$. "Baros" is the Greek for heavy. The high specific gravity of the mineral is felt even by the hand. Barite is the prin-

cipal of the very few barium minerals, and the most widespread anhydrous sulphate after anhydrite.

Chemical composition. BaO 65.7%, SO_3 34.3%. Sr and Ca are found sometimes as isomorphous admixtures. The variety with a high strontium content is known as *barytocelestite.* There are some rare varieties rich in Pb and Ra (hokutolite). Occasionally certain impurities such as Fe_2O_3, clayey, organic, and other matter.

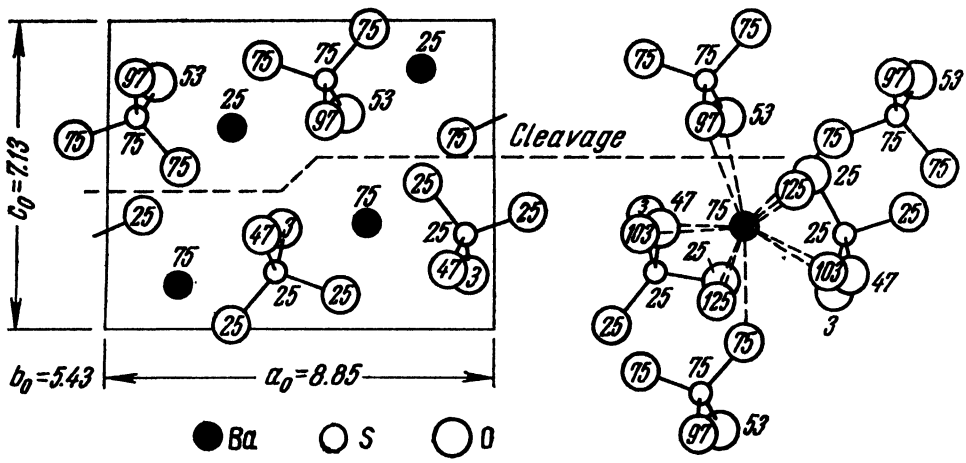


Fig. 232. Crystal structure of barite projected on {010}.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Pnma(D_{2h}^{16})$. $a_0 = 8.85$; $b_0 = 5.43$; $c_0 = 7.13$. **Crystal structure.** Figure 232 shows the projection of a unit cell of the structure on the (010) plane. The Ba^{2+} and S^{6+} ions are spaced at a distance of $\frac{1}{4}$ and $\frac{3}{4}$ of the b height from each other (see the figures). The SO_4 groups are somewhat irregular tetrahedra which, as evident from the figures, are differently orientated. Each Ba ion is surrounded by twelve oxygen ions which belong to seven different SO_4 groups (Fig. 232, on the right). **Habit.** Frequent barite crystals have generally a tabular habit (Fig. 233) owing to the development of the {001} face. Less frequent are prismatic, columnar (Fig. 233) crystals bounded with dominant prism faces {011} or {101} in combination with {001}, and isometric crystals. Occur in a great variety of combinations. Twins are rare; those observed are usually polysynthetic, producing striations on faces. **Aggregates** are commonly granular, less often compact, cryptocrystalline, and earthy. Also observed as stalactites and other flowstone sinter forms with a concentrical banded structure, and globular and ellipsoidal concentrations of radial structure. In cavities, often forms beautiful druses of small crystals.

Colour. Crystals may be colourless and water-transparent. However, commonly barite is coloured white or grey by foreign impurities (microscopic occlusions of gases and liquids), red (iron oxide), yellow or brown (probably iron hydroxides), dark grey and black (bituminous

substances); sometimes it has bluish, greenish, and other tinges. **Lustre**, vitreous, pearly on cleavage surfaces {010}. $n_x = 1.648$, $n_y = 1.637$, and $n_z = 1.636$.

Hardness, 3 to 3.5. Brittle. **Cleavage**, {001}, indistinct. **Specific gravity**, 4.3 to 4.5.

Diagnostic features. Barite has the highest specific gravity among the most common sulphates (only the specific gravity of anglesite is higher). Characteristic features are also perfect unidirectional cleavage, insolubility in hydrochloric acid even on heating (in contrast to all the carbonates). Differs from certain similar silicates in cleavage and other features, and by much lower hardness. Hard to distinguish from celestite without chemical tests.

Decrepitates in the blowpipe flame, only the thin edge fragments become rounded. Colours the flame yellow-green (barium). With soda

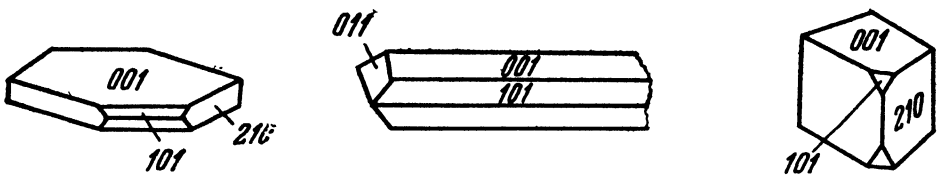


Fig. 233. Barite crystals.

on platinum plate fuses into a transparent mass which on cooling becomes turbid (when fused on charcoal, the mass deliquesces and soaks into the coal). As different from celestite, barium sulphide formed in the reducing flame, when moistened with hydrochloric acid, colours the flame yellow-green instead of carmine-red. In the powdered state slowly dissolves in concentrated sulphuric acid. When water is added, the solution becomes turbid, i.e., $BaSO_4$ separates once more.

Genesis and occurrence. In nature barite is formed in different ways, but only under conditions of increased partial oxygen pressure and at relatively low temperatures. Therefore, like all the other anhydrous sulphates, it never occurs as a magmatogenic product in igneous or deep-seated metamorphosed rocks.

In *hydrothermal* deposits it is rather common. As an accessory mineral, it is found in many sulphide, manganese (with manganite and braunite), iron (with siderite and hematite), and other ores. There are known gold-barite, almost purely barite, barite-calcite, barite-fluorite veins with a minor admixture of quartz and rare sulphides (galena, sphalerite, chalcopyrite, sometimes cinnabar, etc.).

In small amounts, mostly as concretions, barite is also widespread in *sedimentary* rocks, although in a different environment from that of anhydrite, gypsum, and celestite. Thus, it never occurs in salt deposits, very rarely in limestones, but often in sedimentary deposits of manganese (in oxide and carbonate ores) and iron, in argillaceous sandy, and other sedimentary deposits in near-shore zones of seas.

This is explained by the fact that the soluble salts of barium transported from land by surface water form a practically insoluble sulphate of barium at their very first encounter with $[SO_4]^{2-}$ ions in sea water. Nodular barite is found in silts also in contemporary seas.

In the zones of *weathering* of rocks and ore deposits in dry climate, close examination may reveal small barite crystals often of columnar habit associated with gypsum and iron hydroxides.

Barite is a chemically inert mineral and is, therefore, found in the eluvium often as coarse clastic material as well as in the heavy sands residue of placer sluicing operations. However, like all minerals of distinct cleavage and low hardness, barite soon becomes attrited in the places and gradually disappears.

The U.S.S.R. has numerous barite deposits, of which we shall mention only the principal ones. Thus, in Western Georgia there are a number of vein deposits of barite at *Kutaissi*, *Bolnissi*, and other districts in tuffs and effusive rocks (porphyrites). Barite masses of symmetrically banded or colloform texture contain the following impurities: calcite, a negligible amount of quartz, occasionally pyrite, chalcopyrite, and galena. The deposits of *Karakaly* district in the Kopetdag Ridge (Turkmenia) comprise a whole series of veins in sedimentary rocks (sandstones, clay shales, etc.). In some of the veins (Arpaklen) barite is associated with witherite, $BaCO_3$, which in places is pseudomorphous after barite.

A major foreign locality is *Meggen*, Westphalia (Germany), where a sheet-like body of extraordinary length (7 km) accompanied in places by a deposit of sulphides, mostly pyrite, lies at the contact of Mid-Devonian and Upper-Devonian sediments. The genesis of this particular deposit still remains obscure.

Uses. Barite is widely used in many industries.

1. In the form of fine powder as a weighting agent in drilling fluids for cementing unconsolidated rocks in oil-well drilling, for preventing blowouts and strengthening the walls of wells.
2. In chemical industry it is a source of various salts and agents for fireworks, treatment of hides (depilation) sugar refining, manufacture of photographic paper; in ceramics for making enamels, special grades of glass with high refractive indices, in medicine, etc.
3. In the manufacture of rubber and paper, as a filler and weighting agent.
4. For making high-quality lithopone (mixed with ZnO and ZnS) and paints, etc.
5. As the chief constituent of plaster for X-ray laboratories to protect the staff from harmful radiations.
6. Metallic barium is used in certain types of electronic tubes.

CELESTITE, $SrSO_4$. "Celestis" is the Latin for heavenly (the first discovered specimens were sky-blue in colour). Although relatively rare, it is the principal mineral of strontium.

Chemical composition. SrO 56.4%, SO_3 43.6%. At times contains Ca and Ba (often in appreciable amounts).

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group *Pnma* (D_{2h}^{16}). $a_0 = 8.36$; $b_0 = 5.36$; $c_0 = 6.84$.

Crystal structure is exactly the same as that of barite. **Habit.** Crystals resemble closely those of barite. Usually tabular, columnar or prismatic (Fig. 234). **Aggregates** mostly granular, sometimes rod-like, veined, and conchoidal, all of flowstone form. Also occurs in nodules and secretions and in druses in cavities.

Colour. Colourless white, often faintly blue or bluish grey, red or yellow. Occasionally colourless, water-transparent crystals are found. **Lustre**, vitreous to pearly on cleavage surfaces. $n_x = 1.631$, $n_y = 1.624$, and $n_z = 1.622$.

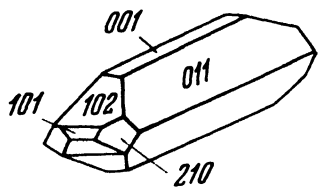


Fig. 234. Celestite crystal.

Hardness, 3 to 3.5. Brittle. **Cleavage**, {001} perfect, {210} distinct, and {010}, indistinct. **Specific gravity**, 3.9 to 4.0.

Diagnostic features. In granular masses differs from carbonates of Mg, Ca, Sr, Ba, etc., by behaviour in acids (when dissolved with heating, carbonates evolve CO_2). Sometimes resembles anhydrite in colour, but differs from it in the direction of cleavage and in higher specific gravity. Often hard to distinguish from barite. Very characteristic reaction for strontium.

Before the blowpipe fuses into a white head, colouring the flame intense carmine-red, especially when moistened with hydrochloric acid (strontium reaction). On charcoal with sodium carbonate gives characteristic sulphur liver. Soluble in strong sulphuric acid. The solution becomes turbid on addition of water.

Genesis and occurrence. More or less considerable quantities of celestite occur as nodules, pockets, and massive bodies in *sedimentary* rocks (dolomites, limestones, gypsiferous clays, marls, etc.). Finds of celestite are often confined to definite horizons of the rocks.

Also found in marine organisms, viz., in skeletons of a certain group of radiolaria. Sometimes in the shells of ammonites and in other fossils as a result of later deposition.

Also occurs in typical but very rare hydrothermal veins with galena, sphalerite, and other sulphides. Has been observed in amygdules of igneous rocks.

Celestite occurs fairly often as secretions in sedimentary gypsiferous Permian rocks in the *Archangel* Region, and Upper and Lower *Volga country* in *Bashkiria*, the *Orenburg Region*, etc. Numerous occurrences are known in the area of the *Caspian Sea* (in Turkmenia, Mangyshlak Island, etc.), and elsewhere in the Soviet Union.

Notable foreign localities are near *Bristol* (Britain), *Westphalia* and *Waldek* (Germany).

Uses. Celestite is the main source of strontium salts used for fireworks (giving a bright carmine-red flame) and in chemical industry: sugar refining (as strontium oxide to extract sugar from molasses), in the manufacture of glass and ceramics (for iridescent glass, specially glazed bricks, etc.). Lately, metallic strontium is used in special alloys, e.g., is added to copper to increase its strength and homogeneity (without decreasing its electrical conductivity).

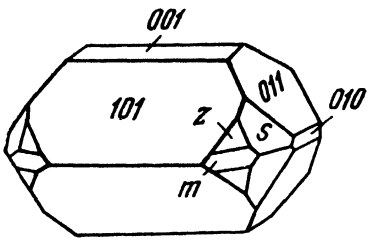


Fig. 235. Anglesite crystal: *s* {232}, *m* {210}, *z* {211}.

ANGLESITE, $PbSO_4$. Discovered on the Anglesey Island (Wales), from which it derives its name.

Chemical composition. PbO 73.6% (Pb 68.3%), SO_3 26.4%. Usually free from impurities. A variety rich in BaO (8.45%) is known.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group *Pnma* (D_{2h}^{16}). $a_0 = 8.45$, $b_0 = 5.38$, $c_0 = 6.93$. **Crystal structure** exactly the same as that of barite. **Habit.** Very many combinations of crystal faces. Usually tabular (Fig. 235), less often short-columnar, and pyramidal. Large crystals are rare. **Aggregates.** Often as crystalline crusts on galena, druses of small crystals, and in compact granular or earthy masses.

Colour. Colourless and often water-transparent. Often coloured grey, yellowish or brown by iron hydroxides, occasionally black owing to microscopic inclusions of undecomposed galena. **Lustre**, adamantine. $n_x = 1.894$, $n_y = 1.882$, and $n_z = 1.877$.

Hardness, 2.5 to 3. Very brittle. **Cleavage**, parallel to {001} distinct, parallel to {210} and {010} indistinct. **Specific gravity**, 6.1 to 6.4.

Diagnostic features. Anglesite is recognised by high specific gravity, adamantine lustre, close association with galena in oxidised ores, and behaviour in the blowpipe flame.

In the blowpipe flame decrepitates and fuses readily. On charcoal with sodium carbonate gives sulphur liver and on further ignition in the reducing flame a lead globule.

Dissolves in concentrated sulphuric acid only on heating. Dissolves completely, however, in KOH (which distinguishes it from celestite and barite).

Genesis and occurrence. As a poorly soluble product of the oxidation of galena and other sulphurous compounds of lead, anglesite is mostly formed in the *oxidised zones* of lead-zinc sulphide deposits, very often associated with the much more common cerussite, $PbCO_3$.

Microscopic examination shows that anglesite is the first oxygen compound of lead resulting from the oxidation of galena on the periphery and parallel to the cleavage, according to the reaction $PbS + O_4 = PbSO_4$. Under the action of carbon dioxide, however, anglesite readily changes in turn to lead carbonate, i.e., cerussite, $PbCO_3$. Being

poorly soluble in water, both minerals usually form white crusts over massive galena which is thus protected from further oxidation*. Therefore, when white nodules of seemingly completely oxidised lead ores are broken, their central portions often constitute solid galena.

It is also characteristic that the total lead content in the oxidised zones is invariably higher than in the primary sulphide ores. This is due to the fact that the constant accessory of galena – sphalerite – and copper sulphides are readily oxidised to well-soluble sulphates which are transported downward, thus enriching the oxidised ores with lead.

Anglesite may also be formed *hydrothermally*, though under specific conditions. Well-developed, often large, crystals occur in those lead-zinc ores which are deposited, judging by the paragenesis and the forms of mineral aggregates, near the daylight surface (probably through mixing with vadose waters saturated with free oxygen). Such are the deposits in Carinthia (the Western Alps) where anglesite crystals are found in cavities side by side with unoxidised sulphides of Fe, Zn, and Pb.

A certain amount of anglesite is always present in the oxidised zones of all galena-bearing sulphide deposits. Without enumerating all of them we shall merely mention that in Soviet literature there are described well-developed anglesite crystals from the Berezovskoye gold deposits (the Urals), from a number of deposits in the Altai mountains, Nerchinsk (eastern Trans-Baikal area), and elsewhere.

Uses. Anglesite mined together with other oxygen compounds of lead in the oxidised zones of lead deposits goes into the smelter.

Summary. The barite group, including anhydrite, has certain important distinctive features. It will be seen from Table 11, that lead

Table 11

Basic Properties of Barite Minerals

Mineral	Hardness	Specific gravity	Colour	Lustre	n_x	n_y	n_z
Anhydrite, $CaSO_4$	3-3.5	2.9	White	Vitreous	1.614	1.576	1.571
Celestite, $SrSO_4$	3-3.5	3.9	Blue	Ditto	1.631	1.624	1.622
Barite, $BaSO_4$	3-3.5	4.5	White	Ditto	1.648	1.637	1.636
Anglesite, $PbSO_4$	2.5-3	6.3	White	Adamantine	1.894	1.882	1.877

* This property is taken advantage of for keeping sulphuric acid in vessels lined with metallic lead. The resultant insoluble $PbSO_4$ film is solid enough to prevent further conversion of lead into a sulphate.

sulphate sharply differs in properties from other similar sulphates of metals. It also differs materially from them in the mode of formation. Sulphates of Ca, Sr, and Ba markedly differ from one another in specific gravity and refractive index.

2. ANHYDRITE AND GYPSUM

These two minerals stand apart both in physical and chemical properties from anhydrous and hydrous sulphates, but are closely linked with each other in the mode of formation and occurrence. Therefore, they will be discussed together.

The so-called calcium hemihydrate, which is easily obtained artificially, has not yet been positively recognised in nature.

ANHYDRITE, $CaSO_4$. The name of the mineral ("waterless") implies that in contrast to gypsum it contains no water.

Chemical composition. CaO 41.2%, SO_3 58.8%. Quite frequently contains strontium as an impurity.

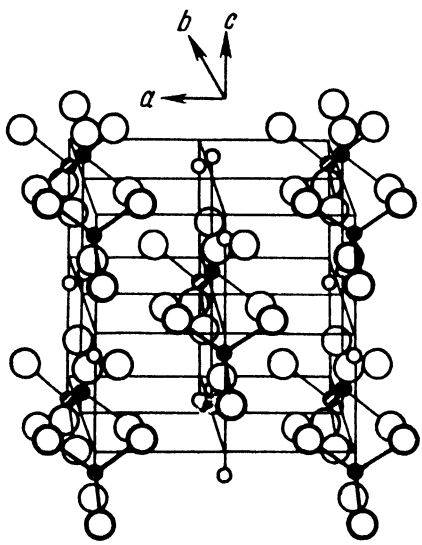


Fig. 236. Crystal structure of anhydrite.

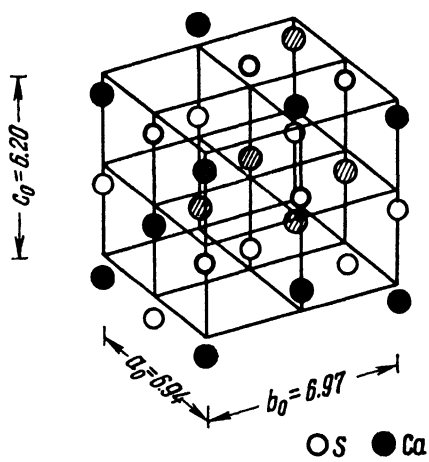


Fig. 237. Arrangement of sulphur and calcium ions in anhydrite structure.

Black circles of calcium ions correspond to those shown in Fig. 238.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Cmcm$ (D_{2h}^{17}). $a_0 = 6.94$; $b_0 = 6.97$; $c_0 = 6.20$. **Crystal structure** is shown in Figs. 236 and 237 and the model of the structure in Fig. 238. The S^{6+} ions are located in the centres of the tetrahedral O^{2-} groups, and each Ca^{2+} ion is surrounded by 8 oxygen ions. It should be noted that the *a* and *b* dimensions in the unit cell are almost equal. The structure, however, cannot be regarded as pseudotetragonal parallel to *c* axis, since the arrangements of ions on the

(010) plane (Fig. 237, left) and on the (100) plane (closer to the observer) are different. The (010) face is centred, while on the (100) face, the Ca^{2+} and $[SO_4]^{2-}$ ions do not form horizontal rows. **Habit**, thick-tabular or prismatic (Fig. 239). Well-formed crystals are rare. **Aggregates.** Usually granular massive sometimes in rod-shaped aggregates.

Colour, white, often with a blue, greyish, sometimes reddish tinge. Colourless water-transparent crystals occur. **Lustre**, vitreous with pearly chatoyancy on cleavage (010). This becomes especially pronounced on heating. $n_x = 1.614$, $n_y = 1.576$, and $n_z = 1.571$.

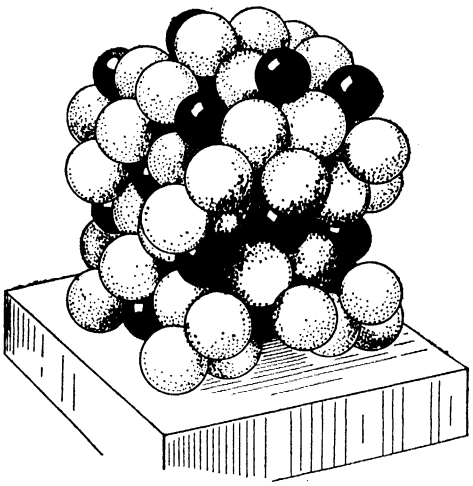


Fig. 238. Model of anhydrite crystal structure oriented as shown in Fig. 237 (cf. arrangement of calcium cations).

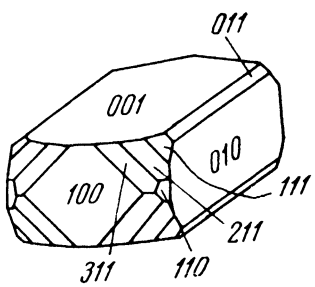


Fig. 239. Anhydrite crystal.

Hardness, 3 to 3.5. **Cleavage**, {010} perfect, {100} and {001} distinct. In these three mutually perpendicular directions, crystals are rather easily split into cubic fragments. **Specific gravity**, 2.8 to 3.0 (for transparent varieties, 2.96). **Other properties.** In the presence of water under atmospheric pressure gradually changes to gypsum, greatly increasing in volume (up to 30 per cent). Increasing external pressure inhibits this conversion.

Diagnostic features. Differs from the other sulphates of the group by lowest specific gravity; direction of cleavage planes; and optical properties (especially birefringence). Anhydrite also differs from marbled masses of carbonate (calcite, dolomite, and magnesite) in that it does not evolve CO_2 in acids. Is distinguished from gypsum by hardness (cannot be scratched with the fingernail).

Before the blowpipe fuses into a white enamel and colours the flame reddish-yellow. Does not fuse with soda or deliliquiesce and soak into the charcoal like barite, but decomposes and yields sulphur liver which stains a silver plate. In powdered form dissolves in sulphuric acid. The solution, in contrast to anhydrous sulphates of Ba, Sr, and Pb does not become turbid on addition of a moderate amount of water. Poorly soluble in hydrochloric acid.

Genesis and occurrence. Anhydrite occurs in huge masses in thick sedimentary strata. As a product of chemical sediments (in lagoons and seas), anhydrite is almost invariably accompanied by gypsum. It is rather easily converted to gypsum in the outcrops. This conversion, according to the data obtained in numerous boreholes and mine workings, may occur down to a depth of 100 to 150 m from the surface (beyond which anhydrite masses are unaltered). At great depths the

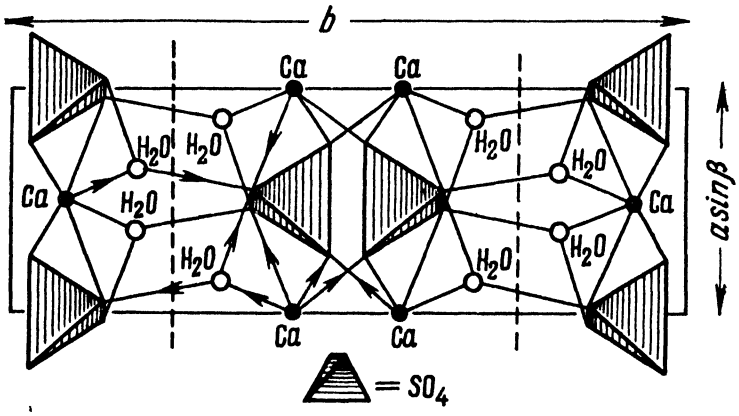


Fig. 240. Crystal structure of gypsum projected on the plane perpendicular to *c* axis. Dotted lines show cleavage direction.

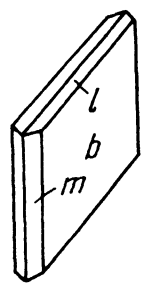


Fig. 241. Platy gypsum crystal: *b* {010}, *l* {111}, *m* {110}.

pressure of the overlying rocks is evidently so great that it prevents any increase of the rock mass volume which accompanied the alteration of anhydrite into gypsum.

Anhydrite often occurs in salt deposits either as individual crystals or as beds and intercalations (sometimes paper-thin) interbedded with halite, sylvite, carnallite, etc.

Relatively seldom anhydrite may be recorded from *hydrothermal* veins, and occasionally in contact-metasomatic deposits. Anhydrite had also occurred in voids in lavas in volcanic regions.

It is quite probable that the thick anhydrite strata in gypsiferous regions have derived from the dehydration of original gypsum strata caused by the great pressure of the overlying rocks. No anhydrite or any other sulphates are found, however, in deeper metamorphic rocks.

Great anhydrite deposits are found at depth in thick gypsiferous Permian strata all along the western foothills of the Urals, in the Archangel, Vologda, Kuibyshev, Gorky regions, Donets Basin, and elsewhere.

Uses. Anhydrite, as well as gypsum, is used chiefly in the production of binding materials (cements). Dense cryptocrystalline varieties are also used for ornamental purposes.

GYPSUM, $CaSO_4 \cdot 2H_2O$. Gypsum is the old Greek name for the mineral.

Chemical composition. CaO 32.5%, SO_3 46.6%, H_2O 20.9%. Usually pure. Mechanical impurities are clayey matter, organic substances (fetid gypsum), minute sand grains, sometimes sulphides, etc.

System, monoclinic; symmetry, prismatic L^2PC. Space group $A2/n(C_{2h}^6)$. $a_0 = 10.47$; $b_0 = 15.12$; $c_0 = 6.28$; $\beta = 98°58'$. **Crystal structure.** According to X-ray data, the mineral has a distinctly laminated structure. Two sheets of the $[SO_4]^{2-}$ anionic groups closely bonded with

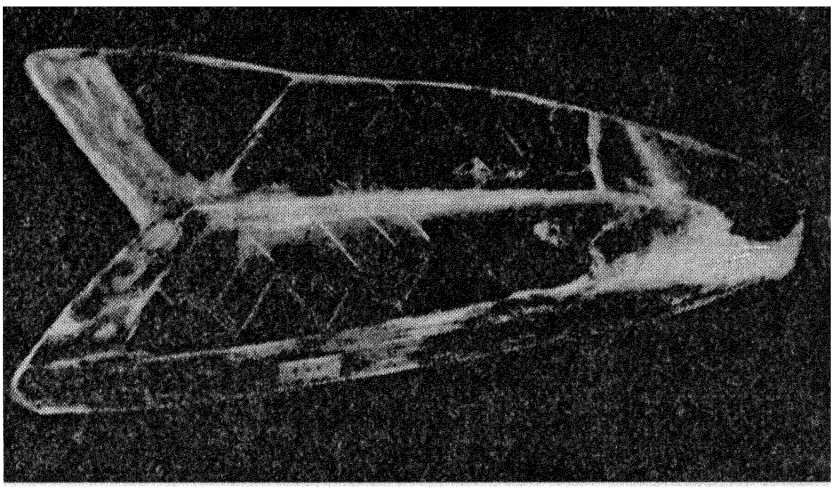


Fig. 242. Transparent swallow-tail gypsum twin.

the Ca^{2+} ions (Fig. 240) compose double layers oriented parallel to the (010) plane. In Fig. 240 these layers are arranged perpendicular to the plane of drawing and follow a vertical direction (the borderlines are dotted). The H_2O molecules are located between the double layers. This explains the characteristic perfect cleavage of gypsum. Each calcium ion is surrounded by six oxygen ions of the SO_4 groups, and by two water molecules. Each water molecule links the Ca ion with one oxygen ion in the same double layer and with another oxygen ion in the adjacent layer (Fig. 240).

Habit. Owing to the predominant development of the {010} faces, crystals are tabular (Fig. 241), rarely columnar or prismatic. The most common prisms are {110} and {111}, sometimes {120}, etc. The faces {110} and {010} are often vertically striated. Penetration twins are common and may be of three types: (1) Gallio twins (100); (2) Paris twins (101), and (3) twins ($\bar{2}09$). It is not always easy to tell them from one another. The first two types have a swallow-tail shape (Fig. 242). In Gallio twins (Fig. 243) the edges of the prism *m* {110} are parallel to the twinning plane, and the edges of the prism *l* {111} form a re-entrant angle, whereas in Paris twins the edges of the prism *l* {111} are parallel to the twinning plane (Fig. 244). **Aggregates.** Occurs in cavities as crystal druses. Compact finely-crystalline aggregates are com-

mon. In cracks sometimes occurs in asbestos-like parallel-florous masses of gypsum with a silky chatoyancy and with the fibres perpendicular to the walls of the cracks. Such gypsum is known as selenite. When gypsum crystallises among loose sandy masses, it contains numerous entrapped sand particles which are clearly visible on the cleavage surfaces of large crystal individuals.

Colour, white. Individual crystals may be colourless and water-transparent. Also grey, honey-yellow, red, brown, and black (depending on the colour of the impurities entrapped during crystallisation).

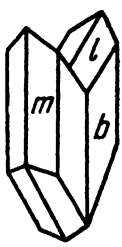


Fig. 243. Gallic penetration twin on (100) *m* {110}, *l* {111}, *b* {010}.

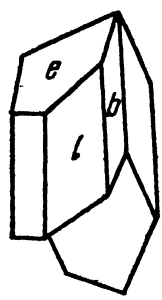


Fig. 244. Paris penetration twin on (101) *l* {111}, *b* {010}, *e* {103}.

Lustre, vitreous, with a pearly chatoyancy on cleavage surfaces. $n_x = 1.530$; $n_y = 1.528$, and $n_z = 1.520$.

Hardness, 1.5 (can be scratched with the fingernail). Very brittle. **Cleavage**, {010} excellent, {100} and {011} distinct. Cleavage fragments are rhombic with angles of 66° and 114°. **Specific gravity**, 2.3. **Other properties.** Well-soluble in water. A remarkable characteristic of gypsum is that its solubility is highest at 37° to 38° and then drops abruptly (Fig. 245). The sharpest decrease in solubility begins at temperatures over 107°, owing to the formation of the "hemi-hydrate" $CaSO_4 \cdot {}^1/_2H_2O$.

When heated under atmospheric pressure, gypsum, as evident from thermographs, starts losing water at 80° to 90° and at 120° to 140° completely changes to the hemi-hydrate, the so-called statuary or plaster gypsum known as plaster of Paris. On mixing this hemi-hydrate with water, a mortar is obtained which soon sets, expanding and evolving heat.

Diagnostic features. A highly characteristic feature of crystalline gypsum is its perfect {010} cleavage and low hardness (can be scratched with the fingernail). Compact marble-like aggregates and fibrous masses are also identifiable by low hardness and the fact that they do not effervesce when moistened with hydrochloric acid.

Before the blowpipe loses water, decrepitates, and fuses into white enamel. In the reducing flame on charcoal gives CaS. Dissolves in water with a little sulphuric acid much more readily than in pure

water. When the acid concentration exceeds 75 g/l, solubility drops sharply. Almost insoluble in hydrochloric acid.

Genesis and occurrence. Gypsum forms in diverse ways in nature.

1. Large masses are formed by *sedimentation* in drying saline lacustrine and marine basins, where gypsum along with NaCl is formed only at the first stages of evaporation when the concentration of other salts in solution is not yet great. When such salts as NaCl and especially $MgCl_2$ reach a certain point of concentration, anhydrite begins to crystallise, followed by other more soluble salts. Thus, gypsum in these basins must be one of the early chemical sediments. Indeed, in many salt deposits the gypsum (and anhydrite) beds alternating with those of rock salt occupy the lower part of the deposit and are often underlain only by chemically sedimented limestones.

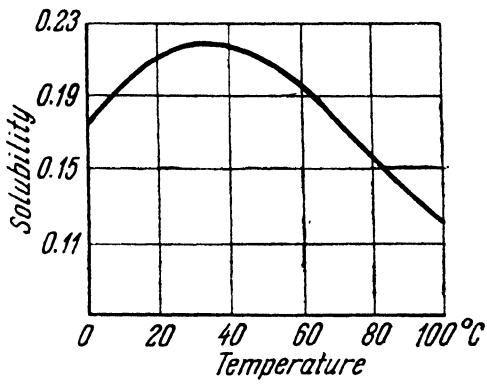


Fig. 245. Relation between gypsum solubility and temperature.

2. Considerable amounts of gypsum derive from the *hydration of anhydrate* in sedimentary deposits under the action of surface water under low external pressure (at the maximum average depth of 100 to 150 m), according to the following reaction:

$$CaSO_4 + 2H_2O = CaSO_4 \cdot 2H_2O$$

The reaction is accompanied by a large increase in volume (up to 30 per cent) which involves numerous and complex local disturbances in the mode of occurrence of the gypsiferous strata. The majority of huge gypsum deposits in the world have been formed in this way. Massive gypsum in cavities sometimes contains pockets of large, often transparent crystals.

3. In deserts and semideserts gypsum frequently occurs as veinlets and nodules in *the crust of weathering* of rocks of most diverse composition. It may be formed on limestones by the action of water enriched in sulphuric acid or dissolved sulphates. Sometimes occurs in the oxidised zones or sulphide deposits, though not in as large amounts as might be expected. This is so because, in most cases, sulphide ores contain pyrite or pyrrhotite, the oxidation of which (especially of the former) substantially increases the sulphuric-acid content of the surface water. The acidulated surface water considerably increases the solubility of gypsum. Hence, in a number of deposits gypsum is more common in the upper zones of primary ores, where it occurs in cracks together with other sulphates.

4. Gypsum is comparatively rarely found as a typically *hydrothermal* mineral in sulphide deposits formed at low pressures and tempe-

ratures. In such deposits it occurs sometimes in large crystals in cavities, and contains inclusions of chalcopyrite, pyrite, sphalerite, and other minerals.

Such minerals as calcite, aragonite, malachite, quartz and other minerals frequently occur pseudomorphous after gypsum and vice versa.

Sedimentary gypsum deposits are found all over the world in strata of different geological ages. Without enumerating them, we shall merely say that in the U.S.S.R. thick gypsiferous Permian strata occur in the Western Urals, Bashkiria and Tataria as well as in the Archangel, Vologda, Gorky, and other regions. Numerous Upper Jurassic deposits are found in the Northern Caucasus, Daghestan, Turkmenia, Tajikistan, Uzbekistan, etc.

Uses of gypsum are many and varied, especially in building.

1. Plaster of Paris (semi-calcined gypsum) is used for casts, moulds, "rock" lath, stucco, and wall plaster, in surgery, as filler for heavy white paper, etc.); in building as a binding material in masonry and for plaster floorings; in making bricks, window-sills, staircases, etc.

2. Uncalcined (natural) gypsum is used chiefly as a retarder in cement, for decorative and statuary purposes, as an ornamental stone (especially Ural selenite), in the preparation of paints, enamels, glazes, as a flux in smelting oxidised nickel ores, etc.

3. SULPHATES OF ALKALI METALS

Besides anhydrous and hydrous sodium sulphates (thenardite and mirabilite) we shall describe in this group binary salts with alkaline earth metals (polyhalite and kainite).

THENARDITE, Na_2SO_4. **Chemical composition.** Na_2O 43.7%, SO_3 56.3%. Occasionally contains small amounts of K_2O, and as a mechanical impurity, $CaSO_4$.

System, orthorhombic, symmetry, rhombic dipyramidal $3L^23PC$. Space group $Fddd(D_{2h}^{24})$. $a_0 = 9.75$; $b_0 = 12.29$; $c_0 = 5.85$. Crystals are dipyramidal in habit (Fig. 246), sometimes tabular, owing to the development of the {001} pinacoid and the {101} prism. Twins are frequent (Fig. 246). Often occurs in druses or granular aggregates.

Colour. Colourless, transparent, sometimes with a reddish tinge. **Lustre**, vitreous. $n_x = 1.485$, $n_y = 1.474$, and $n_z = 1.464$.

Hardness, 2 to 3. Brittle. **Cleavage**, {010} perfect, {101} distinct, and {100} imperfect. **Specific gravity**, 2.66. **Other properties.** Soluble in water. Precipitates from oversaturated solutions (in pure water) only at temperatures over 32.5°. Below this temperature crystallisation of mirabilite, $Na_2SO_4 \cdot 10H_2O$, takes place. Therefore, at room temperature in humid air, thenardite is hydrated and covered with a white crust of hydrous sodium sulphate. With time decomposes to powder.

Diagnostic features. In crystals differs from its mineral associates (mirabilite, astrakhanite, etc.) by crystallisation system, and in granular aggregates by chemical reactions.

Infusible in the blowpipe flame, colours the flame intense yellow (Na reaction). Readily soluble in water. Taste subsaline.

Genesis and occurrence. Thenardite is formed in certain drying salt lakes together with mirabilite, crystallising directly from the brine supersaturated with Na and SO_4 ions. Also derives from the dehydration of mirabilite, e.g., in the upper layer of the material thrown up on the shore during storms (in the Caspian Sea), or in underground (i.e., not of recent formation) sodium sulphate deposits, and also in hot deserts.

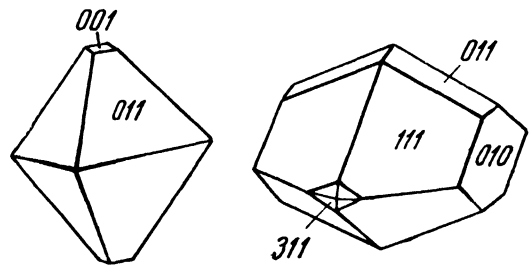


Fig. 246. Thenardite dipyramidal crystal and twin.

Occurs in some volcanic regions (Vesuvius), at fumaroles.

A large buried deposit of thenardite in Pleocenic strata is located at *Kyuren-Dag* near the Azun-Su railway station, beyond the Caspian Sea. Together with mirabilite it occurs as lenses in sandy-clayey sediments. Also occurs in contemporary lakes in the *Kulunda Steppe* (North-Western Kazakhstan), north of the Caspian Sea (Lake Shashinskoye) in the *Shemakha* district (Transcaucasia), and elsewhere.

Uses. Extracted together with mirabilite and used in the manufacture of glass, soda, etc.

MIRABILITE, $Na_2SO_4 \cdot 10H_2O$. The old name: "sal mirabile Glauberi" (the wonderful salt of Glauber). Synonym: Glauber salt.

Chemical composition. Na_2O 19.3%, SO_3 24.8%, H_2O 55.9%. Mirabilite owes many of its properties to high content of crystallisation water.

System, monoclinic; symmetry, prismatic L^2PC. Crystals are short-columnar in habit parallel to the *b* axis or to the *c* axis (Fig. 247). Usually in massive granular aggregates and also in crusts and coatings.

Colour. Colourless and transparent, sometimes turbid with yellow, bluish, or greenish tinges. **Lustre,** vitreous. Refractive indices extremely low: $n_x = 1.398$, $n_y = 1.396$, and $n_z = 1.394$.

Hardness, 1.5 to 2. Very brittle. **Cleavage,** {100} perfect. Fracture in other directions conchoidal. **Specific gravity,** 1.48. **Other properties.** In dry air loses gradually all its water, changes to thenardite, and turns into a white pulverulent substance. Taste cool, slightly bitter-saline.

Diagnostic features. As a mineral rich in H_2O molecules bonded within the crystal structure, mirabilite has the lowest specific gravity and refractive indices of all the readily soluble hydrous sulphates and chlorides. Differs from soda ($Na_2CO_3 \cdot 10H_2O$) in that it does not

evolve carbon dioxide under the action of hydrochloric acid. At 32° deliquesces or rather dissolves in its own crystallisation water.

Genesis and occurrence. Is formed in large masses in salt lakes saturated with sodium and sulphate anions in the course of evaporation of water at temperatures below 33° (provided the solution contains no other soluble salts) or with decreasing temperature in autumn and winter. If evaporation of water from a solution of the same composition takes place at temperatures higher than 33°, anhydrous sodium sulphate called thenardite will crystallise. In the presence of dissolved sodium chloride (almost always the case in salt lakes) thenardite crystallises at lower temperatures.

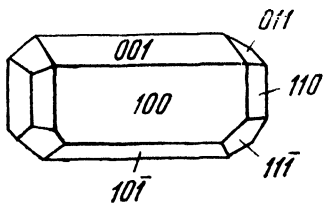


Fig. 247. Mirabilite crystal.

In the Gulf of Kara-Bogaz (the Caspian Sea) in winter when the temperature of water drops below 6°, great amounts of mirabilite are precipitated on the bottom and are partly thrown upon the shore by storms forming billows of white salt. In summer, the mirabilite in the gulf water once again passes into solution, while on shore its upper layers are dehydrated to thenardite. The numerous small dried-up lakes of the Northern Caspian region, North-Eastern Kazakhstan (Kulunda Steppe), Northern Caucasus (south of Stavropol), Transcaucasia, the Crimea, etc., contain large masses of mirabilite and thenardite, with layers of halite, sometimes gypsum, and other minerals.

The most important foreign localities for the occurrence of mirabilite are the Great Salt Lake in Utah (U.S.A.) and lakes in Mexico and Argentine.

Uses. Mirabilite is used mainly for containing potash by the Leblanc process (fusion with limestone and coal), as well as in the production of glass, paints, etc. It is used in medicine as a purgative.

POLYHALITE, $K_2MgCa_2[SO_4]_4 \cdot 2H_2O$. **System,** triclinic; symmetry, pinacoidal. Crystals rare, commonly tabular. Aggregates, compact, fibrous, rod-like.

Colour, white with a grey or yellowish tinge, and also brick-red. **Lustre,** vitreous. $n_x = 1.567$; $n_y = 1.562$; and $n_z = 1.548$.

Hardness, 2.5 to 3. **Cleavage,** {101} perfect. **Specific gravity,** 2.72 to 2.78. Before the blowpipe readily loses water and fuses into an opaque bead. Water leaches out the salts of K and Mg leaving a residue corresponding to gypsum in composition.

Polyhalite is formed from brines rich in Mg, K, and Ca within a relatively broad range of temperatures from 0° to 80°. Occurs in deposits in the Stassfurt district as a "polyhalite stage" between the anhydrite and kieserite strata. Sometimes it is intercalated with thin layers of halite. Also occurs in salt deposits at Ischle, Halistadt (Austria), in Texas, New Mexico (U.S.A.), and elsewhere.

As a potassium salt it is used for the manufacture of artificial fertilisers.

KAINITE, $KMg[SO_4]Cl \cdot 3H_2O$ or $MgSO_4 \cdot KCl \cdot 3H_2O$. System, monoclinic; symmetry, prismatic. Usually in granular massive. Rare crystals are either tabular or prismatic in habit.

Colour, yellowish- or greyish-white, sometimes red. Lustre, vitreous. $n_x = 1.516$; $n_y = 1.505$; and $n_z = 1.494$. Hardness, 2. Cleavage, {001} perfect. Specific gravity, 2.1.

Fusible in the blowpipe flame. Well soluble in water. Taste, bitter saline. Non-hygroscopic (in contrast to carnallite).

Widely occurs in the salt deposits at Stassfurt associated with schoenite, $K_2Mg[SO_4]_2 \cdot 6H_2O$; carnallite, kieserite, halite, etc. Considerable kainite is found at Kalush (Western Ukraine).

A material for artificial fertilisers and potassium salts.

4. HYDROUS SULPHATES OF DIVALENT METALS

Here we shall review some sulphates of magnesium, iron, and copper, especially those rich in H_2O.

EPSOMITE, $MgSO_4 \cdot 7H_2O$. Named after the mineral springs at Epsom, England, in which it occurs. Synonym: Epsom salt.

Chemical composition. MgO 16.3%, SO_3 32.5%, H_2O 51.2%. May contain $Mn^{\cdot\cdot}$ and $Fe^{\cdot\cdot}$ as isomorphous admixtures. Certain varieties rather rich in divalent iron (ferroepsomite) and also in nickel (nickel-epsomite) have been established.

System, orthorhombic; symmetry, rhombic tetrahedral $3L^2$. Space group $P2_12_12_1(D_2^4)$. $a_0 = 11.94$; $b_0 = 12.13$; $c_0 = 6.865$. A rather unstable monoclinic modification in the form of pseudohexagonal plates can be obtained artificially. Crystals precipitating from brines are pseudotetragonal prismatic (Fig. 248) or acicular. Occurs in compact sinters and earthy aggregates.

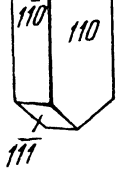


Fig. 248. Epsomite crystal.

Colour, white; sometimes colourless and transparent. **Lustre**, vitreous. $n_x = 1.461$, $n_y = 1.455$, and $n_z = 1.433$.

Hardness, 2 to 2.5. Very brittle. **Cleavage**, {010} highly perfect, and {101} distinct.

Specific gravity, 1.68. **Other properties.** Taste, bitter, subsaline. In dry air gradually loses water and becomes turbid. Dehydration proceeds unevenly: at 100° epsomite loses five water molecules, at 132° the sixth water molecule, and at 218° to 238° the last molecule. On losing one water molecule in dry air, changes to magnesium hexahydrous sulphate.

Diagnostic features. Epsomite is very similar to hydrous sulphates of more complex composition, and can be distinguished from them only by chemical tests. Has a characteristic bitter saline taste.

Gives off water upon heating. On ignition yields an infusible white mass. Well-soluble in water.

Genesis and occurrence. Epsomite forms in the course of evaporation of the brine of magnesia-rich salt lakes and is one of the first of the highly hydrated and magnesium sulphates to precipitate. As the brine gets thicker, magnesium heptahydrous sulphate becomes unstable yielding place to magnesium hexahydrous sulphate known as hexahydrite, $MgSO_4 \cdot 6H_2O$.

Occurs as efflorescences on the surface of rocks, as crusts, capillary or acicular crystals on the walls of caves in calcareous rocks, abandoned mine workings, and other cavities near the surface; evidently as a result of crystallisation of percolating magnesial-sulphate waters.

Epsomite is formed most frequently as crystalline precipitates in magnesial sulphate salt lakes: *Elton*, *Jelon*, *Malinov* in the lower Volga country in certain Crimean lakes (Sasyk-Sivash, and others); Jaman-Klych, north of the Sea of Aral in Kazakhstan, etc.

Notable foreign lakes are in the U.S.A., Mexico, Egypt, China, and elsewhere.

Uses. Epsomite, as the other magnesium sulphates, is used in textile, paper-making, sugar-refining, chemical, pharmaceutical, and other industries.

HEXAHYDRITE, $MgSO_4 \cdot 6H_2O$. System, monoclinic; symmetry, prismatic. Synonym: sacchite. Occurs in thick tabular, spear-shaped crystals or in fibrous masses. Twins on (001) and (110).

Colour, white, sometimes with a light-green tinge. Lustre, pearly. $n_x = 1.456$, $n_y = 1.453$, and $n_z = 1.426$.

Hardness, 2. Cleavage, {100} perfect. Specific gravity, 1.75. Well-soluble in water.

Occurs in magnesial sulphate salt lakes in the Crimea, Astrakhan Region, and elsewhere. Precipitates from evaporating brine after epsomite.

KIESERITE, $MgSO_4 \cdot H_2O$. **Chemical composition.** MgO 29.0%, SO_3 58.0%, H_2O 13.0%.

System, monoclinic; symmetry, prismatic L^2PC. Rare crystals are dipyramidal. Usually occurs in compact crystalline-granular aggregates.

Colour. Seldom colourless and transparent; commonly turbid, white with a yellowish tinge. **Lustre**, vitreous. $n_x = 1.584$, $n_y = 1.533$, and $n_z = 1.520$.

Hardness, 3.5. Brittle. **Cleavage**, on {110} and {111} prisms perfect. **Specific gravity**, 2.57. **Other properties.** In humid air gradually changes to epsomite. A powdered mass mixed with a small amount of water sets like plaster of Paris.

Diagnostic features. Differs from similar hydrous sulphates (epsomite, kainite, etc.) in optical constants and composition.

In the blowpipe flame decrepitates, loses water and fuses readily. Slowly dissolves in water. Crystallises among the last minerals from complex, concentrated, magnesia-rich sulphate brines at temperatures above 18-20°.

Genesis and occurrence. In salt lakes kieserite very rarely crystallises directly from the magnesia-rich sulphate brine (its range of stability at lower temperatures is very small).

Usually occurs in buried salt deposits probably deriving from the more water-abundant magnesium sulphates (epsomite and hexahydrite), through dehydration under pressure.

In quantity (up to 30 per cent of total mass), kieserite is found in the Stassfurt salt deposits (Germany) in association with halite, carnallite, polyhalite, anhydrite, etc.

Uses. A source of bitter salt (epsomite) the uses of which have been described above.

MELANTERITE, $FeSO_4 \cdot 7H_2O$. "Melanteros" is the Greek for blacker. Probably, the first to be discovered was the rare grey-black variety. Is readily converted to black leather mordants and dyes.

Chemical composition. FeO 25.9%, SO_3 28.8%, H_2O 45.3%. May contain isomorphous admixtures of Mg, Ni, Zn, Cu, and sometimes Mn.

System, monoclinic; symmetry, prismatic L^2PC. $P2_1/c$ (C_{2h}^5). $a_0 = 15.34$; $b_0 = 12.98$; $c_0 = 20.02$. **Habit**, rhombohedral, sometimes acicular or capillary. More often massive in the form of veinlets or sinters.

Colour, light-green, sometimes dark-grey, or greyish black. **Lustre**, vitreous. $n_x = 1.486$; $n_y = 1.478$, and $n_z = 1.471$.

Hardness, 2. Very brittle. **Cleavage**, {001} perfect, {110} distinct. **Specific gravity**, 1.8 to 1.9.

Diagnostic features. May be distinguished positively from other readily soluble sulphates only by chemical analysis. A characteristic feature is the presence of divalent iron.

On heating deliquesces, dissolving in its own crystallisation water. On losing water turns into a pulverulent mass of anhydrous sulphate which turns brown in the reducing flame on charcoal (owing to the oxidation of its divalent iron).

Genesis and occurrence. Melanterite crystallises from supersaturated sulphate waters under oxygen deficiency conditions. Therefore is never found in the oxidised zones. Usually occurs below the oxidised zone in cracks and cavities in semi-decomposed pyrite-rich ores in association with gypsum and other sulphates. Also occurs in clays in coal deposits (the source material for it is probably pyrite, often present in them).

In the U.S.S.R. melanterite occurs in Kazakhstan, Central Asia, and Siberia. Found in the *Blyava* pyrite deposit (Southern Urals) as veinlets and accumulations in cavities in the upper horizons of semi-decomposed pyrite ores. Some black varieties of melanterite have been found there.

Uses. Natural occurrences are rarely large. Artificial melanterite is used as a mordant and in making paints: Prussian blue and black and dark dyes for woolens and leather and also for the preparation of ink and chemicals. It should be noted that heptahydrosulphate of ferrous iron with certain tanning agents yields a stable black pigment.

CHALCANTHITE, $CuSO_4 \cdot 5H_2O$. "Chalcos" is the Greek for copper, "anthe" flowers ("copper flowers"). Synonym: copper vitriol.

Chemical composition. CuO 31.8%, SO_3 32.1%, H_2O 36.1%. Impurities: Fe, sometimes Zn, Co, and Mg (magnochalcanthite).

System, triclinic; symmetry, pinacoidal. Space group $P1(C_i^1)$. $a_0 = 6.11$; $b_0 = 10.673$; $c_0 = 5.95$; $\alpha = 97°35'$; $\beta = 107°10'$; $\gamma = 77°33'$. Crystals are rare, short-prismatic and tabular. Usually occurs massive with stalactitic radial-fibrous structure.

Colour, azure, deep-blue, sometimes with a greenish tinge. **Lustre,** vitreous. $n_x = 1.543$, $n_y = 1.537$, and $n_z = 1.514$.

Hardness, 2.5. Very brittle. **Cleavage**, {110} imperfect. Fracture, conchoidal. **Specific gravity,** 2.1 to 2.3.

Diagnostic features. Identifiable by sky-blue colour and high solubility in water; however for more positive identification, chemical analysis should be resorted to.

On heating gradually loses water and changes first to trihydrous sulphate and then to monohydrous sulphate, becoming white and opaque. Readily soluble in water yielding a blue solution. An iron needle immersed in the solution, is coated with metallic copper.

Genesis and occurrence. Chalcanthite forms in the oxidised zones of copper sulphide deposits in dry climate. As stalactites occurs on the walls of abandoned unventilated mines driven through the oxidised zones of copper deposits.

In the U.S.S.R., chalcanthite occurs in a number of copper deposits: Mednorudyanskoye (Nizhny Tagil), Turya (Northern Urals), Kedabek (Transcaucasia), etc. Large masses are extremely rare.

Uses. Artificial chalcanthite is used as a pesticide in vineyards, and in the chemical dyeing, and other industries.

The presence of this mineral in ores shows that mine waters are rich enough in dissolved copper sulphate to warrant recovery of metallic copper by precipitation with scrap iron. This is done by passing mine waters through tanks in which copper is deposited on iron shavings.

5. ALUNITE GROUP

We shall consider under this heading a characteristic group of basic binary sulphates of Al and Fe with univalent (K, Na, NH_4) and some divalent (Pb) metals.

It should be noted that compounds with large univalent cations (K, NH_4) and occasionally with Pb^{2+} are pseudocubical and crystal-

lise in the ditrigonal pyramidal symmetry (in which the α-angle of the rhombohedron is close to 90°), whereas compounds with smaller cations (Na and Ag) are lower in symmetry order and pseudohexagonal.

ALUNITE, $KAl_3[SO_4]_2[OH]_6$. Synonym: alumstone. The colloidal variety rich in adsorbed water is known as loewigite.

Chemical composition. K_2O 11.4%, Al_2O_3 37.0%, SO_3 38.6%, H_2O 13.0%. Very often half of K_2O is replaced by Na_2O (natroalunite). Loewigite may contain rare earths.

System, trigonal; symmetry, ditrigonal pyramidal L^33P. Space group $R3m(C_{3v}^5)$. $a_0 = 6.96$; $c_0 = 17.35$. Rare small crystals are rhombohedral, pseudocubical, or thick-tabular (Fig. 249). Usually in fine-granular, earthy, sometimes fibrous masses.

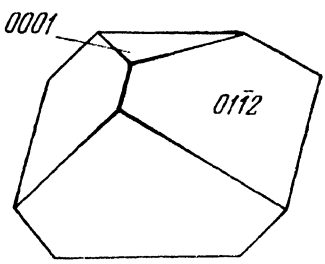


Fig. 249. Alunite crystal.

Colour, white with greyish, yellowish, and reddish tinges. **Lustre**, vitreous, sometimes pearly on cleavage surfaces. $n_x = 1.592$ and $n_y = 1.572$ (for natroalunite 1.585).

Hardness, 3.5 to 4. **Cleavage**, {0001} distinct. **Specific gravity**, 2.6 to 2.8.

Diagnostic features. In finely-crystalline masses alunite may be easily confused with many white hydrous minerals. The best way to identify it is by chemical tests.

Before the blowpipe decrepitates without fusing. Loses water only on ignition. With soda yields sulphur liver. When moistened with a solution of cobalt nitrate assumes a deep-blue coloration (aluminium reaction). Insoluble in water and hydrochloric acid. Dissolves with difficulty in concentrated sulphuric acid. Ignited alunite placed in water gives alum in the solution.

Genesis and occurrence. Alunite forms as extensive impregnations in igneous rocks rich in alunite-forming alkaline feldspars under the action of low-temperature sulphurous *hydrothermal* solutions. This alteration of rocks is called "alunitisation". Is also found in some hydrothermal veins.

Rare alunite concretions occur in sands, clays, bauxites, probably of exogenous origin.

As irregular yellowish or pinkish inclusions alunite is found in heavily altered tuffs (clastic rock of igneous origin) at *Zaglik* (Azerbaijan). At *Zhuravlinskoye* (25 km up the Chusovaya River from the Chusovskaya railway station) alunite with hydrargillite and kaolin forms pockets and veinlets of exogenous origin in the disintegration zone of limestones.

Uses. Alunite-bearing rocks are a source of alum and aluminium sulphate. For the uses of these products see "Alum". Lately alunite is used as a source of alumine.

JAROSITE, $KFe_3[SO_4]_2[OH]_6$. Named after the place of discovery, Barranco Jaroso (Spain). Synonym: utahite.

Chemical composition. K_2O 9.4%, Fe_2O_3 47.9%, SO_3 31.9%, H_2O 10.8%. Quite frequently contains small amounts of sodium and selenium and also SiO_2, Al_2O_3, etc., as mechanical impurities.

System, trigonal; symmetry, ditrigonal pyramidal L^33P. Often massive granular or earthy, also in druses of small rhombohedral crystals in cavities.

Colour, ochreous-yellow, often with a definite brown tinge. **Streak**, yellow. **Lustre**, vitreous to adamantine. $n_y = 1.820$, $n_z = 1.715$.

Hardness, 2.5 to 3.5. **Cleavage**, {0001} distinct. **Specific gravity**, 3.15 to 3.26.

Diagnostic features. Externally resembles ochreous limonite. Differs from it by chemical reactions and also by greasy feel contrasting with the rough sand-like feel of limonite.

In the blowpipe reducing flame yields a magnetic mass. Does not dissolve in water, but is soluble in hydrochloric acid. Gives a $BaSO_4$ precipitate from a solution of BaCl. In the closed tube, gives water with an acidic reaction.

Genesis and occurrence. Jarosite is a rather widely distributed mineral, formed in the *oxidised zones* of iron-sulphides, chiefly pyrite, deposits under the conditions of an arid climate and also after pyrite in certain sediments.

In moderate-temperature climates with abundant precipitation it is formed very rarely, since the iron sulphides decompose and are altered directly to iron hydroxides.

It has been demonstrated experimentally that jarosite precipitates from sulphate water contacting atmospheric oxygen and therefore containing trivalent iron.

Jarosite is not very stable in water or air, yielding iron hydroxides on hydrolysis.

Pseudomorphs of jarosite after cubic crystals of pyrite impregnated in rocks and after marcasite and pyrite concretions in clays are frequent.

Large masses of jarosite occur in the *Blyavinskoye* pyrites deposit (Southern Urals), in which it has survived in an old oxidised zone underlying an iron-hat zone composed of hydrohematite and hematite; jarosite also occurs at *Maykain* (Bayanaul district, south-west of Pavlodar, Central Kazakhstan).

Uses. When found in large pure masses, jarosite is a material for polishing powders (Fe_2O_3) made by calcining.

6. ALUM GROUP

The term alum stands for normal binary sulphates of aluminium and alkalis crystallising in the cubic system with 12 water molecules. Halotrichite, i.e., sulphate of Fe and Al with 22 H_2O molecules, will also be described here.

POTASSIUM ALUM, $KAl[SO_4]_2 \cdot 12H_2O$. **System**, cubic; symmetry, didodecahedral $4L_6^3 3L^2 3PC$. **Chemical composition.** K_2O 9.9%, Al_2O_3 10.8%, SO_3 33.8%, H_2O 45.5%.

Colourless. **Lustre**, vitreous, $n = 1.456$ (often anisotropic). **Hardness**, 2. **Specific gravity**, 1.76. Readily fusible before the blowpipe. Soluble in water. Solubility at 20° is 151 g/l.

Found in earthy masses, efflorescences, crusts, less often as massive granular aggregates.

Occurs in the so-called "alum earths" in the Tambov and Ulyanovsk regions, North Caucasus (Zelenchuk River), in Daghestan, Turkmenia (Kara-Kum desert), Uzbekistan (Shorsu), at the Blyavinskoye pyrite deposit in the Urals (in the lower part of the oxidised zone together with other sulphates), on the right bank of the Oka River (a tributary of the Angara River in Siberia), etc.

Potassium alum has numerous uses: as a mordant in dyeing, in printing shops, in leather and paper manufacture, in medicine, for varnishes, etc. It is recovered by leaching from alum earths and subsequent evaporation of the solution. However, the bulk of alum is obtained artificially from bauxites or as a by-product of other chemical processes.

SODA ALUM, $NaAl[SO_4]_2 \cdot 12H_2O$. Synonym: solfatarite. Has never been recognised positively in nature. Readily obtained artificially. Has been observed as parallel-fibrous masses in cracks in rocks.

Colourless. **Lustre**, vitreous. **Hardness**, 3. **Specific gravity**, 1.73. $n = 1.439$ (for the artificial compound). Natural specimens proved to be optically anisotropic, either because they were partially dehydrated or belonged to a different modification—mendozite. On exposure to air, soda alum is dehydrated and altered to tamarugite, $NaAl[SO_4]_2 \cdot 6H_2O$. Has been described in the solfataras of Pozzuoli near Naples.

HALOTRICHITE, $FeAl_2[SO_4]_4 \cdot 22H_2O$. System, monoclinic; symmetry, dihedral axial L^2. Often occurs in asbestos-like veinlets of snow-white colour with a silky chatoyancy. Hence its name (translated into English means "hairy salt").

Hardness, 2 to 2.5. **Specific gravity**, 1.89 to 2.04. Dissolves in water. In the candle flame melts in its own crystallisation water and solidifies in drop-like forms.

It is formed from sulphate water rich in aluminium and ferrous oxide, under the conditions of acute deficiency of free oxygen below the oxidised zone of pyrites, as, for example, in the Blyavinskoye deposit (Southern Urals).

Also found in pyrite-bearing clays and in coal seams where it is formed as a product of the decomposition of pyrites in the oxidised zone and of the decomposition of argillaceous matter by the evolving sulphuric acid.

CHROMATES

Naturally-occurring salts of chromic acid are very few. The $[CrO_4]^{2-}$ complex anion is capable of forming crystal structures with the large Pb^{2+} cation. Chromate of K^{1+} are extremely rare.

Chromates are formed only in an environment with high oxygen concentration. Although they may occur with sulphates, chromates form neither isomorphous mixtures nor binary salts with them. It has been shown experimentally that $PbCrO_4$ and $PbSO_4$ can intermix in the solid state only at high temperatures. It also has been shown that the metastable $PbCrO_4$ modification crystallising in the orthorhombic system is isostructural with $BaSO_4$.

CROCOITE, $PbCrO_4$. "Crocos" is the Greek for saffron (named for its orange-yellow colour). The element Cr was discovered in crocoite from the Urals in 1797. The mineral has first been recognised in the days of Lomonosov (in the middle of 18th century).

Chemical composition. PbO 68.9%, CrO_3 31.1%. May contain a little silver. The zinc-bearing variety called iossaite has a specific gravity of 5.2 (has not been studied in detail).

System, monoclinic; symmetry, prismatic L^2PC. Space group $P2_1/n(C_{2h}^5)$. $a_0 = 7.10$; $b_0 = 7.40$; $c_0 = 6.80$; $\beta = 102°27'$. Crystals are frequent and occur exclusively in cracks. **Habit**, prismatic parallel to the c axis, sometimes acute rhombohedroidal with {110} and {$\bar{1}$01} faces (Fig. 250) and octahedroidal with {$\bar{1}$11} and {111} faces. Also in druses of rod-like crystals in cracks.

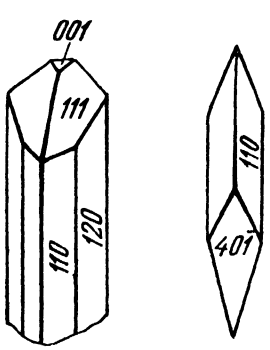


Fig. 250. Crocoite crystals.

Colour, orange-red. On exposure to light fades with time. **Streak**, orange-yellow. **Lustre**, adamantine. $n_x = 2.66$, $n_y = 2.37$, and $n_z = 2.31$.

Hardness, 2.5 to 3. Brittle. **Cleavage**, {110} distinct. **Specific gravity**, 6.0.

Diagnostic features. Highly characteristic features are bright red colour, rod-like or prismatic crystal habit and high specific gravity.

Readily fusible in the blowpipe flame giving a lead globule. The bead of salt of phosphorus and borax assumes an emerald-green colour (chromium reaction). Soluble in hot hydrochloric acid with evolution of chlorine and precipitation of $PbCl_2$. Turns brown and dissolves in KOH.

Genesis and occurrence. Crocoite is formed in the oxidised zone of lead ore deposits near ultrabasic igneous rocks which, upon weathering, may yield at least minor amounts of chromic acid evolving through the disintegration of chromium-bearing silicates and chrome-spinellids. Very well known is the crocoite from the *Berezovskoye* gold deposit (near Sverdlovsk), first described in 1766 by Academician I. G. Leman. It occurs in cracks in beresite (altered granite-porphyry)

as elongated prismatic crystals oriented parallel to the walls. Sometimes associated with galena. On *the Island of Tasmania* large druses of crocoite crystals up to 10 cm long occur in serpentinites. Also occurs in many other deposits.

Because of its sparse distribution is of no commercial importance.

CLASS 5.

MOLYBDATES AND TUNGSTATES

Molybdenum and tungsten are found in the fifth and sixth periods of the periodic system. These elements, just as other pairs in the periods, viz., Zr and Hf, Nb and Ta, are characterised by almost equal atomic and ionic radii owing to the so-called lanthanidic compression, and hence have equal atomic and ionic volumes. Therefore, both elements, as the other pairs, might be expected to yield wide series of isomorphous mixtures in the course of the formation of minerals.

In nature, however, isomorphous mixtures of compounds of this class are very rare. Molybdenum and tungsten play materially different parts in the geochemical processes of mineral formation.

Molybdenum, as has been mentioned when sulphides were discussed, has a distinct affinity for sulphur. The bulk of this element occurs in the earth's crust as a *sulphide*, MoS_2. Spectral and chemical analyses show its presence as an admixture to many sulphurous compounds. Its oxygen compounds seldom occur in nature and are chiefly confined to the *oxidised zone* of ore deposits.

Tungsten, on the other hand, yields almost exclusively *oxygen* compounds in the form of tungstates in the processes of mineral formation. Tungsten sulphide known as tungstenite, WS_2, is so rare that it has never been found in a quantity sufficient for detailed mineralogical study. Only recently it has been found in a more considerable quantity in the form of pseudomorphs after scheelite that have been studied by O. M. Rimskaya-Korsakova. It should also be noted that most tungstates are relatively *high-temperature* formations.

Among the few minerals of this class two principal groups stand out.

1. Tungstates of $Fe^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, and Zn. Molybdates of these metals are so far unknown, with the exception of ferrimolybdite.

2. Molybdates and tungstates of stronger divalent metallic ions with larger ionic radii, such as Ca, Pb, and partly Cu.

1. WOLFRAMITE GROUP

Included in this group are the minerals of the $MnWO_4 - FeWO_4$ (hübnerite-ferberite) isomorphous series. Since the minerals have many common properties, we shall describe in detail only the most widespread wolframite, $(Mn, Fe)WO_4$, a species of intermediate composition,

mentioning in passing the important characteristics of the end members of this series.

WOLFRAMITE, (Mn, Fe)WO_4. At first it was named wolfram (1758) which is the German translation of "Lupi spuma", a Latin term meaning "wolf foam" or "wolf cream", deriving from the property of the mineral, when admixed to tin ores, to produce foam on the surface of the smelted tin. The element tungsten was discovered later; sometimes it is also called wolfram after the mineral.

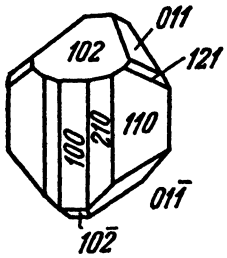


Fig. 251. Wolframite crystal.

Chemical composition. A. K. Boldyrev, suggested to classify as wolframite the varieties containing 25 to 75 molecular per cent of $MnWO_4$, i.e., 5.9 to 17.6 weight per cent of Mn. Varieties containing less than 5.9 per cent Mn are called ferberite, and those containing 17.6 to 23.4 per cent, hübnerite. The WO_3 content is about 75 per cent. Impurities are Mg (up to 0.5%), sometimes CaO, Ta_2O_5, Nb_2O_5, SnO_2, etc.

System, monoclinic; symmetry, prismatic L^2PC. Space group $P2/c(C_{2h}^4)$. $a_0 = 4.78$; $b_0 = 5.73$; $c_0 = 4.98$; $\beta = 90°26'$. Frequent crystals are thick tabular or prismatic (Fig. 251), sometimes flattened parallel to {100}. Some individuals from certain deposits are very large (20 cm and larger). Vertical faces are often striated parallel to the c axis. Twins are parallel to (100), sometimes to (001). Also occurs in massive coarse-granular aggregates.

Colour, brownish black. Hübnerite usually has a pinkish or violet tinge; ferberite, black. **Streak**, brown, for ferberite darker to black, for hübnerite lighter to yellowish brown and even yellow. **Lustre**, on cleavage surfaces mirror-like, adamantine and greasy in other directions. Hübnerite in thin fragments is translucent. Refractive indices for hübnerite are $n_x = 2.32$, $n_y = 2.22$, and $n_z = 2.17$, becoming higher with increasing iron content: in the almost opaque ferberite n_y goes up to 2.40 (Li-light).

Hardness, 4.5 to 5.5. Brittle. **Cleavage**, {010} perfect. **Specific gravity**, 6.7 to 7.5. Ferruginous varieties have a relatively high specific gravity. Iron-rich varieties are weakly magnetic.

Diagnostic features. Wolframite has characteristic brownish-black colour, dark-brown streak, high specific gravity, perfect unidirectional cleavage (in distinction from black sphalerite, whose cleavage is multidirectional, and also from columbite, tantalite, cassiterite, whose cleavage is imperfect).

On intensive ignition in the blowpipe flame on charcoal fuses into a magnetic globule. When a wolframite-soda flux is boiled with tin in water acidulated with hydrochloric acid, it gives a light-blue solution (W reaction). Gives the Mn and Fe reactions with borax. Insoluble in hydrochloric acid.

Genesis and occurrence. Wolframite occurs chiefly in quartz and *hydrothermal quartz* veins often confined to granite masses. Occasionally associated with cassiterite, molybdenite, arsenopyrite, pyrite, chalcopyrite, etc.

In *greisens*, i.e., in the portions of granite masses heavily altered by pneumatolytic action, wolframite is associated with such minerals as micas, topaz, fluorite, tourmaline, sometimes with beryl, cassiterite, molybdenite, etc.

Sulphide veins containing wolframite in paragenesis with chalcopyrite, molybdenite, pyrite, bismuthinite, sphalerite, etc., are known.

Less often and usually in small quantities, it occurs in *pegmatite* dikes in granites.

Mineralogically interesting is the frequent endogenous replacement of scheelite crystals by wolframite both on the periphery and along the cracks. In turn, scheelite often replaces wolframite.

In the oxidised zone exposed to weathering, wolframite is altered, though with difficulty, into the so-called tungsten ochre. In this process, divalent iron is oxidised into the trivalent modification. As a result, the crystal lattice breaks down and earthy yellow-brown or brown masses are formed, consisting mainly of hydrotungstate of trivalent iron (ferritungstite). Sometimes yellow-green tungsten oxides called tungstite, or meymacite, H_2WO_4, are formed.

Hübnerite, which breaks down in much the same manner, yields black "psilomelanic" accumulations containing WO_3. It should be noted that the psilomelane nodules present in eluvium, even at a considerable distance from the primary deposit, contain up to a few per cent WO_3.

Commonly, however, in the vicinity of primary deposits, wolframite, as a relatively inert mineral, usually passes into placers. But it is characteristic that with increasing distance from the primary deposits, the fragments of the wolframite minerals are comparatively quickly attrited and finally disappear altogether. This is due to the relative brittleness of the minerals which is enhanced by their perfect cleavage.

The world's largest wolframite deposits are in South China, Yunan and Kiangsi provinces (Hsihuashan), and also in northern Viet-Nam, South Burma and the Malacca Peninsula. In the United States, there are a number of deposits in Colorado, South Dacota, Nevada, and elsewhere. In Europe, wolframite deposits are found in Portugal and Spain.

Uses. The minerals of this group are the principal source of tungsten which has numerous applications.

1. Nonferrous metallurgy consumes 85 to 90 per cent of the total output of tungsten for special self-hardening steels used in high-speed cutting tools.

2. Tungsten is a component of the so-called stellites, i.e., alloys of tungsten with Cr, Co, etc., which are employed in special-purpose

tools and superhard alloys such as "pobedit", "vidia", "volomite", etc. These alloys are used for the manufacture of drill bits.

3. Tungsten is used for incandescent lamp filaments, targets in X-ray tubes, etc.

4. Tungsten compounds are used in the chemical industry, in colouring glass and porcelain, and for other purposes.

2. SCHEELITE GROUP

This group comprises both tungstates and molybdates of Ca and Pb crystallising in the tetragonal system; only a lead tungstate modification crystallising in the monoclinic system is known.

POWELLITE, $CaMoO_4$. **Chemical composition.** CaO 28%, MoO_3 72%. Some varieties contain an isomorphous admixture of WO_3 (up to 8%).

System, tetragonal; symmetry, dipyramidal L^4PC. Space group $I4_1/a$. $a_0 = 5.23$; $c_0 = 11.44$. **Crystal structure**, analogous to that of scheelite (see below). Occurs as earthy-foliated pseudomorphs after molybdenite. Separate crystals are dipyramidal in habit, sometimes tabular along {001}. The faces {112} are often obliquely striated.

Colour, pale yellow, in crystals yellow-green. **Streak**, light with a yellowish or greenish tinge. **Lustre**, adamantine. $n_x = 1.984$ and $n_y = 1.974$.

Hardness, 3.5. Brittle. **Cleavage**, none. **Specific gravity**, 4.25 to 4.52.

Diagnostic features. Powellite pseudomorphs after molybdenite are readily identifiable by relict platy forms and pale-yellow colour. Crystals are characteristically dipyramidal and give the Mo and Ca reactions.

Before the blowpipe fuses into a semi-transparent mass. With salt of phosphorus in the oxidising flame yields yellowish-green bead, and a dark-green bead in the reducing flame. Soluble in hydrochloric acid. A dilute HCl solution in the presence of excess NH_3 with ammonium oxalate gives a calcium oxalate precipitate.

Genesis and occurrence. As has been stated earlier, powellite often occurs as pseudomorphs after molybdenite in the *oxidised zones* of molybdenum deposits, deriving probably from the reaction of molybdenic acid, formed by oxidation, with calcium-bearing surface waters. With time it is gradually leached out, leaving cavities in quartz in place of the molybdenite crystals.

Exogenous powellite frequently occurs in virtually all oxidised zones of molybdenite deposits, whereas endogenous powellite is rare.

Uses. As compared with molybdenite, is of secondary importance, because it rarely occurs in quantity.

SCHEELITE, $CaWO_4$. Named after the Swedish chemist Scheele (1742-1786), the discoverer of tungstatic acid in this mineral (tungsten in wolframite was discovered later).

Chemical composition. CaO 19.4%, WO_3 80.6%. Occasionally contains an isomorphous admixture of MoO_3 (up to 10%). There is also a copper-bearing variety called *cuproscheelite* with a CuO content of up to 7%. At times contains rare earths (mostly of the cerium group).

System, tetragonal; symmetry, dipyramidal L^4PC. Space group $I4_1/a(C_{4h}^6)$. $a_0 = 5.246$; $c_0 = 11.349$. **Crystal structure** is shown in Fig. 252. The unit cell is a centred tetragonal prism. The arrangement of the anionic tetrahedral WO_4 groups and Ca cations is clearly shown in the diagram. **Habit**, octahedral (Fig. 253), sometimes tabular along {001}. The faces (112) sometimes show oblique striations. Penetration twins on (110) and (001) are fairly often. **Aggregates.** Mostly as irregular inclusions, less often massive.

Colour. Rarely colourless, usually grey, yellow, greenish yellow, brown,

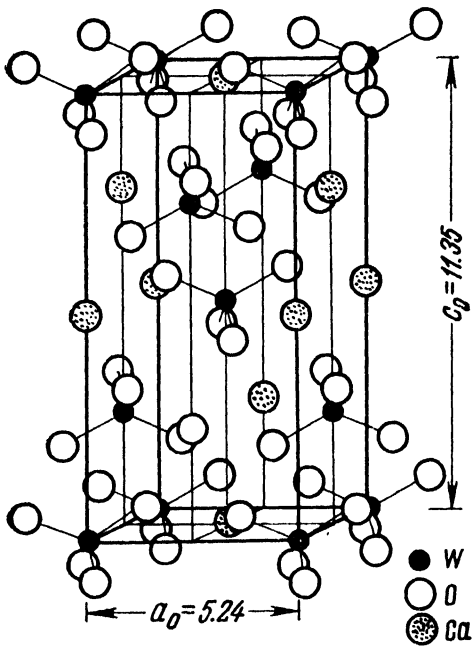


Fig. 252. Crystal structure of scheelite.

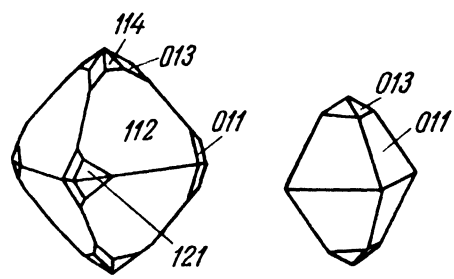


Fig. 253. Scheelite crystals.

and even red. **Streak**, white. **Lustre**, slightly greasy, adamantine. $n_x = 1.937$ and $n_y = 1.920$.

Hardness, 4.5. Brittle. **Cleavage**, {111} distinct. Fracture uneven. **Specific gravity**, 5.8 to 6.2. **Other properties.** In cathode rays usually fluoresces bright blue.

Diagnostic features. In silicate rocks scheelite is sometimes scarcely noticeable. Can be recognised by the naked eye only through long experience. In crystals it is identifiable by octahedral cleavage, while on fracture and in aggregates by rather strong slightly greasy lustre, rather distinct cleavage, high specific gravity, and reaction for tungsten. Highly characteristic is its blue fluorescence in cathode rays. This property is widely made use of for identification in situ and even for a rough estimate of its content in the ore.

Fusible with difficulty in the blowpipe flame. Soluble in hydrochloric and nitric acids, decomposes with evolution of yellow tungstatic acid, $H_2WO_4 \cdot H_2O$, which is soluble in ammonia. Solution in hydrochloric acid when boiled with tin acquires a beautiful deep-blue colour.

Genesis and occurrence. Scheelite occurs relatively often as a *hydrothermal* mineral in deposits of different ores.

Small amounts are sometimes found in pegmatites. The biggest deposits, however, are of *contact-metasomatic* origin. In these it is associated with silicates (garnets, pyroxenes, etc.), quartz, and frequently with sulphides, such as molybdenite. It is often found in wolframite-bearing, auriferous, and other vein deposits.

In the oxidised zone scheelite is not very stable. On the surface, quartz veins sometimes have cavities in the place of leached scheelite. Nevertheless, scheelite quite often shows in the heavy concentrates of placer washing.

Notable foreign localities for the occurrence of scheelite are the contact deposits in western U.S.A., the great deposit in Malaya where it often occurs in association with cassiterite in metamorphosed limestones and schists, as well as in quartz veins, also in northern *Tasmania*, and elsewhere.

Uses. Both scheelite and wolframite ores are a source of tungsten. For the uses of the metal see "Wolframite".

WULFENITE, $PbMoO_4$. **Chemical composition.** PbO 61.4%, MoO_3 38.6%. Occasionally contains admixtures of CaO, CuO, MgO, WO_3, rarely CrO_3 and V_2O_5.

System, tetragonal; symmetry, pyramidal L^4. **Habit.** Often in square tablets, less often in combinations of obtuse and acute pyramids (Fig. 254). Massive crystal aggregates are rare.

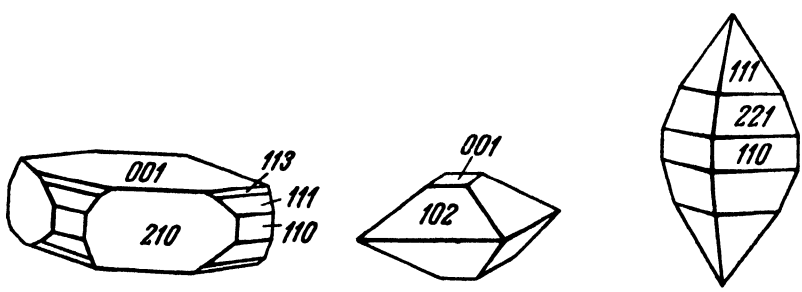


Fig. 254. Wulfenite crystals.

Colour is wax- or honey-yellow, grey, brown, sometimes orange, or even red. **Streak**, white or very faintly coloured. **Lustre**, adamantine, greasy on fracture. $n_y = 2.40$ and $n_z = 2.28$.

Hardness, 3. **Cleavage**, {111} distinct. **Specific gravity**, 6.3 to 7.0.

Diagnostic features. Characteristic honey-yellow colour, tabular habit, adamantine lustre, high specific gravity, and paragenesis with other minerals of lead in the oxidised zone.

Fusible in the blowpipe flame. On charcoal with soda yields a lead globule. With salt of phosphorus in the oxidising flame gives yellow-green, and in the reducing flame, dark-green bead (Mo reaction).

Dissolves slowly in hydrochloric acid becoming covered with a white coating of $PbCl_2$.

Genesis and occurrence. As a salt poorly soluble in water it is rather often found in the *oxidised zones* of lead-zinc deposits. May derive its molybdenum from two sources: either from the molybdenic acid brought by waters percolating from the wall rocks or through oxidation and concentration of the molybdenum dispersed in the sulphides within the deposit.

Usually wulfenite occurs as small crystals and crystalline crusts on the walls of leaching cavities. It may also occur pseudomorphous after other lead minerals in the oxidised zone, in particular cerussite. In this case, wulfenite is associated with cerussite, anglesite, and galena.

It is also found in low-temperature hydrothermal deposits of lead-zinc ores.

Uses. When found in quantity, wulfenite together with other oxidised lead minerals, is a source of lead and molybdenum.

3. HYDROUS MOLYBDATES AND HYDROUS TUNGSTATES

This division includes a very brief description of as yet inadequately studied hydrous salts of trivalent iron.

FERRIMOLYBDITE, $Fe_2\cdots[MoO_4]_3\cdot 7H_2O$. **System**, orthorhombic. Occurs in fibrous or scaly masses of sulphur-yellow colour. $n_y = 1.87$ to 2.05, $n_x = 1.753$ to 1.79, and $n_z = 1.72$ to 1.78.

Hardness, 2. **Cleavage**, {001} distinct. **Specific gravity**, 4.5. Readily fusible. Soluble in acids and NH_4OH.

An alteration product of molybdenite. Occurs in the oxidised zones of ore deposits.

FERRITUNGSTITE, $Fe_2\cdots[WO_4][OH]_4\cdot 4H_2O$. **System**, hexagonal. Occurs in microscopic plates and scaly aggregates of light-yellow or brownish-yellow colour. $n_y = 1.80$, and $n_z = 1.72$. Other physical properties as yet unknown. Decomposes in acids with evolution of yellow WO_3. As a product of wolframite oxidation is found in the Deer Trail deposit, in Washington (U.S.A.), and elsewhere.

CLASS 6.

PHOSPHATES, ARSENATES, AND VANADATES

General. This class includes comparatively numerous mineral species of diverse composition. Their total quantity by weight in the earth's crust is relatively small, however.

The $[PO_4]^{3-}$, $[AsO_4]^{3-}$, and $[VO_4]^{3-}$ trivalent anions are rather large, and therefore the most stable *anhydrous* compounds of the AXO_4

type may be expected from the combination of these anions with trivalent large cations. In the introduction to the description of oxygen salts it was stated that such cations are ions of rare earths and Bi. Compounds with small cations are, as a rule, much more extensively represented among all typically oxygen salts by *hydrous* normal salts (with hydrated cations).

Phosphates of divalent metals, with additional anions (OH, F, O, sometimes Cl) or in the form of acid phosphates are most stable, also when the compounds contain relatively large cations (Ca, Sr, and sometimes Pb); characteristic for arsenates and vanadates are compounds with Pb, Cl being an additional anion, and finally binary compounds of Pb or Ca with Cu, Zn, Mg, and sometimes with Mn$^{\cdot\cdot}$. Calcium is also known to form hydrous acid salts.

In this connection it would be relevant to compare dihydrous salts, the phosphate and arsenate of Ca, with the sulphate of Ca (gypsum), all of which crystallise in the monoclinic system and have many properties in common.

	a_0	b_0	c_0	β	Hardness	Sp. gr.
Gypsum, $CaSO_4 \cdot 2H_2O$	10.47	15.15	6.28	98°58′	2	2.31
Brushite, $CaHPO_4 \cdot 2H_2O$	10.47	15.15	6.28	95°15′	2	2.25
Pharmacolite, $CaHAsO_4 \cdot 2H_2O$	10.97	15.40	6.29	96°36′	2-2.5	2.64

This is another proof that the H^{1+} cation, being very small, has practically no effect on the size of the crystal structure. The $[SO_4]^{2-}$ and $[PO_4]^{3-}$ anions, as seen from the above, are of exactly the same size, and the $[AsO_4]^{3-}$ anion is somewhat larger. While the refractive indices in these minerals increase with anion size from gypsum to pharmacolite, the birefringence of all these minerals remains practically the same. The specific gravity of the minerals fully corresponds to the atomic weights of the cations in the complex anions (S^{6+}, P^{5+}, and As^{5+}).

As it should have been expected, the phosphates and arsenates of divalent small cations (Mg, Fe$^{\cdot\cdot}$ (Ni, Co$^{\cdot\cdot}$, Cu$^{\cdot\cdot}$, Zn) form highly characteristic hydrous normal salts with 8, 4, and 3 H_2O molecules.

Univalent metals (Na, Li) form, as a rule, binary compounds with Al^{3+}, and also a series of rare complex hydrous salts.

A special place among hydrous salts, with regard to composition, is occupied by the so-called uran-micas and complex vanadates.

Highly interesting are the phenomena of heterovalent isomorphism which are quite frequent in this class of compounds, especially in phosphates. Most vivid examples are the isomorphous substitutions of anionic radicals.

Thus, the $[PO_4]^{3-}$ trivalent anion may be replaced by similarly built and equidimensional anions such as divalent $[SO_4]^{2-}$ and tetravalent $[SiO_4]^{4-}$. This substitution may proceed in a variety of ways.

1. Isomorphous substitution in the anionic portion of a compound takes place without affecting the composition and charge of the cat-

ionic portion. In this case, the magnitude of the total anionic charge should remain unchanged. This happens when the divalent $[SO_4]^{2-}$ anion enters into the composition of the mineral simultaneously with the replacement of the trivalent $[PO_4]^{3-}$ anion by the tetravalent $[SiO_4]^{2-}$ anion. Only in this case can the total anionic charge remain unchanged.

In this case, the crystal structure and physical properties of the minerals naturally remain the same. It may be added that in the cationic portion too the Ca^{2+} ions may be simultaneously replaced by equidimensional Na^{1+}, Y, and TR ions (with the composition and charge of the anionic portion remaining unchanged).

2. Isomorphous substitution in the anionic portion of a compound may take place simultaneously with the replacement of ions in the cationic portion by cations of a different valency. Thus, it has long been known that monazite, $CePO_4$, occasionally contains considerable SiO_2, i.e., the $[SiO_4]^{4-}$ anion, and that at the same time a corresponding amount of Th^{4+}, and occasionally U^{4+} and Zr^{4+}, is isomorphously admixed to Ce^{3+}. Recently Soviet scientist I.D. Borneman-Starynkevich showed by means of delicate chemical analyses that in certain monazites the isomorphous admixture of Ca^{2+} is accompanied by the divalent $[SO_4]^{2-}$ anion entering into the composition of the anionic portion. Therefore, the general chemical formula for such monazite varieties should be written as (Ce, Th, Ca) $[PO_4, SiO_4, SO_4]$.

It should be noted that heterovalent isomorphism does not necessarily require a strict quantitative balance between ions of the cationic and anionic portions. However, it does require: (1) equality of positive or negative total charges; (2) equality or proximity of the size of replacing ions, and (3) preservation of the total number of cations and anions in the course of replacement (except when one of the cations is an H^{1+} proton).

We shall not dwell on the general characteristics of physical properties of the most diverse minerals of this class. Since they vary widely, it seems more appropriate to review them for each individual group of minerals.

As for the mode of formation of the vast majority of minerals of this extensive class, especially hydrous compounds, they are associated with exogenous processes (in the oxidised zones of ore and sedimentary deposits). The endogenous minerals are almost exclusively the phosphates the majority of which is formed during the final stages of magmatic processes, mainly in pegmatites, and sometimes in hydrothermal veins. Apatite (calcium phosphate) also occurs in magmatic deposits (in nepheline-syenites).

Since the salts of this class include widely diverse hydrous and anhydrous compounds, all these minerals, in distinction from sulphates, fall into two large groups:

(1) anhydrous phosphates, arsenates and vanadates;

(2) hydrous phosphates, arsenates and vanadates.

Anhydrous Phosphates, Arsenates, and Vanadates

The anhydrous compounds of this class are represented in nature by a considerable number of minerals. In addition to the *normal* salts of orthoacids there are some rare species of *acid* salts. Much more common are *basic* salts.

1. MONAZITE GROUP

MONAZITE, (Ce, La. . .)PO_4. "Monazen" is the Greek for solitary (hence the word monk). Usually occurs as single crystals.

Chemical composition. The content of oxides of rare earths (chiefly Ce and La) may be as high as 50 to 68 per cent; may contain an isomorphous admixture of Y_2O_3 (up to 5 per cent). P_2O_5 content usually from 22 to 31.5%. Often contains also an isomorphous admixture of ThO_2 (5 to 10%, sometimes as high as 28 per cent), in some instances ZrO_2 (up to 7%) with SiO_2 (up to 6%), and sometimes CaO accompanied by SO_3.

Thus, from the standpoint of crystallochemistry, the mineral provides a graphic example of heterovalent isomorphism. The chemical formula for such varieties of monazite should look as follows: (Ce, La, Th, Ca) [PO_4, SiO_4, SO_4]. Negligible amounts of MgO, MnO, PbO, Fe_2O_3, Al_2O_3, and H_2O are also present.

System, monoclinic; symmetry, prismatic L^2PC. Space group $P2_1/n(C_{2h}^5)$. $a_0 = 6.79$; $b_0 = 7.04$; $c_0 = 6.74$; $\beta = 104°24'$. **Habit**, usually tabular {100} (Fig. 255), less often prismatic, isometric, and pyramidal. Most common forms are pinacoids {100}, {010}, {101}, prisms {110}, {011}, etc. Often striated. Twins on (100) and (001). Usually occurs as small crystals. Some large individuals, however, have weighed up to several kilograms.

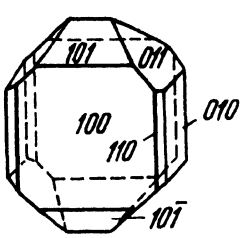


Fig. 255. Tabular monazite crystal.

Colour, yellowish brown, brown, red, rarely green. **Lustre**, strong vitreous, greasy. $n_x = 1.837$, $n_y = 1.787$, $n_z = 1.785$.

Hardness, 5 to 5.5. **Cleavage**, sometimes perfect parallel to {001}. **Specific gravity**, 4.9 to 5.5. **Other properties.** Often radioactive (the presence to ThO_2).

Diagnostic features. In pegmatites and granites it is usually identified by characteristic tabular habit of opaque crystals of dark-yellow or reddish-brown colour.

Almost infusible in the blowpipe flame. Powdered monazite moistened with sulphuric acid colours the flame green. Dissolves with difficulty in hydrochloric acid giving a white precipitate. With borax, gives a yellow or yellowish-red bead when hot, which becomes colourless on cooling.

Genesis and occurrence. The mineral usually occurs in *pegmatites*, sometimes in *granites* and *gneisses* in paragenesis with feldspars, zircon ($ZrSiO_4$), in some cases, with magnetite, ilmenite, and other min-

erals. Occasionally found in dolomite veinlets of hydrothermal origin in association with magnetite.

Upon weathering of primary deposits, chemically inert monazite is concentrated in valley and beach placers.

Notable monazite deposits are in the pegmatites of *Madagascar* (Ancasoba and Mount Volhambohitra) where very large crystals are found. Also occurs in very large valley and beach placers in *Brazil* (Minas Geraes) where it is recovered on a commercial scale.

Uses. Monazite is the chief source of thorium and the rare earths and is mined almost exclusively from placers.

Rare earths, in the main cerium, have most diverse uses. At present they are employed chiefly in pyrophoric alloys and cerium carbon-arc electrodes for search lights. They are also used in the manufacture of special glass permeable to light but impermeable to ultraviolet and most of heat rays, in strong and light alloys (of cerium with magnesium, aluminium, etc.), as catalysts in the production of chemicals, in dyes, etc.

XENOTIME, YPO_4. "Xenos" is the Greek for alien, "timi", honour.

Chemical composition. The theoretical Y_2O_3 content should be 63.1%. Commonly contains small amounts of rare earths (Er, Ce) sometimes ThO_2, UO_2 (up to 5%), ZrO_2 (up to 3%), SnO_2,SiO_2 (up to 9%), etc. A variety known as *hussakite* contains up to 6% of SO_3 (and probably CaO).

System, tetragonal; symmetry, ditetragonal dipyramidal $L^4 4L^5 5PC$.

Habit. Occurs in prismatic crystals similar to those of cassiterite and zircon, and also massive. Closely resembles the rutile group in crystal structure. Crystals are usually a combination of {110}, {010} and {011}. Other forms are rare.

Colour, yellowish brown, red, grey. **Streak**, light brown or reddish. **Lustre**, vitreous, waxy, or greasy. $n_x = 1.815$ and $n_y = 1.720$.

Hardness, 4 to 5. Fracture uneven. Brittle. **Cleavage**, {100} perfect. **Specific gravity**, 4.45 to 4.59. **Other properties.** Often radioactive.

Diagnostic features. Easily distinguished from zircon, rutile, and cassiterite by lower hardness and, in thin polished sections, by different optical properties.

Infusible in the blowpipe flame. Insoluble in usual test acids. When moistened with sulphuric acid, colours the flame bluish green.

Genesis and occurrence. Occurs in granites and pegmatites as small disseminated crystals, often in association with zircon, with which it may develop oriented intergrowths, with apatite, orthite, monazite, etc.

As a relatively inert compound, xenotime passes into placers upon the destruction of the primary deposits.

The most notable localities for xenotime-bearing pegmatites and placers are in Brazil (Minas Geraes), Norway (Hitterö near Arendal, Kragerö in Telemarken), Sweden (Itterby), and elsewhere.

2. APATITE GROUP

The apatite group comprises compounds of the $A_2[XO_4]_3Z$ type in which the cations are Ca^{2+}, Pb^{2+} and, in certain isomorphous admixtures, TR^{3+}, Y^{3+}, Mn^{2+}, and Sr^{2+}, the additional anions being F^{1-}, Cl^{1-}, $[OH]^{1-}$, O^{2-}, and $[CO_3]^{2-}$.

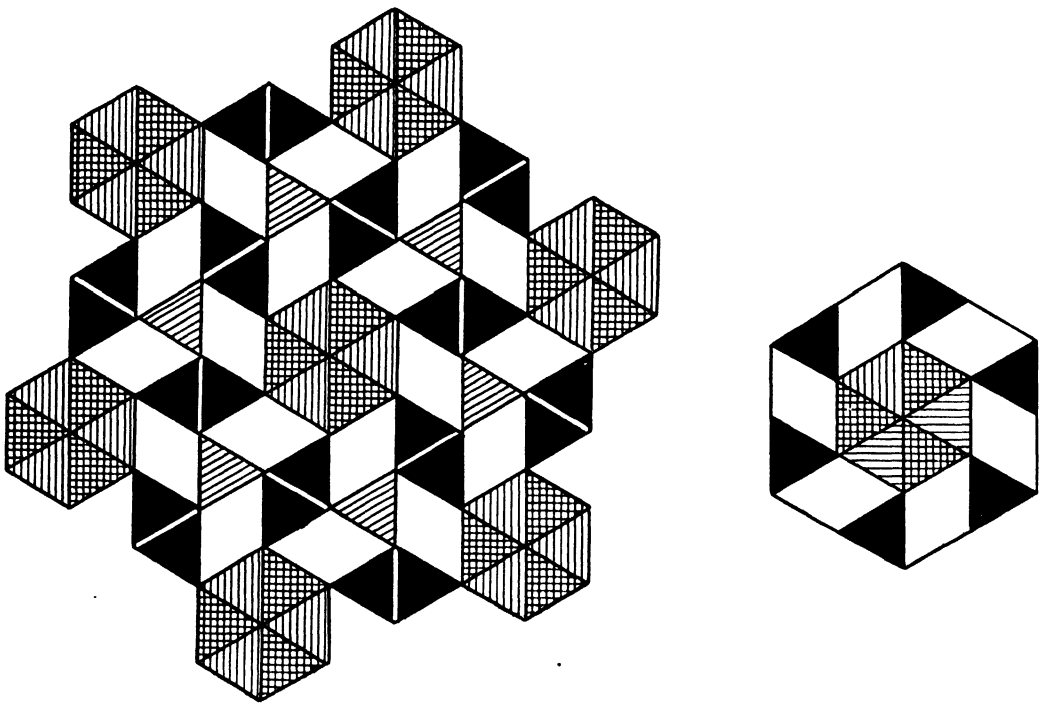


Fig. 256. Crystal structure of apatite projected parallel to *c* axis.

Left—general view of structure on plan; right—hexagonal portion of structure cut out along light dividing lines (figure on the left), and containing a fluorine anion in the centre. Black — PO_4 tetrahedra; horizontally shaded and checkered portions—columns of complex structure composed of trigonal prisms with $Ca^{\cdot\cdot}$ cations; obliquely shaded triangles—simple prisms with $Ca^{\cdot\cdot}$ cations.

The remarkable feature of this group is that the $[PO_4]^{3-}$ anionic group may be partly replaced by a weaker $[SiO_4]^{4-}$ anion, but in combination with a stronger $[SO_4]^{2-}$ anion (provided the cationic valences do not change).

FLUOR- and **CHLORAPATITES,** $Ca_5[PO_4]_3F$ and $Ca_5[PO_4]_3Cl$. "Apatao" is the Greek for *I deceive.* Formerly it was often mistaken for other minerals of prismatic or rod-like habit (beryl, diopside, tourmaline, etc.).

Chemical composition. Fluorapatite: CaO 55.5%, P_2O_5 42.3%, F 3.8%. Chlorapatite: CaO 53.8%, P_2O_5 41%, Cl 6.8%. Fluorapatite is more widespread. Often F is present in addition to negligible amounts of Cl, OH, and CO_3 (carbonate-apatite). Sometimes isomorphous ad-

mixtures to CaO are Na_2O, rare earths, mainly Ce_2O_3 (up to 5%), MgO (up to a few per cent); insignificant amounts of Fe_2O_3, Al_2O_3, etc.

System, hexagonal; symmetry, dipyramidal L^6PC. Space group $C6_3/m(C^2_{6h})$. Fluorapatite: $a_0 = 9.36$; $c_0 = 6.88$. Chlorapatite: $a_0 = 9.52$; $c_0 = 6.85$.

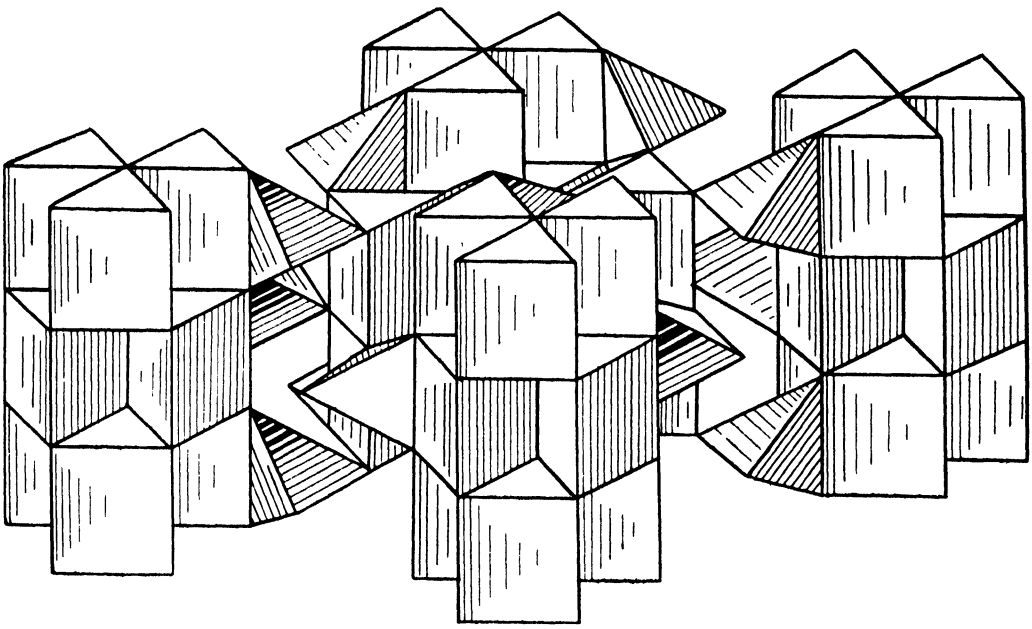


Fig. 257. Structure of apatite in axonometric projection.
Fluorine anions concentrated on sixfold spiral axes, surrounded with trigonal calcium prisms.

Crystal structure. The unit cell projected on the plane (0001) is rhombic (Fig. 256), the fluorine ions occupying the corners of the rhombohedron. The Ca ions, according to N.V. Belov, are inside the trigonal prisms which form columns parallel to *c* axis (Fig. 257). The columns are of two kinds: some of them have more complex structure consisting of three prisms in a given layer, with different orientation around the sixfold axis in each layer, the structural pattern, as a whole, thus acquiring hexagonal habit (Fig. 256, right); other columns are simple, consisting of single trihedral prisms (Fig. 256). All these columns are held together by the PO_4 tetrahedra which alternate with empty octahedra in the vertical direction. The fluorine anions are located in the centre of two layers of trigonal prisms. As for carbonate-apatite, according to Belov, the $[PO_4]$ radical is partly replaced by $[CO_3F]$, which explains the increased fluorine content of this variety.

Habit. Frequently occurs in cavities as well-developed ingrowths or overgrowths of crystals in the form of hexagonal prisms and needles, less often as short-columnar or tabular forms (Fig.258). The most common faces are the prism $\{10\bar{1}0\}$, pinacoid $\{0001\}$, dipyramids $\{10\bar{1}1\}$,

{11$\bar{2}$1}, etc. The faces of the prisms may have vertical striations. In some hydrothermal iron ore deposits and pegmatites there also occur tubular ("hollow") hexagonal crystals of apatite. **Aggregates.** It is also widely distributed in granular, compact, cryptocrystalline, crossveined, and earthy masses. Widespread in sedimentary rocks in diverse concretionary forms, usually containing numerous tiny inclusions of other minerals (quartz, glauconite, calcite, etc.). These accumulations

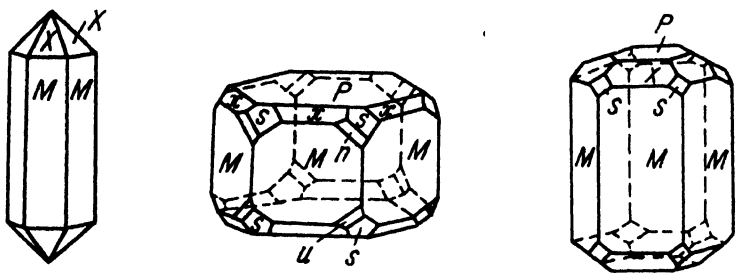


Fig. 258. Apatite crystals:
M {10$\bar{1}$0}, P {0001}, X {10$\bar{1}$1}, S {11$\bar{2}$1}, n {21$\bar{3}$1}.

The presence of the last form indicates that there are no vertical planes of symmetry.

are commonly named *phosphorites* (phosphate rocks). Occurs as pseudomorphs after the bones of animals, pieces of wood, often with all the details of structure faithfully preserved, as recognised under the microscope.

Colour. Colourless (transparent), white, more often pale green to emerald-green, light blue, yellow, brown, violet. **Lustre**, vitreous and greasy on fracture. Pure fluorapatite: $n_y = 1.633$ and $n_z = 1.629$.

Hardness, 5. Brittle. Fracture uneven, sometimes conchoidal. **Cleavage**, {0001} imperfect. **Specific gravity**, 3.18 to 3.21.

Diagnostic features. Crystals are characterised by hexagonal prismatic habit. Are distinguished from similar crystals of beryl and aquamarine by lower hardness.

Fusible with difficulty, even in thin fragments in the blowpipe flame. Powder moistened with sulphuric acid colours the flame bluish green. Dissolves in nitric, hydrochloric and sulphuric acids. Nitric solution with ammonium molybdate gives the phosphorus reaction.

Genesis and occurrence. Being one of the latest *magmatic* minerals, apatite occurs as microscopic grains in many igneous rocks in alkaline rocks (nepheline-syenites), occasionally as granular masses in association with silicates (nepheline, sphene, zircon, vesuvianite, etc.). Such, for instance, is the famous deposit in the *Hibiny mountains* on the Kola Peninsula.

In large rod-like or prismatic crystals it is found in many *pegmatites* of acid and alkaline igneous rocks. Excellent crystals of apatite are found in the *Slyudyanka* deposit near Lake Baikal. Sometimes

occurs in *contact-metasomatic* formations in paragenesis with various minerals.

Is also found in some *hydrothermal* vein deposits as an accessory of such minerals as cassiterite, fluorite, etc. In Alpine-cleft veins short-columnar and even flat crystals of apatite are observed.

In the process of *weathering* of phosphorus-enriched limestones in karsts and leaching cavities there are formed accumulations of brown phosphorites with a concentrically-banded structure similar to that of agates.

Many large deposits of calcium phosphates are formed in marine sedimentary rocks through a complex biochemical process and are confined to definite stratigraphic horizons. The phosphorites in the form of concretions and nodules (Fig. 43) of most diverse shapes, less often massive, occur in argillaceous and glauconitic sands and sandstones.

Phosphorites may also form out of guano, the excrements of sea fowl on desert coasts composed of limestones or other calcium-bearing rocks.

Large phosphorite deposits are found in the Ukraine. A notable deposit is located in the South-Russian depression where a phosphorite-bearing horizon outcrops intermittently in the Upper Cretaceous sediments over a vast area from Podolia (Western Ukraine) to the Volga shores (near Saratov); its northern boundary intrudes into the Kursk Region, and the southern boundary runs across the southern rim of the Donets Basin. The phosphorite is heavily mixed with sand and occurs in nodules or relatively thin beds. Another major deposit of massive laminated high-grade phosphorite has been discovered recently in the *Kara-Tau* mountains (Southern Kazakhstan) in Lower Paleozoic strata. Massive phosphorite of varying dark hues sometimes has an oölitic structure.

The most important foreign localities are the huge beds of phosphorites (phosphate rock) of Permian age which occur in the *United States* (Idaho, Wyoming, Utah, Montana), and the deposits in Lower Tertiary strata along the coast of *Algeria*, *Tunisia* and *Morocco*.

Uses. The principal use of apatite and phosphorites (up to 90 per cent) is for the production of fertilisers (various superphosphates and thermophosphates). Apatites are a source of phosphoric acid and various salts as well as of phosphorus, an important material for safety matches. Fluorine-rich apatites yield hydrofluosilicic acid, as a by-product. Apatite also goes to make the so-called bone china.

PYROMORPHITE, $Pb_5[PO_4]_3Cl$. "Pyros" is the Greek for fire; "morphe", form.

Chemical composition. PbO 82.0%, P_2O_5 15.4%, Cl 2.6 %. Sometimes contains CaO (up to 8-9%), and As_2O_5 (up to 4%). Occasionally an admixture of chromium is observed (probably as CrO_3) which colours the mineral bright red; rarely V_2O_5.

System, hexagonal; symmetry, dipyramidal L^6PC. **Crystal structure** is analogous to that of apatite (see above). **Habit.** Usually occurs in prismatic or columnar crystals (Fig. 259). May occur in barrel-shaped, acicular, often in parallel-intergrown crystals. **Aggregates.** Apart from common druses of small crystals, often occurs as crystalline reniform and globular formations.

Colour. Various tinges of green, yellow, and brown. Less common are varieties coloured bright red or orange-yellow by chromium. The colouring is often banded. **Streak**, white, sometimes yellowish. **Lustre**, adamantine, greasy. $n_y = 2.050$ and $n_z = 2.042$.

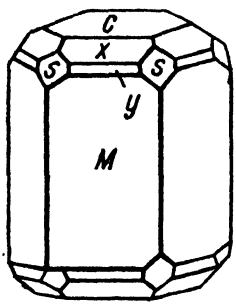


Fig. 259. Pyromorphite crystal: $c\{0001\}$, $M\{10\bar{1}0\}$, $y\{20\bar{2}1\}$, $x\{10\bar{1}1\}$, $S\{11\bar{2}1\}$.

Hardness, 3.5 to 4.0. Brittle. Practically no cleavage. **Specific gravity**, 6.7 to 7.1, diminishing to 5.9 for calcium-rich varieties.

Diagnostic features. Pyromorphite crystals differ from apatite by specific gravity and adamantine lustre. Often indistinguishable from mimetesite and vanadinite without chemical tests.

In the blowpipe flame fuses very easily into a bead which upon cooling rapidly crystallises into a polyhedral form. Ignited with soda, gives a lead globule. On charcoal gives a yellow coating of $PbCl_2$. Soluble in nitric acid, and also in KOH (if it contains no lime).

Genesis and occurrence. Pyromorphite is a mineral of almost exclusively *exogenous* origin, being formed in the oxidised zones of sulphide lead and lead-zinc deposits (as druses of small crystals and crystalline crusts in leaching cavities). The source of phosphoric acid are probably the surface waters reacting with lead minerals.

Often pseudomorphous after cerussite and galena. Reverse cases, i.e., replacement of pyromorphite by galena on the periphery of crystals, are also observed under certain specific conditions.

Pseudomorphous after pyromorphite are also vanadinite, vauquelinite, wulfenite, calamine, chalcedony, and calcite.

Has been recognised from certain low-temperature vein deposits as an *endogenous* mineral.

Lastly, pyromorphite often occurs as an accessory mineral in the oxidised zones of many deposits.

In the U.S.S.R., it is found in the oxidised zones of the *Berezovskoye* gold deposit in the Urals (together with crocoite). Excellent crystals of pyromorphite with an admixture of a negligible quantity of As_2O_5 have been recorded from *Shilka* and *Zerentuy* deposits (Eastern Trans-Baikal area) at *Kyzyl-Espe* (Kazakhstan), and elsewhere.

Uses. Together with the other lead minerals of the oxidised zone pyromorphite is a source of lead. It rarely occurs in considerable amounts.

MIMETESITE, $Pb[AsO_4]_3Cl$. "Mimetes" is the Greek for imitator – reference to its similarity to pyromorphite.

Chemical composition. PbO up to 74.9%, As_2O_5 up to 23.2%, Cl up to 2.4%. Often contains P_2O_5, Sb_2O_5, also CaO up to 10-14%, and occasionally BaO and CrO_3, as isomorphous admixtures.

System, hexagonal; symmetry, dipyramidal L^6PC. **Habit.** As a rule, in prismatic (Fig. 260), often acicular forms. Barrel-shaped, tabular and dipyramidal crystals are also known. **Aggregates.** In cavities, as druses and rosettes of small crystals, crusts, more seldom as sinter-like and earthy masses.

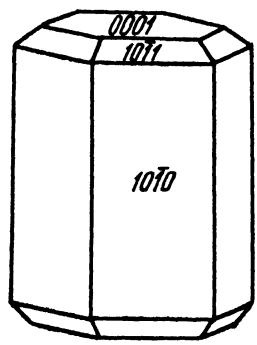


Fig. 260. Mimetesite crystal.

Colour. Pure varieties are colourless and transparent. More often honey-yellow, brown or green. **Streak**, white. **Lustre**, adamantine, greasy. $n_y = 2.135$ and $n_z = 2.120$.

Hardness, 3.5. Brittle. Fracture conchoidal, uneven. Practically no cleavage. **Specific gravity**, 7.19 to 7.25.

Diagnostic features. May be positively distinguished from pyromorphite and vanadinite only by chemical tests.

Before the blowpipe on charcoal fuses with more difficulty than pyromorphite, and giving off vapours of oxidised arsenic with a garlic smell gives a lead globule. Dissolves in sulphuric and hydrochloric acids with separation of $PbSO_4$ and $PbCl_2$ in the form of a poorly soluble precipitate.

Genesis and occurrence. Like pyromorphite, occurs in the *oxidised zones* of sulphide lead-zinc deposits, but much less often than the former. The sources of arsenic in this case are probably oxidised arsenides, sulphoarsenides, and sulphoarsenites, such as arsenopyrite and grey ores present as impurities in primary lead ores. Reference has also been made in literature to the formation of endogenous mimetesite in a low-temperature *hydrothermal* deposit at Lilli in the Sica-Sica province (Bolivia) in veinlets with quartz, chalcedony, calcite, etc.

In the U.S.S.R., reniform masses and crystals have been found in a number of lead-zinc deposits in Eastern Trans-Baikal area (Nerchinsk district): Trekhsvyatitelsky, Spasskoye, Klichkinskoye, Kadainskoye deposits, and also Kyzyl-Espe (Kazakhstan), and elsewhere.

Outside the Soviet Union, the deposit of Tsumeb (South-Western Africa) is notable for its large well-formed crystals; other localities are Chihuahua (Mexico) and Tintic in Utah (U.S.A.).

VANADINITE, $Pb_5[VO_4]_3Cl$. Named after the important element vanadium contained in the mineral.

Chemical composition. PbO 78.3%, V_2O_5 19.3%, Cl 2.4%. Sometimes contains negligible amounts of P_2O_5, As_2O_5, etc.

System, hexagonal; symmetry, dipyramidal L^6PC. **Habit.** Crystals are, as a rule, small and of prismatic (Fig. 261) or acicular habit. Often

in small crystals in the form of hollow prisms or narrow dipyramids forming crystal druses in cavities, and parallel intergrowths of prismatic crystals (Fig.262). Occurs in reniform aggregates with a radial-fibrous or fibrous structure.

Colour, yellow, brown, sometimes red. **Streak**, white or pale yellow. **Lustre**, adamantine, greasy. $n_y = 2.354$ and $n_z = 2.299$.

Hardness, 3.0. Brittle. Fracture uneven. **Cleavage**, none. **Specific gravity**, 6.66 to 7.10.

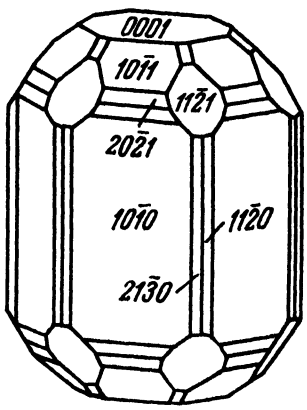


Fig. 261. Vanadinite crystal.

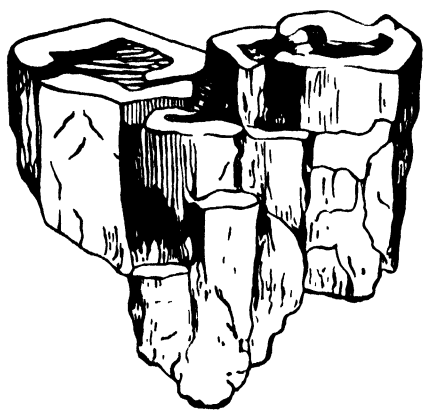


Fig. 262. Intergrowth of imperfectly developed vanadinite crystals.

Diagnostic features. Vanadinite is less hard than pyromorphite and mimetesite. Blowpipe and chemical tests are required, however, for more positive identification.

In the blowpipe flame on charcoal decrepitates, readily fuses into a black shiny mass, which in the reducing flame gives a lead globule, and a yellow coating of $PbCl_2$ on charcoal. In the reducing flame the salt of phosphorus bead is reddish yellow, turning purely green (vanadium reaction) on cooling. The powdered mineral, when dissolved in a drop of dilute nitric acid on a slide and completely evaporated, gives a dark-red residue (other minerals of the group give a white or grey residue).

Genesis and occurrence. Like pyromorphite and mimetesite, is formed in the oxidised zones of lead-zinc sulphide deposits, mostly in carbonate rocks. Occasionally pseudomorphous after pyromorphite.

In the *Suleyman-Sai* deposit (Southern Kazakhstan) large quantities of vanadinite have been found as well-developed crystals, earthy and friable masses and crusts coating remnants of unoxidised fine-grained galena. Notable foreign localities are at *Broken Hill* (Northern Rhodesia) and *Lamentos* (Mexico), where vanadinite, descloizite, and wulfenite characteristically accumulate in the lower parts of the oxidised zone.

Uses. When found in quantity, vanadite-bearing ores are an economic source of vanadium.

Summary. It follows from the above description that the minerals of this group, along with common properties, have considerable differences determined by their chemical composition. A comparison of their principal characteristics is given in Table 12.

Table 12

Basic Characteristics of the Apatite Group Minerals

Mineral	Specific gravity	Hardness	Refractive index		Lustre
			n_y	n_z	
Fluorapatite, $Ca_5[PO_4]_3F$ ..	3.2	5	1.633	1.629	Vitreous
Pyromorphite, $Pb_5[PO_4]_3Cl$	6.9	3.5-4	2.050	2.042	Adamantine
Mimetesite, $Pb_5[AsO_4]_3Cl$ ..	7.2	3.5	2.135	2.120	Ditto
Vanadinite, $Pb_5[VO_4]_3Cl$ ...	7.0	3.0	2.354	2.299	Ditto

A comparison of the properties of pyromorphite, mimetesite and vanadinite shows that with increasing replacement of P in the XO_4, complex anion by As and V, the hardness of the mineral decreases and the refractive index increases. The differences in specific gravity are not conspicuous since the content of heavy metal (lead) is strongly predominant over the other elements.

The considerable distinctions between the properties of apatite and the minerals just reviewed are quite natural.

3. AMBLYGONITE-TRIPLITE GROUP

AMBLYGONITE, $LiAl[PO_4]F$. **System**, triclinic. Occurs in large, poorly formed crystals. **Colour**, white with greenish, bluish, yellowish, and other tinges. Translucent. **Lustre**, vitreous; pearly on cleavage surfaces. **Hardness**, 6. Brittle. **Cleavage**, {001} excellent. **Specific gravity**, 2.98 to 3.15.

Before the blowpipe fuses readily with intumescence. Colours the flame red (presence of lithium). With powdered magnesium gives the phosphorus reaction. Soluble in sulphuric acid.

Has been recorded from pegmatite dikes associated with other lithium-bearing minerals at Estremadura (Spain), Herbon, Maine (U.S.A.), and elsewhere.

LITHIOPHILITE, Li (Mn, Fe) PO_4. Rare. **System**, orthorhombic. **Colour**, pale pink, yellow, red-brown, light blue. **Streak**, white or faintly coloured. **Lustre**, vitreous. **Hardness**, 4.5 to 5. **Cleavage**, {001} perfect, {010} less perfect. **Specific gravity**, 3.5.

Fuses readily before the blowpipe flame colouring the flame red. Soluble in acids. Gives reactions for Mn, Fe, and P.

Has been recorded from pegmatites with quartz, beryl, and lithium minerals at Branchville, Connecticut (U.S.A.), and elsewhere. In the oxidised zone is subject to alteration.

TRIPLITE, $(Mn, Fe)_2[PO_4]F$. Contains isomorphous admixtures of Ca and Mg. **System**, monoclinic. Sometimes massive. **Colour**, brown or pink. **Hardness**, 4 to 5. **Cleavage**, poor. **Specific gravity**, 3.44 to 3.87.

Before the blowpipe fuses readily into a black magnetic globule; with borax in the oxidising flame gives a violet bead (Mn). With powdered Mg gives the phosphorus reaction. Soluble in hydrochloric acid.

Occurs in pegmatite dikes in association with quartz, beryl, apatite, fluorite, and other minerals, and also in some hydrothermal veins. In the U.S.S.R., has been found in hydrothermal deposits in Buryatia in association with quartz, rhodochrosite, etc. Is subject to alteration in the oxidised zone.

Hydrous Phosphates, Arsenates, and Vanadates

1. VIVIANITE GROUP

The minerals of this group are hydrous normal phosphates and arsenates with 8 water molecules hydrating the cations of iron, nickel, and cobalt.

VIVIANITE, $Fe_2^{\cdot\cdot}[PO_4]_2 \cdot 8H_2O$. **Chemical composition.** FeO 43.0%, P_2O_5 28.3%, H_2O 28.7%. Often contains ferric oxide which has developed from the ferrous form on further oxidation.

System, monoclinic; symmetry, prismatic L^2PC. Space group $C2/m(C_{2h}^3)$. $a_0 = 10.01$; $b_0 = 13.43$; $c_0 = 4.70$; $\beta = 104°30'$. **Habit**, commonly prismatic (Fig. 263), rod-like, acicular. **Aggregates.** Often occurs in radial-fibrous, stellate, reniform, globular aggregates, and also as earthy masses (blue iron earth).

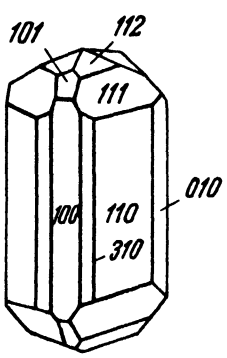


Fig. 263. Vivianite crystal.

Colour. Unaltered vivianite is light-coloured or even colourless and transparent; on partial oxidation in the air becomes greyish blue or greyish green, dark blue to black-blue. **Streak.** Unoxidised varieties colourless. Oxidised varieties bluish white, blue or brown. **Lustre**, vitreous; pearly on cleavage surfaces. $n_x = 1.633$, $n_y = 1.603$, and $n_z = 1.579$.

Hardness, 1.5 to 2. Brittle. **Cleavage**, {010} excellent. **Specific gravity**, 2.95.

Diagnostic features. Partly oxidised varieties may be identified by greenish-blue or blue colour, streak, and low hardness. Also very characteristic are radial-acicular, rod-like, stellate aggregates, quite frequently occurring in cavities in accumulations of iron hydroxides, in fossil bones and shells.

In the reducing flame turns red and fuses into a grey lustrous magnetic globule. With salt of phosphorus gives the characteristic iron bead. Heated in the glass tube, yields much water, the reaction of which is neutral, intumesces, and turns grey with red spots. Readily soluble in hydrochloric and nitric acids.

Genesis and occurrence. Vivianite is formed through exogenous processes in a reducing environment. Its phosphorus is often derived from organic remains. Commonly found in phosphorus-rich sedimentary iron ores, and also in peat bogs (as an earthy variety) associated with siderite and other ferrous oxide minerals. Is subject to alteration in the oxidised zone.

Vivianite occurs in many deposits in the U.S.S.R. Well-known are crystalline radiated aggregates in shells and cavities in the brown iron ores of the Kerch Peninsula (the Crimea) and on the Taman Peninsula. Earthy vivianite is widely distributed in bog iron ores, e.g., in the Moscow Region.

Uses. When found in quantity, is a source of cheap blue pigment.

ANNABERGITE, $Ni_3[AsO_4]_2 \cdot 8H_2O$. Named after the place of occurrence (Annaberg in Saxony). Synonym: nickel bloom.

Chemical composition. NiO 37.5%, As_2O_5 38.5%, H_2O 24.0%. Sometimes contains a negligible isomorphous admixture of Co, Fe, Mg, rarely Ca.

System, monoclinic; symmetry, prismatic L^2PC. Crystals capillary and rare. Usually observed as earthy masses.

Colour, apple-green to dark green. **Streak**, slightly greenish. **Lustre**, vitreous. $n_x = 1.687$, $n_y = 1.658$, and $n_z = 1.622$. **Hardness**, 2.5 to 3. Brittle. **Cleavage**, {010} perfect. **Specific gravity**, 3.0.

Diagnostic features. Characteristic green colour and association with nickel arsenides such as niccolite and chloanthite, from which it usually derives.

Fuses in the reducing blowpipe flame evolving arsenic and giving a greyish-black globule. Readily soluble in acids. With dimethyl glyoxyme gives a vivid nickel reaction.

Genesis and occurrence. Confined exclusively to the oxidised zones of ore deposits, the primary ores of which contain nickel arsenides. As a rule, they are replaced directly by annabergite.

Occurs in quantity in nickel-arsenide deposits at Annaberg and Schneeberg in Saxony. Finds in the Urals, North Caucasus, and elsewhere in the Soviet Union are of mineralogical interest only.

ERYTHRITE, $Co_3[AsO_4]_2 \cdot 8H_2O$. "Erythros" is the Greek for red. Synonym: cobalt bloom.

Chemical composition. CoO 37.5%, As_2O_5 38.5%, H_2O 24.0%. Occasionally contains isomorphous admixtures of Ni, Mg, Fe, Ca, and also foreign matter as mechanical impurities.

System, monoclinic; symmetry, prismatic L^2PC. Rare crystals are small. **Habit**, acicular or thin-platy. Usually in earthy masses.

Colour, crimson to peach-red, dark pink. **Streak**, pale red. **Lustre** of crystals, vitreous; pearly on cleavage surfaces. $n_x = 1.701$, $n_y = 1.663$, and $n_z = 1.629$.

Hardness, 1.5 to 2.5, for earthy masses 1. **Cleavage**, {010} excellent. **Specific gravity**, 2.95.

Diagnostic features. Readily identifiable by pink or red colour, earthiness, and association with cobalt arsenides: cobaltite and smaltine.

Before the blowpipe fuses into a grey bead giving an arsenical (garlic) odour, and colouring the flame light blue. Very characteristic are the deep blue beads of borax and salt of phosphorus. In the closed tube yields much water. Soluble in hydrochloric acid colouring the solution pink-red.

Genesis and occurrence. Like annabergite, occurs in the oxidised zones of the deposits whose ores contain cobalt arsenides. May be pseudomorphous after smaltine.

Is found in the same deposits as annabergite, since arsenides of nickel and cobalt mostly occur together. However, certain deposits contain cobalt arsenides only and, therefore, erythrite is not accompanied by annabergite. Such are the deposits of Dashkesan (Azerbaijan), Ak-Jilga (the Alai range in Central Asia), etc.

2. SCORODITE GROUP

SCORODITE, $Fe^{\cdots}[AsO_4]\cdot 2H_2O$. "Scorodon" is the Greek for garlic. Has been named for its characteristic garlic odour given off when it is struck with a hammer.

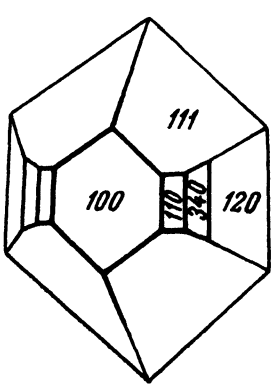


Fig. 264. Scorodite crystal.

Chemical composition. Fe_2O_3 34.6%, As_2O_5 49.8%, H_2O 15.6%. Varieties containing up to 7.1% of Al_2O_3 known as *alumoscorodite*. Massive scorodite is often contaminated with foreign matter.

System, orthorhombic; symmetry, dipyramidal $3L^23PC$. Space group *Pcab* (D_{2h}^{15}). $a_0 = 10.28$; $b_0 = 10.00$, $c_0 = 8.90$. **Habit**, dipyramidal, sometimes in combination with prisms (Fig. 264). Frequently observed in finely-crystalline druses. Usually in compact earthy masses.

Colour, greenish white, apple-green, brownish grey, sometimes white (in cryptocrystalline earthy masses). *Pitticite*, an impure partly hydrolysed variety coloured by iron hydroxides, is reddish brown. $n_x = 1.79$ to 1.81, $n_y = 1.77$ to 1.79, and $n_z = 1.76$ to 1.78.

Hardness, 3.5. Brittle. **Fracture**, uneven. **Cleavage**, {100}, {001}, and {201} imperfect. **Specific gravity**, 3.3.

Diagnostic features. Characteristic pale-green hues of minute pyramidal crystals in cavities or of continuous, often dull, masses. Highly

aracteristic is the association with residual unreplaced arseno-
rite.

Readily fusible before the blowpipe, colouring the flame light blue
d giving off the garlic odour. On charcoal with soda gives a black
agnetic slag. Readily soluble in hydrochloric acid and, to some ex-
nt, in nitric acid. A KOH solution rapidly colours scorodite powder
ddish brown.

Genesis and occurrence. Scorodite forms sometimes considerable
asses in the oxidised zones of arsenopyrite-rich deposits. Usually
velops metasomatically directly after arsenopyrite and löllingite.

In the U.S.S.R., occurs in many arsenopyrite-rich sulphide ore
posits. In the *Brich-Mulla* deposit (north-east of Tashkent) scoro-
te has been found in large quantities both as granular massive and
cryptocrystalline gel-like formations with a waxy lustre of vari-
s colours: white, all shades of green, brown, and even black. Scoro-
te also occurs at *Takeli* in the Karamazar ridge (Tajikistan), at
chkar and *Jetygar* (Southern Urals), *Zapokrovskoye* (Eastern Trans-
ikal area), etc.

3. URANITE GROUP

This group includes the rather numerous hydrous basic phosphates,
senates, and vanadates which are mostly binary salts of divalent
etals, such as Cu^{2+} and Ca^{2+}, followed by Mg^{2+}, Fe^{2+}, Mn^{2+}, Ba^{2+},
$^{2+}$, and K^{1+} with U^{6+}; the latter is believed to form a $[UO_2]^{2+}$
tionic group with additional O^{2-} anions. The most common among
em are compounds with eight water molecules. It should be men-
ned that by far not all mineral species of the group occurring in
ture have been identified.

The important characteristic of the uranites is perfect unidirec-
nal cleavage, in which respect they resemble micas.

Their crystal structures are characteristically laminated. The
minae are probably double sheets composed of XO_4 tetrahedral
oups, linked by U^{6+} cations having sixfold oxygen coordination. Cu,
, Ba cations and H_2O molecules may be located between such layers.

The water-rich varieties on exposure to air are dehydrated owing
the low vapour pressure of the environment, the process being
pecially intensified by heating. This involves changes in the physical
operties, especially of specific gravity and refractive indices.

The minerals of the group are distinguished by bright-yellow or
een colour, iridescent chatoyancy on cleavage surfaces, comparative-
low hardness, good solubility in acids, and strong radioactivity.
ese compounds are easily produced artificially from cold solutions
appropriate composition and concentration.

Lastly, practically all these minerals occur under the same condi-
ns, being the products of the oxidation of uranium deposits. When
und in commercial quantity, these minerals are of economic impor-
nce as a source of uranium, radium, and, sometimes, vanadium.

TORBERNITE, $Cu[UO_2]_2[PO_4]_2 \cdot 12H_2O$. **Chemical composition.** According to the analytical data available: CuO 7.73%, UO_3 57.50%, P_2O_5 14.50%, H_2O 20.30%. Very closely agrees with the theoretical composition. At 45°C four water molecules disappear, the mineral changing to metatorbernite.

System, tetragonal; symmetry, ditetragonal dipyramidal $L^4 4L^2 5PC$. Space group $I4/mmm(D_{4h}^{17})$. $a_0 = 7.06$; $c_0 = 20.5$. **Habit.** Crystals are small, well-formed, and tabular (Fig. 265). Usually in scaly masses and pulverulent coatings. Tabular crystals are of a square contour on {001} faces. Intergrowths with autunite have been observed.

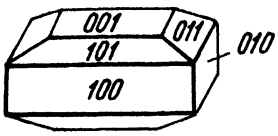


Fig. 265. Torbernite crystal.

Colour, emerald green. **Lustre**, vitreous, pearly on cleavage surfaces. $n_y = 1.590$ to 1.592, and $n_z = 1.576$ to 1.582.

Hardness, 2 to 2.5. **Cleavage**, {001} perfect. **Specific gravity**, 2.3 to 3.6. Strongly radioactive.

Diagnostic features. Characteristic are perfect cleavage (micaceous), and bright-green colour. Torbernite may be distinguished from other green minerals by optical constants and chemical tests.

Before the blowpipe fuses into a black bead. With soda in the reducing flame yields a copper globule. Dissolves in nitric acid; when ammonia is added, the solution turns blue (copper) giving a yellow precipitate.

Genesis and occurrence. Forms in the oxidised zones of pegmatites and hydrothermal and also sedimentary and other uraniferous deposits. Usually is found in small quantities on the walls of cracks and leaching cavities, often on limonite, sometimes in association with autunite and other secondary uranium minerals.

Torbernite is a relatively widespread mineral.

AUTUNITE, $Ca[UO_2]_2[PO_4]_2 \cdot 8H_2O$. Named after a locality in France.

Chemical composition. CaO 6.1%, UO_3 62.7%, P_2O_5 15.5%, H_2O 15.7%. Sometimes contains impurities of BaO, MgO, Fe_2O_3, etc. (usually in negligible amounts). Autunite may also contain actinium and polonium.

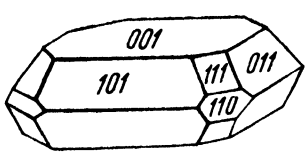


Fig. 266. Autunite crystal.

System, tetragonal; symmetry, ditetragonal dipyramidal $L^4 4L^2 5PC$. Space group $J4/mmm$ (D_{4h}^{17}). $a_0 = 7.00$; $c_0 = 20.67$. **Habit.** Crystals are thin-tabular (Fig. 266), micaceous, square. Interfacial angles are close to those of torbernite. Druses of small crystals or scaly aggregates are sometimes observed.

Colour, green, greenish yellow, sulphur-yellow. **Lustre**, on cleavage surfaces pearly. $n_x = 1.594$, $n_y = 1.590$, and $n_z = 1.571$.

Hardness, 2 to 2.5. Brittle. **Cleavage**, {001} highly perfect, {100}

and {010} less perfect. **Specific gravity**, 3.05 to 3.19. Strongly radioactive. Luminescent. In ultraviolet radiation fluoresces yellow-green.

Diagnostic features. May be positively distinguished from other similarly coloured uranites by spectral and chemical analyses.

Slightly intumesces before the blowpipe flame and fuses into a black globule. Colours the flame orange-red (Ca). In the closed tube, yields much water. With borax shows the reaction for uranium. Soluble in nitric acid colouring the solution green.

Genesis and occurrence. Like all the uranites, is formed in the oxidised zones of uranium deposits.

Autunite occurs in a fairly numerous deposits: Autun in the Loire department (France), Schneeberg, Johanngeorgenstadt in Saxony (Germany), Redruth in Cornwall (Britain), pegmatites of Madagascar, and elsewhere.

TYUYAMUNITE, $Ca[UO_2]_2[VO_4]_2 \cdot 8H_2O$. Discovered by Soviet scientist K. A. Nenadkevich at Tyuya-Muyun (Ferghana).

Chemical composition. CaO 5.87%, UO_3 59.96%, V_2O_5 19.06%, H_2O 15.11%. Sometimes contains as negligible impurities Na_2O, K_2O, MgO, CuO (up to 4%), SiO_2, etc.

System, orthorhombic, symmetry, rhombic dipyramidal $3L^23PC$. $a_0 = 10.63$; $b_0 = 8.36$; $c_0 = 20.40$. **Habit**, thin-tabular (Fig. 267). Common forms: {100}, {010}, {110}, {120}, {001}, {101}, and {111}. **Aggregates.** Thin-scaly earthy masses and also as coatings and crusts in cavities.

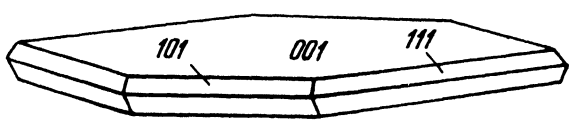


Fig. 267. Tyuyamunite crystal.

Colour, bright yellow (canary), sometimes with greenish or slightly orange tinge. **Lustre**, strong, pearly on cleavage surfaces. $n_x = 1.895$, $n_y = 1.870$, and $n_z = 1.670$.

Hardness, 1. Brittle. **Cleavage**, {001} perfect, {010} and {100} distinct. **Specific gravity**, 3.68 (varies depending on water content). Strongly radioactive.

Diagnostic features. Distinguishable from other uranites only by chemical tests and optical constants. In finely-dispersed masses resembles the bright-yellow efflorescence of certain iron sulphates. Is distinguished from the latter by poor solubility in water and radioactivity.

Readily fusible in the blowpipe flame. With borax gives a distinct reaction for uranium (in the absence of copper). In the closed tube, yields much water. Readily soluble in acids. With hydrogen peroxide, gives a reaction for vanadium. In appropriate solutions and concen-

trations the Ca^{2+} cation is capable of being replaced by two K^{1+}, resulting in the formation of carnotite.

Genesis and occurrence. Together with other exogenous minerals, tyuyamunite occurs in the oxidised zone of uranium-bearing deposits. It is also formed in the presence of organic matter with which vanadium minerals are often associated in general.

Tyuyamunite may quite possibly be formed after carnotite in sedimentary rocks through the action of waters containing calcium bicarbonate. The possibility of potassium being replaced by calcium has been confirmed experimentally.

In the U.S.S.R., usually occurs as earthy masses associated with gypsum in cracks in sedimentary rocks containing organic remains. A notable foreign locality are the vanadium-bearing sandstones of Colorado (U.S.A.).

CARNOTITE, $K[UO_2]_2[VO_4]_2 \cdot 3H_2O$. Named after A. Carnot.

Chemical composition. K_2O 10.44%, UO_3 63.41%, V_2O_5 20.16%, H_2O 5.99%. Sometimes contain as impurities Na_2O, MgO, CaO, a very negligible quantity of CuO, PbO, etc.

System, monoclinic; symmetry, rhombic prismatic L^2PC. Space group $P2_1/a(C_{2h}^5)$. $a_0 = 10.47$; $b_0 = 8.41$; $c_0 = 6.91$; $\beta = 103°40'$. Usually in pulverulent masses and coatings.

Colour, bright yellow to greenish yellow. **Lustre**, strong; pearly on cleavage surfaces. $n_x = 1.950$, $n_y = 1.925$, and $n_z = 1.750$.

Hardness, 2 to 2.5. Brittle. **Cleavage**, {001} perfect. **Specific gravity**, 4.46. Strongly radioactive.

Diagnostic features. Has much in common with tyuyamunite, but differs from it in optical constants.

Before the blowpipe fuses readily into a black globule and colours the flame pale violet (should be viewed through blue glass which filters out the yellow tint of sodium). With borax gives a uranium bead. Readily soluble in acids. With hydrogen peroxide gives the vanadium reaction. Its powder, when slightly moistened with hydrochloric acid, turns blood-red, this indicating the presence of vanadium.

Genesis and occurrence. Occurs in the weathered zone of sedimentary rocks, chiefly in sandstones enriched in organic matter. First discovered in Jurassic vanadium-bearing sandstones in *Utah* and *Colorado* (U.S.A.).

Also found in the calcareous sandstones of *Katanga* (Congo), *Radium Hill* (Australia), and many other places.

4. TURQUOISE GROUP

The group includes pentahydrous basic phosphates of Cu, Al, and Fe^{3+} crystallising in the triclinic system. We shall limit the present discussion to turquoise.

TURQUOISE, $CuAl_6[PO_4]_4[OH]_8 \cdot 5H_2O$. Synonym: kallait (the old name for turquoise). A variety rich in iron (Fe_2O_3 20 to 21%) is called *rachleite*.

Chemical composition. CuO 0.57%, Al_2O_3 36.84%, P_2O_5 34.12%, H_2O 19.47%. May contain various impurities.

System, triclinic; symmetry, pinacoidal. Commonly occurs in cryptocrystalline reniform masses or crusts, veinlets, and irregular masses.

Colour, sky-blue, apple-green, greenish grey. **Lustre**, waxy. $n_x = 1.65$, $n_y = 1.62$, and $n_z = 1.61$.

Hardness, 5 to 6. Rather brittle. **Cleavage**, {001} perfect, {010} distinct. **Fracture**, slightly conchoidal. **Specific gravity**, 2.60 to 2.83.

Diagnostic features. Characteristic colour and waxy lustre. Sometimes, however, it is necessary to resort to chemical tests to distinguish it from similar chrysocolla and other copper minerals.

Before the blowpipe decrepitates turning brown. Colours the flame pale green. In the closed tube, yields much water. With borax and salt of phosphorus gives the reaction for copper. Soluble in acids. Gives the phosphorus reaction.

Genesis and occurrence. Turquoise is formed in the zone of weathering, often together with limonite, through the action of cupriferous surface solutions on rocks containing alumina (feldspars) and phosphorus (apatite). A variety known as bone turquoise or odontolite is represented by fossil bones and teeth coloured blue. The organic genesis of such turquoise is readily visible in polished sections under the microscope.

The best turquoise has come for centuries from the *Madan* deposit near Nishapur (Iran) where it was formed together with limonite as irregular masses and thin veinlets in weathered igneous rocks, trachyte. It is from there that gem turquoise has come to Europe via Turkey. Other localities worth of mention are: *Vadi-Magara* (Sinai Peninsula), *Kara-Tyube* (south of Samarkand), etc.

Uses. Best coloured varieties (sky-blue) are used as gemstones. Varieties of inferior quality may be coloured artificially.

CLASS 7. BORATES

General. This class includes salts of boric acids such as orthoacid HBO_3, metaboric acid, HBO_2, and the so-called polyboric acids.

These hypothetical polyboric acids are deduced by subtracting a certain number of H_2O particles from the corresponding number of normal orthoacid particles. The most common in nature are salts of the following boric acids:

$$H_3BO_3 - H_2O = HBO_2 \qquad 5H_3BO_3 - 7H_2O = HB_5O_8$$
$$4H_3BO_3 - 5H_2O = H_2B_4O_7 \qquad 6H_3BO_3 - 7H_2O = H_4B_6O_{11}$$
$$5H_3BO_3 - 6H_2O = H_3B_5O_9 \qquad 7H_3BO_3 - 8H_2O = H_5B_7O_{13}, \text{ etc.}$$

Borates may contain Al^{3+}, Fe^{3+}, and Mn^{3+} cations which are known to form salts in combination with divalent cations of small

ionic radii (Mg and Fe^{2+}). The class also includes acidic and basic orthosalts of Mg^{2+}, which in one case are combined with Ti^{4+}. Calcium occurs in binary salts only.

All these *orthoborates* occur exclusively as anhydrous compounds. Normal orthoborates are insoluble not only in water, but even in acids (or are decomposed by them with difficulty), fusible at high temperatures and have very high or high hardness.

Polyborates, besides the Mg^{2+} cation, may contain larger Ca^{2+} and Na^{1+} cations, and occur almost invariably as hydrous salts. Polyborates of Na^{1+} and other strong cations are readily soluble in cold water, while binary borates of Na^{1+} and Ca^{2+} are soluble in hot water. Anhydrous polyborates of Mg (e.g., boracite) are gradually hydrated in water at room temperature, in which respect they differ from orthoborates.

The behaviour of boron in the course of natural processes shows some other interesting features as well. Whereas at low temperatures B_2O_3 is replaced by CO_2, at high temperatures the process is reversed. Borates may be replaced by carbonates in the course of weathering which has been observed at the Inder deposit. In contact-metasomatic deposits, on the other hand, there have been found borates formed by replacement in limestones.

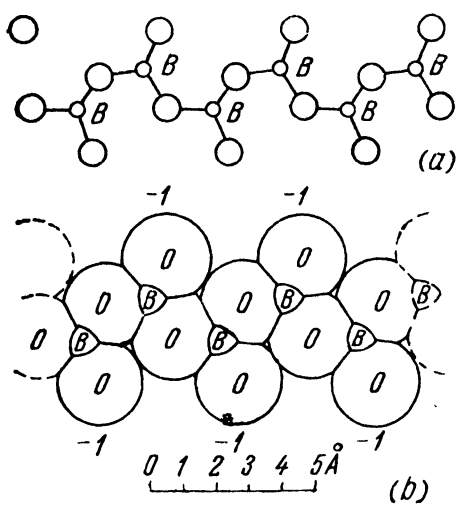


Fig. 268. Chains of BO_3 groups. *a* – position of ionic centres; *b* – view of chain in crystal structure.

Boron is a rather mobile element, being transported by water solutions containing such constituents as Cl, OH, and especially F which has a strong chemical affinity for boron. Therefore, the concentration and formation of boric compounds take place in the *residual products* of geological processes, partly in pegmatites and hydrothermal environment (orthoborates, borosilicates), but for the most part in boron-enriched drying salt basins (polyborates and, rarely, hydrous borosilicates).

Borates are closer to silicates in a number of crystallochemical properties than to any other oxysalts. Borates that contain simple anionic groups $[BO_3]^{3-}$ and $[BO_4]^{5-}$ in their crystal structures differ but slightly from typical oxysalts, including the orthosilicates with their $[SiO_4]^{4-}$ groups. In contrast to salts of other types, however, borates, as well as silicates may contain more complex anionic $[BO_3]^{3-}$ groups interlocked to form common triangular apexes (Fig. 268), which gives rise to the so-called extended anions in the form of negatively charged chains, layers, frameworks, etc., characteristic of polyborates.

Anhydrous Borates

Anhydrous borates are represented mostly by salts of orthoboric acid (normal, acid, and basic). There are few minerals that may be classified as meta- and polyborates.

ASCHARITE, $MgHBO_3$ or $2MgO \cdot B_2O_3 \cdot H_2O$. Named after a geographical location: Ascharix, a former Roman province (Aschersleben in Saxony). Synonym: szaibelyite (the term used in the U.S.A.).

Chemical composition. MgO 47.91%, B_2O_3 41.38%, H_2O 10.71%. May contain Mn and negligible F.

System. Orthorhombic. Occurs in friable chalk-like, more seldom in compact masses of parallel-fibrous or thin-acicular structure.

Colour, white. **Lustre**, vitreous, in friable masses dull. $n_x = 1.650$, $n_y = 1.646$, $n_z = 1.575$.

Hardness, 3 to 3.5. In friable chalk-like masses smears the fingers. **Specific gravity**, 2.65.

Diagnostic features. Ascharite may be identified tentatively when it is found in paragenesis with other borates. Positive recognition is possible only by measurement of optical constants and by chemical analyses.

Before the blowpipe fuses into enamel and strongly colours the flame green (presence of boron). Insoluble in water. Soluble with difficulty in acids. Yields the bulk of its water at temperatures above 800°.

Genesis and occurrence. Ascharite occurs most often as a secondary mineral in salt-bearing sedimentary deposits of borates. It is formed in the conditions of a hot arid climate as a product of the natural reworking and dehydration of other, chiefly hydrous, boracic compounds. May accumulate metasomatically in clays. In leaching cavities occurs as colloform reniform masses of radial or acicular structure.

Cases are known when it has been found in contact-metasomatic deposits in limestones or dolomites associated with serpentine (magnesium hydrosilicate), magnetite, and other minerals.

Notable foreign localities are Aschersleben and Neustassfurt (Saxony), Rézbanya (Rumania), Nevada (U.S.A.).

Uses. When found in large quantities together with other borates, ascharite is of economic importance.

Borates are a source of boric acid, which has various uses. The chemical industry uses boric acid to make different boric salts. Together with borax it is used in enamels for iron ware (its expansion coefficient approaches that of the metal), for impregnating candle wicks to keep them upright when burning, in tanning, pharmaceutics, etc.

Furthermore, borax is used in making lamp-glass and other kinds of glass subject to temperature fluctuations such as "pyrex" (B_2O_3 11.8%), for laboratory utensils (the optical lenses made by Zeiss are

made of glass containing 56 per cent B_2O_3). Since borax dissolves metal oxides, it is indispensable as a flux which prevents formation of oxides on the surface of soldered joints.

Borax is also added to paper pulp in the manufacture of high-grade glossy and noninflammable papers, and articles therefrom. Boron compounds are also important fertilisers; correctly dosed, they help to balance plant nutrition with potassium salts, and thus to increase crop yields.

Of late, boron has been used extensively in highly efficient jet fuels. Boron carbides (B_6C, B_4C, and B_3C) are good abrasives. Borides of W, Ti, and Ta are very hard and refractory. Boron steel is used in atomic piles.

BORACITE, $Mg_3B_7O_{13}Cl$. **Chemical composition.** B_2O_3 62.1%, MgO 30.7%, Cl 8.1%.

System. Pseudocubic. Above 265° becomes cubic. Below 265° converts to an orthorhombic modification. Space group of the high-temperature modification $F\bar{4}3c(T_d^5)$. $a_0 = 12.10$. **Habit**, cubic or octahedral (Fig.269). Also occurs as continuous close-grained marble-like masses.

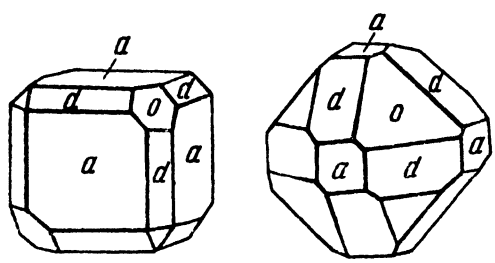


Fig. 269. Boracite crystals: *a* {100}, *o* {111}, *d* {110}.

Colour, white with greyish, yellowish or greenish tinge. **Lustre**, vitreous, strong. $n_x = 1.673$, $n_y = 1.667$, and $n_z = 1.662$.

Hardness, 7. **Cleavage**, none. Fracture conchoidal. **Specific gravity**, 2.95.

Diagnostic features. Characteristic crystals in the cubic system which in thin polished sections under the microscope show optical anisotropy and complex texture. High hardness (7) and rather high specific gravity are also distinctive features of boracite.

Before the blowpipe fuses rather easily into a white enamel globule, colouring the flame green. Insoluble in water. Dissolves slowly in hydrochloric acid. On weathering absorbs water and becomes fibrous (evidently altering to a different mineral).

Genesis and occurrence. Occurs in salt deposits with carnallite, sylvite, halite, gypsum, anhydrite, and other minerals. Evidently forms in the process of metamorphism through dehydration of hydrous borates of magnesium. Is found at Stassfurt in Anhalt, at Luneburg in Hannover (Germany) and other deposits. Has commercial importance.

Hydrous Borates

Almost all the hydrous salts reviewed here are polyborates of Mg, Na, and Ca.

BORAX, $Na_2B_4O_7 \cdot 10H_2O$. **System**, monoclinic. Space group $C2/c(C_{2h}^6)$. $a_0 = 11.82$; $b_0 = 10.61$; $c_0 = 12.30$; $\beta = 106°35'$. **Habit.** Sometimes occurs in large prismatic crystals (Fig. 270). Also widespread as earthy masses.

Colour. Colourless but usually white with greyish, yellowish, bluish, or greenish tinges. **Lustre**, vitreous, greasy.

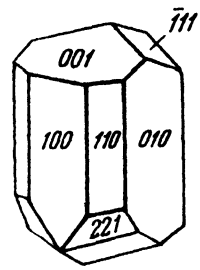


Fig. 270. Borax crystal.

Hardness, 2 to 2.5. **Cleavage**, {110} imperfect. **Specific gravity**, 1.69 to 1.72.

Diagnostic features. Characteristic boron colouring of the flame. Other characteristic features are rather low hardness and ready solubility in water. Can be distinguished from similar boronatrocalcite only by chemical tests (borax does not contain any calcium).

In the blowpipe flame after much swelling fuses into a transparent globule. Dissolves in water, the solution showing a slightly alkaline reaction. Taste, sweetish-alkaline, weak.

On exposure to air is readily dehydrated, becomes turbid and finally alters to a fine white powder (probably tincalconite or kernite). In the fused state is capable of dissolving metal oxides. For uses see "Ascharite".

Genesis and occurrence. Is formed in drying boron-bearing salt lakes. In large masses, together with other sodium salts, occurs along lake shores in Kashmir and Tibet; in some lakes in California; in the region of the Death Valley (San Bernardino) where it probably derives from the leaching of colemanite or kernite. In the U.S.S.R., borax deposits occur near mud cones in the Crimea.

BORONATROCALCITE, $NaCaB_5O_9 \cdot 8H_2O$. Named for the elements entering into its composition. Although the choice of the name is not quite fortunate, since there is another borate of the same qualitative composition (probertite, $NaCaB_5O_9 \cdot 5H_2O$). Synonym: ulexite.

Chemical composition. Na_2O 7.7%, CaO 13.8%, B_2O_3 43.0%, H_2O 35.5%. May contain negligible K_2O and MgO and some foreign matter. **System**, triclinic; symmetry, pinacoidal (?). Occurs as nodules and reniform masses of asbestos-like, acicular or matted fibrous structure. Occasionally in thin platy aggregates.

Colour, white. **Lustre**, vitreous, silky. $n_x = 1.519$, $n_y = 1.505$, and $n_z = 1.496$.

Hardness, 1. **Cleavage**, visible under the microscope, is in three directions crossing at right angles and thus giving the plates a rectangular habit. **Specific gravity**, 1.65.

Diagnostic features. Characteristic low hardness, frequent asbestos-like structure with silky lustre and insolubility in water. For positive identification, chemical tests and measurements of optical constants are necessary.

Swells in the blowpipe flame and fuses readily into a transparent bead with occluded bubbles. Colours the flame green. Almost insoluble in cold water. Dissolves in hot water. Readily soluble in acids.

Genesis and occurrence. Occurs in dried boron-bearing salt lakes, especially in salines in hot arid climate. May derive from hydroboracite or inyoite ($Ca_2B_6O_{11} \cdot 13H_2O$) through the weathering of salt domes containing borates. This is possible from hydroboracite if the concentration of sodium in the percolating solutions is high enough; otherwise boronatrocalcite may be altered to inyoite. In the static zone, the mineral develops metasomatically in enclosing rocks, particularly in clays, in the process of evaporation of water from solutions.

In the U.S.S.R., occurs sporadically. In large masses it is found in the dried salt lakes in the *Death Valley* (California); *Wales Desert* near Kern; at *Lange* (Los Angeles) with colemanite and also in the arid regions of Nevada such as *Esmeralda*, in dry regions of *Tarapaca* (Chile), and elsewhere.

Uses. Like other borates, when found in quantity is a source of boric compounds. For uses see "Ascharite".

HYDROBORACITE, $MgCaB_6O_{11} \cdot 6H_2O$. The name has no connection with boracite, from which it materially differs in composition. MgO 9.9%, CaO 13.9%, B_2O_3 49.5%, H_2O 26.7%. May contain very negligible quantities of alkalis. Identified by Academician G. I. Hess in 1833.

System, monoclinic. Occurs in acicular and fibrous aggregates, sometimes beautiful spherolitic and stellate sinter formations.

Colour. Colourless or white, rarely pink, red, or grey. **Lustre**, vitreous. $n_x = 1.571$, $n_y = 1.534$, and $n_z = 1.522$.

Hardness, 2. Brittle. **Cleavage**, {010} perfect. **Specific gravity**, 2.167.

Diagnostic features. Externally indistinguishable from similar borates without optical and chemical analyses.

Fuses readily before the blowpipe flame into a bead which does not become turbid on cooling; colours the flame green. Almost insoluble in water, even on boiling. Soluble in acids on slight heating.

Genesis and occurrence. Occurs in boron-bearing deposits of rock salt accompanied with strata of gypsum, anhydrite and clays. The clay beds are enriched in hydroboracite due to the general ability of clays to adsorb different substances, perhaps predominantly boric salts.

In the course of formation of salt domes, the hydroboracite in the zone of weathering becomes unstable under the action of percolating waters and is either re-deposited or gradually replaced by more stable borates (boronatrocalcite, inyoite, colemenite, and ascharite) formed metasomatically or deposited in leaching cavities (caverns and karsts)

in horizons lying at varying depths. Thus, considerable masses of secondary borates are formed together with gypsum as caps over salt domes.

Notable foreign localities for hydroboracite are at *Stassfurt* (Germany) and at Inyo California (U.S.A.).

Uses. Found in quantity, hydroboracite is an important material for the chemical industry as a source of boric compounds. See also "Ascharite".

COLEMANITE, $Ca_2B_6O_{11}\cdot 5H_2O$. **System**, monoclinic. Crystals are short-columnar, dipyramidal in habit. More often occurs in granular spherolite masses.

Colour, white. **Lustre**, vitreous. $n_x = 1.614$, $n_y = 1.592$, and $n_z = 1.586$.

Hardness, 4. **Cleavage**, {010} perfect. **Specific gravity**, 2.44. Insoluble in water. Soluble in hydrochloric acid on heating.

Large deposits of colemanite associated with gypsum and other boron minerals are found in California and Nevada (U.S.A.) in dried salt lakes and salines in districts with a hot arid climate. In Chile, near Bacos del Toro, colemanite is deposited from hot springs. In small masses it occurs at the Inder deposit.

PANDERMITE, $Ca_4B_{10}O_{19}\cdot 7H_2O$. Synonym: priceite. System, monoclinic or triclinic. Occurs as compact white metacolloidal reniform masses with dull conchoidal fracture. $n_x = 1.593$, and $n_z = 1.574$.

Hardness, 3.5. Specific gravity, 2.43. Behaviour before the blowpipe and in acids is similar to that of colemanite.

The mineral was first discovered near the port of Panderma, in the Sea of Marmora (Turkey). Occurs at *Inyo* and elsewhere in California (U.S.A.). Is found in quantity as compact masses at the *Inder* deposit of borates (north of the Caspian Sea).

CLASS 8.

SILICATES

General. The class of silicates includes a vast number of minerals—about one-third of all mineral species known in nature. Their share becomes even more important if their distribution and weight in the earth's crust are taken into consideration.

A. Y. Fersman has estimated that the silicates make up 75 per cent of the earth's crust. If we add to this another 12 per cent of free silica (mostly in the form of quartz and opal), the tremendous importance of silicium in geochemistry in general will become perfectly clear.

Many silicates are essential rock-forming minerals not only in all magmatic rocks, their hydrothermally altered varieties and contact-

metasomatic formations, but also in their weathering products and in many sedimentary rocks (chiefly clays and shales), and also in various crystalline schists. They are also important constituents of practically all deposits of economic minerals as accessory minerals of ores and, in a number of cases, as bearers of important metals (Ni, Zn, Be, Zr, Li, Cs, Rb, U, TR, etc). Quite a few nonmetallic economic minerals are silicates. This includes asbestos, kaolin, bleaching clays and feldspars which are materials for refractories, ceramics, etc., not to speak of building materials. A number of silicates (emerald, aquamarine, tourmaline, topaz, rhodonite, nephrite, etc.) have long been used as gemstones and ornamental stones.

The principal elements entering into the composition of silicates are:

Na, K, Li		
Ca, Mg, $Fe^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, Be		Si, Zr, Ti
Al, $Fe^{\cdot\cdot\cdot}$, B		O, F, H (as H^{1+}, $[OH]^{1-}$, and H_2O)

Numerous other elements (Rb, Cs, Ba, Sr, Pb, Zn, Ni, Co, Cu, Bi, Sb, Cr, V, Sc, Y, TR, Th, Sn, U, Nb, S, Cl, C in the form of $[CO_3]^{2-}$, and P) are present in relatively rare mineral species of the class.

In spite of the comparative fewness of principal elements (cited above) entering into the composition of silicates, an extraordinary variety of natural silicate compounds, often of highly complex constitution and variable composition, is observed in nature.

The chemical composition of oxygen salts of the classes reviewed heretofore was expressed by rather simple formulas. Among the silicates the number of such simple compounds is relatively small. In a great number of cases chemical analysis data do not permit evolving simple formulas because of the presence of numerous impurities and certain variability of composition of the mineral species. This cannot be explained either by errors in the analyses or by the microscopic foreign inclusions in the minerals analysed. The complexity of the composition is due to the crystallochemical features of the compounds, as will be seen from the descriptions of individual mineral groups.

The constitution of silicates. The chemical nature of silicates was thoroughly studied by such eminent scientists as Vernadsky, Tchermak, Groth, Clarke, and many others even before the advent of the X-ray methods.

Attempts were made to solve this highly complicated problem by careful comparison of the empirical formulas of minerals, making use of the valences of individual elements that were known at that time; by detailed investigation of the chemical and physical properties of minerals and of synthetic products obtained in the laboratory; by the study of the behaviour of minerals, and especially of their decomposition products, under natural conditions. All this resulted in the establishment of a number of empirical dependences. This was a stupendous job.

Numerous indirect deductions served as a basis for diverse, often controversial hypothetical concepts of the constitution of many silicates of complex composition for which various structural formulas were suggested. A number of postulates advanced with amazing intuition (by Vernadsky) have been fully borne out today. Some, however, have not been corroborated by the data of the modern precise methods of research.

Inadequate as they may seem today, the early hypotheses have played their indisputable historical role in the development of the mineralogy of silicates. But for this research, especially in ascertaining the properties of the minerals, deciphering of a number of most intricate crystal structures, particularly of feldspars, would have been hampered considerably.

We shall dwell now on some terms which have been adopted in the literature on mineralogy.

On the basis of the concepts of the molecular structure of matter, the silicates were interpreted as salts (acid, normal, and basic) of numerous hypothetical acids: silicic, alumosilicic, titanozirconosilicic, and so forth. From this standpoint the silicates proper were divided into:

(1) orthosilicates, or salts of an H_4SiO_4 acid;
(2) metasilicates, or salts of an H_2SiO_3 acid;
(3) pyrosilicates, or salts of an $H_6Si_2O_7$ acid, etc.

Whereas the compounds of the first type do have many properties, including the structure of the crystal lattice, characteristic of typical salts, analogous to the previously described phosphates, sulphates, etc., in the salts of the other two types, especially those rich in silica, these features are much less pronounced. Compounds of the latter type actually occupy an intermediate position between typical salts and oxides (e.g., SiO_2).

It should also be mentioned that in literature one finds other less appropriate terms for types of silicates based on the quantitative ratio between oxygen atoms of the SiO_2 anhydride and those of the bases (derived from empirical formulas). The orthosilicates (e.g., forsterite $2MgO \cdot SiO_2$) were called *monosilicates* because the ratio of oxygen atoms for SiO_2 and MgO (2 : 2) was 1. The metasilicates were called *disilicates* (e.g., enstatite $MgO \cdot SiO_2$); albite $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$ was thus called *trisilicate*.

The current concept of the constitution of silicates has developed mainly on the basis of general laws of crystal chemistry.

X-ray study of scores of silicates of widely varying composition has led to the following highly important conclusions with regard to the specific features of crystal structures of these compounds.

1. In all the silicates studied each Si^{4+} ion is always surrounded by four O^{2-} ions occurring at the corners of a tetrahedron (Fig. 271). The bonding of the oxygen ions with silicon is much stronger than

with other metals acting as cations in the crystal structure of silicates. The dimensions of these silicon-oxygen tetrahedra are almost invariable. The Si—O distance is about 1.6Å. This and the other X-ray data confirm that the Si—O linkage is largely covalent.

Thus, the silicon-oxygen tetrahedron, i.e., $[SiO_4]^{4-}$ group, is the fundamental structural unit of all silicates.

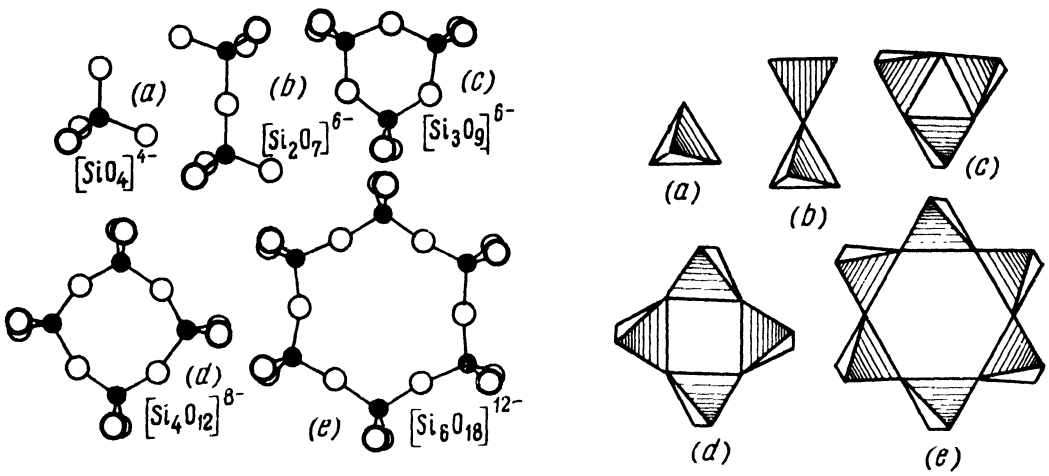


Fig. 271. Types of individual groups of silicon-oxygen tetrahedra (in two representations).

a —single isolated $[SiO_4]^{4-}$ tetrahedron; *b* —group of two $[Si_2O_7]^{6-}$ tetrahedra linked by a shared apex; *c*—group of three tetrahedra linked in a $[Si_3O_9]^{6-}$ ring; *d*—group of four tetrahedra linked in a $[Si_4O_{12}]^{8-}$ ring; *e* —group of six tetrahedra linked in a $[Si_6O_{18}]^{12-}$ ring.

2. The silicon-oxygen tetrahedra in the crystal structures of the silicates may be either independent SiO_4 unit cells or may be linked together in a number of ways to form complex anionic radicals. *The tetrahedra are linked only by sharing corners*, never by sharing edges or faces. Most complete linkage is obviously achieved when all the four tetrahedron apexes are shared by the adjacent SiO_4 tetrahedra. This is precisely the case of crystal structures of minerals of the quartz group (cf. Figs. 182 and 183) with the general formula SiO_2.

Therefore, the Si : O ratio in the complex anionic radicals of the silicates may vary from 1:4 to 1:2.

3. Depending on whether the silicon-oxygen tetrahedra are linked and on the nature of the linkage, the complex anionic radicals assume different spatial forms.

Here are the most typical examples:

(a) The complex anionic radical has the form of an *isolated* $[SiO_4]^{4-}$ tetrahedron (Fig. 271*a*) held in the structure by cations of other metals. The total negative charge of each such group is 4 (each oxygen ion giving to silicon only half of its negative charge which is 2). This type of structure is widely represented in the orthosilicates, such as zircon, $Zr[SiO_4]$; forsterite, $Mg[SiO_4]$; garnet, $Ca_3Al_2[SiO_4]_3$, and many others.

(b) The complex anionic radical has the form of isolated $[Si_2O_7]^{6-}$ *groups* consisting of two interlinked SiO_4 silicon-oxygen tetrahedra with a common apex (Fig. 271*b*). The total negative charge of this group is obviously 6. The oxygen ion occurring at the common apex is electrostatically inert. Therefore, the active oxygen ions, whose residual negative charges are neutralised in the crystal structure by

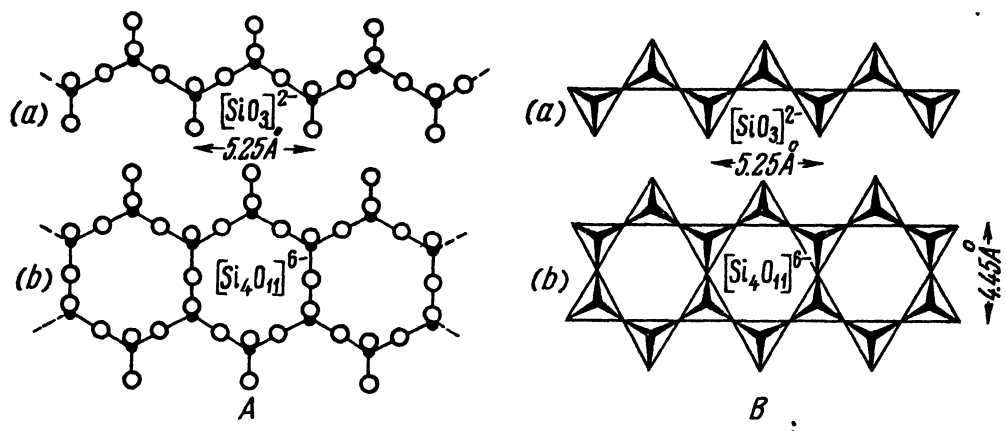


Fig. 272. Types of unidimensional continuous chains of silicon-oxygen tetrahedra (in two representations).

a—single $[SiO_3]^{2-}_{\infty}$ chain, *b*—double $[Si_4O_{11}]^{6-}_{\infty}$ chain (ribbon). Tetrahedral apexes facing viewer are shown by thicker lines (*B*).

metallic cations, occur at the two opposite ends of the anionic radical (Fig. 271*b*). Compounds (pyrosilicates) with such complex anionic radicals are few, e.g., thortveitite, $Sc_2[Si_2O_7]$.

(c) The complex anion consists of three, four, and six silicon-oxygen tetrahedra sharing two apexes and thus forming closed *flat isolated rings* (Fig. 271*c*, *d*, and *e*). In this case the complex anions will be respectively expressed as $[Si_4O_9]^{6-}$, $[Si_4O_{12}]^{8-}$, and $[Si_6O_{18}]^{12-}$. The total valence of each such radical depends on the number of the outer oxygen ions, each having the non-compensated negative valence. Examples are benitoite, $BaTi[Si_3O_9]$, and beryl, $Be_3Al_2[Si_6O_{18}]$. Under the older classification, the compounds of this structural type were grouped with the metasilicates, $R''[SiO_3]$, solely on the basis of its chemical formula. It should be added that N. V. Belov has demonstrated that certain silicates (milorite and tourmaline) possess a new type of anions in the form of complexes consisting of double (two-tier) rings.

(d) The complex anions constitute *unidimensional continuous chains* of linked silicon-oxygen tetrahedra. In the upper part of Fig. 272 there is shown a simple *single chain* in which each tetrahedron is linked to the adjacent tetrahedra by sharing two corners with inert oxygen ions, while two active oxygen ions in each tetrahedron are so arranged that one of them occurs above the Si ion (on the plane of the

drawing) and the other is offset alternately upward and downward. The metallic cations are located between these *linearly extended* radicals.

As in the previous type, in each silicon-oxygen tetrahedron, two oxygen ions completely belong to the Si ion, while the two others (the inert ones) are equally shared, as it were, by the adjacent tetrahedra. In the sum total, each Si ion holds three oxygen ions, two of which have one free valence each. Thus the composition and valence of such radicals may be expressed as follows: $n[SiO_3]^{2-}$, where $n = \infty$ and indicates polymerisation. This type of the acid radical structure is characteristic of the group of pyroxenes which are classed as typical metasilicates expressed by the general formula $R'' [SiO_3]$. Here, however, as in the previous type of crystal structures, there are no isolated SiO_3 anionic radicals.*

In the lower part of Fig. 272*b* there is shown a *double chain* or rather a band of continuously linked silicon-oxygen tetrahedra corresponding to a single chain reflected across a plane perpendicular to the drawing and parallel to the axis of the chain. Such band-type linkage of silicon-oxygen tetrahedra is characteristic of the amphiboles. It can be easily calculated that the composition and valence of such radicals within the limits of one period (5.25 Å) is expressed by the formula $[Si_4O_{11}]^{6-}$.

It should be noted that in the silicon-oxygen tetrahedra the Si ion may be partially replaced by the Al ion which is also surrounded by four oxygen ions.

Recently, at the Research Institute of Crystallography of the U.S.S.R. Academy of Sciences, N. V. Belov and other workers have established a new type of anionic radical in the form of a silicon-oxygen $[Si_3O_9]^{6-}$ chain characteristic of the minerals of the wollastonite group, $CaSiO_3$, and also in the form of double silicon-oxygen $[Si_6O_{17}]^{10-}$ chains characteristic of the OH-bearing xonotlite, $Ca_6[Si_6O_{17}] [OH]_2$.

(e) The complex anions have the form of *two-dimensional layers* of silicon-oxygen tetrahedra. In the structure of such layered radicals, the tetrahedra are linked together by sharing three common apexes to form continuous sheets (Fig. 273) having the pattern of a hexagonal lattice. The active oxygen ions (one from each tetrahedron) are all oriented in the same direction (above or beneath the plane of the drawing) thus forming a special active layer in the tetrahedral sheet. The chemical formula of such anionic layer within a hexagon should be written as $[Si_2O_5]^{2-}$. Some of the Si ions in the silicon-oxygen tetrahedra are often replaced by Al ions with fourfold coordination. Each such sheet is in some way linked to other structurally identical sheets

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* Both for this complex anionic radical and for all the subsequent forms of tetrahedra linkage we shall enclose in brackets a tentative unit which in this case stands for the unit length of one period of the chain, i.e., 5.25 Å (Fig. 272). Thus the formula of the anionic radical of the pyroxenes will be $[Si_2O_6]$.

by a layer of active oxygen ions and through metallic cations. Examples of such crystal structures are found in lamellar minerals possessing excellent unidirectional cleavage: micas, talc, chlorites, etc.

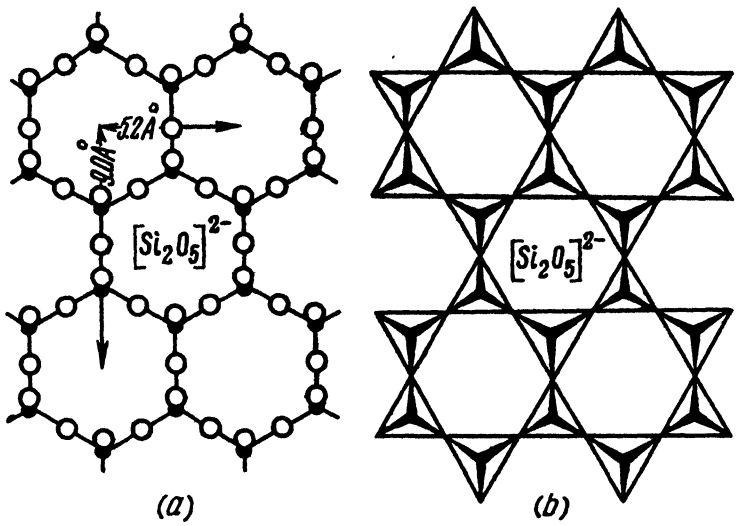


Fig. 273. A sheet of $[Si_2O_5]^{2}_{\infty}$ hexagonal silicon-oxygen tetrahedra.

(f) The complex anions are comprised of *three-dimensional frameworks* of silicon-oxygen tetrahedra, in which each oxygen ion is shared by two adjacent tetrahedra. There is not a single tetrahedral corner with an active oxygen ion in it. As we have already noted, such frameworks are found in minerals of the quartz group, which constitute, as it were, pure anhydride with the SiO_2 formula. Similar structures are observed, however, also in silicates (Fig. 274). It is true that in such cases, some of the Si^{4+} ions are always replaced by Al^{3+} ions with the same coordination number (this problem will be reviewed separately later). The general chemical formula of complex anions with a framework structure may be written as $[(Si_{n-x}Al_x O_{2n}]^{x-}$. Because of the partial substitution of Al^{3+} for the Si^{4+} ions (the total number of oxygen ions remaining the same), the radical has a certain residual negative charge, as can be easily calculated. Examples are feldspars $Na[Si_3AlO_8]$, $Ca[Si_2Al_2O_8]$, and many other minerals. The Na, Ca, and other cations which balance the residual negative valence of the anionic frameworks are enclosed within the frameworks (in the respective "voids" of the structure).

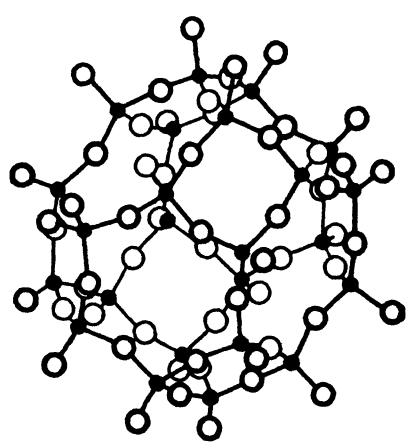


Fig. 274. Aluminium-silicon-oxygen framework in crystal structure of nosean.

Thus, the general features of the crystallochemistry of silicates outlined on the basis of the division of complex anions of the SiO_4 tetrahedra into 0-, 1-, 2-, and 3-dimensional radicals may be tabulated as follows. (Table 13).

Table 13

Types of Silicon-oxygen Anions on the Basis of Si:O Ratios

Si:O	Formula and type of anion	Charge of anion	Charge per 1 Si	Examples
1:4	$[SiO_4]$ tetrahedron	−4	−4	Forsterite, $Mg_2[SiO_4]$
2:7	$[Si_2O_7]$ double tetrahedron	−6	−3	Thortveitite, $Sc_2[Si_2O_7]$
1:3	$[Si_3O_9]$ ring	−6	−2	Benitoite, $BaTi[Si_3O_9]$
1:3	$[Si_6O_{18}]$ ring	−12	−2	Beryl, $Be_3Al_2[Si_6O_{18}]$
1:3	$[SiO_3]n$ chain	$-2n$	−2	Diopside, $CaMg[Si_2O_6]$
4:11	$[Si_4O_{11}]n$ band	$-6n$	−1.5	Tremolite, $Ca_2Mg_5[Si_4O_{11}]_2[OH]_2$
2:5	$[Si_2O_5]n$ sheet	$-2n$	−1	Talc, $Mg_3[Si_2O_5]_2[OH]_2$
1:2	$[(Al_xSi_{n-x})O_{2n}]$ framework	$-x$	−	Albite, $Na[Si_3AlO_8]$

4. One of the principal and most remarkable features of the constitution of many silicates is the role of the Al ions in their crystal structures.

Before the advent of X-ray methods, some authorities maintained that the Al ions, by analogy with Mg, K, Na, and other metals, played the role of bases in the silicates, whereas V. I. Vernadsky argued that the Al of the silicates entered into the composition of the acid radicals along with Si and, therefore, he deduced numerous alumosilicic acids, their anhydrides and salts (alumosilicates).

The problem was solved by means of X-ray examination of the crystal structures of the silicates. It has been demonstrated that *alumosilicates* do exist among the silicates. In many cases, however, the existence of silicates of aluminium was also established in a large number of cases, often together with other metals.

Thus, Al^{3+} plays a dual role in the constitution of the silicates, i.e., either as a constituent of the anionic radicals, surrounded, like Si^{4+}, by four oxygen ions; or as an independent cation which, alone or

together with other metal cations, neutralises the negative anionic charge, and is surrounded, like Mg^{2+}, by six oxygen or hydroxyl ions. In quite a few cases, in one and the same silicate some Al ions occur in the anionic radical and some in the cations which occupy the spaces between the negatively charged radicals.

In the light of these discoveries, many hitherto puzzling aspects of the problem have found a rational explanation on the basis of most precise physical data, in full conformity with the properties of the minerals. We shall repeatedly turn to this problem in the description of individual groups of silicates.

Thus in the alumosilicates the oxygen ions around Al^{3+} have the same fourfold coordination as around Si^{4+}. The possibility of the silicon-oxygen tetrahedra being replaced by alumooxygen tetrahedra may be inferred on a purely geometrical basis: the ratio of the O^{2-} and Al^{3+} ionic radii is 0.43, i.e., comes close to the boundary between the possible fourfold coordination as for Si^{4+}, and sixfold coordination as for Mg^{2+}. However, the replacement of Si^{4+} by Al^{3+} is fraught with important consequences that essentially affect the constitution of alumosilicates.

Indeed, whereas the SiO_4 silicon-oxygen tetrahedron has four unsaturated valences, the AlO_4 alumooxygen tetrahedron has five $(8-3=5)$. Hence, each alumooxygen tetrahedron in the complex anionic radical increases its negative charge by a unit which has to be balanced by some positively charged cation in accordance with the stereometric structure of the given compound. This can be easily demonstrated on the example of compounds possessing crystal structures of the framework type.

Quartz,	Si_4O_8
Albite,	$Na[Si_3AlO_8]$
Nepheline,	$Na_2[Si_2Al_2O_8]$
Anorthite,	$Ca[Si_2Al_2O_8]$, etc.

The Si : Al ratio need not to be an integer, but the equilibrium of negative and positive charges is absolutely essential for the stability of a crystal structure. This is why the data of chemical analyses of the alumosilicates do not always simply correspond to the chemical formula of the mineral analysed. For instance, the general formula of hornblende is written as:

$$(Ca, Na)_{2-3}(Mg,Al)_5[(Si,Al)_4O_{11}]_2[O,OH]_2$$

where the Al : Si ratio in the radical may vary from 1 : 3 to 0.

It should be noted that the formation of the AlO_4 group is possible under certain definite conditions. Frameworks composed of tetrahedral AlO_4 and SiO_4 groups may be formed when the lattice structure contains relatively large cations with a low charge (Na^{1+}, K^{1+}, Ca^{2+}, Ba^{2+}, etc.). Such are the numerous members of the groups of feldspars

and zeolites. Characteristically, when alkaline and alkaline-earth metals are leached, the AlO_4 groups collapse, and in the kaolinite, which results from the decomposition of feldspars, Al^{3+} is already in *sixfold* coordination. The same is true of other types of crystal structure whose anionic radicals include an AlO_4 component.

In an alumina-rich environment, AlO_4 groups are formed at high temperatures. It has been shown experimentally that such minerals as kaolinite and disthene, all of whose Al^{3+} is always in sixfold coordination, partly alter under such conditions (1400 to 1500°) to sillimanite or mullite, i.e., to silicates which also contain AlO_4 groups with fourfold coordination. It should be noted that their heating curves show pronounced exothermal effects, fully conforming to the point of rearrangement of the crystal structure.

In this connection, mention should be made of the so-called kaolin nucleus. Observing the natural breakdown of minerals and studying experimental research data, V. I. Vernadsky came to the conclusion that alumosilicates, feldspars in particular, should contain a specific $Al_2Si_2O_7$ nucleus, highly stable in natural environment. The very idea of a close tie between Al and Si in alumina-bearing silicates was of invaluable assistance in the subsequent X-ray deciphering of the extremely complex structures of the alumosilicate minerals. It has been found, however, that by far not all the alumina-bearing silicates were alumosilicates, i.e., compounds in which Al plays the same part as Si. Even the alumosilicates proper, with their continuous spatial extension of alumo-silica-oxygen radicals, strictly speaking, contain no detached or isolated groups like the hypothetical "kaolin nucleus". Kaolinite itself, a product of weathering of the alumosilicates, in effect proved to be a silicate of aluminium, not an alumosilicate or "alumosilicic acid".

5. Many silicates contain so-called additional anions: O^{2-}, $[OH]^{1-}$, F^{1-}, Cl^{1-}, $[CO_3]^{2-}$, etc., neutralising the excess positive charge of the cations. Presumably, in some cases, the $[OH]^{1-}$ and F^{1-} may replace the oxygen ions within the complex anionic radicals; usually, however, such replacement takes place when the O ions do not enter into the composition of the silicon-oxygen tetrahedra.

Finally, a number of silicates contain H_2O, mostly of zeolitic nature. The H_2O molecules are usually very weakly held in the voids or channels of crystal structures.

6. In all the silicates the number of oxygen ions exceeds that of ions of the other elements. Since the oxygen ions have considerably longer ionic radii than the cations, it is only natural that the size of unit cells depends primarily, as in other oxygen compounds, on the number of oxygen ions per cell and on their spatial positions.

Hence, silicates that are the members of the same isomorphous series should have the same number of oxygen ions.

7. Phenomena of heterovalent isomorphism along with isovalent isomorphism are widespread in the minerals of the silicate group.

A classical example of heterovalent isomorphism is the plagioclase series: $Na[Si_3AlO_8]-Ca[Si_2Al_2O_8]$. Here Na^{1+} is replaced by Ca^{2+} of about the same volume. The accompanying increase of the positive charge by a unit is balanced by a corresponding substitution in the radical: one Si^{4+} ion being replaced by an Al^{3+} ion, or one $[SiO_4]^{4-}$ anion by an $[AlO_4]^{5-}$ anion, i.e., the negative charge is also increased by a unit.

Thus, the above and many other similar instances strictly bear out the conclusion that the components of isomorphous mixtures must have: (a) the same number of oxygen ions, since the size of the unit cells changes little; and (b) the same total valence of the replaced and the replacing ions ($Na^{1+}\ Si^{4+} = Ca^{2+}\ Al^{3+}$, $Ca^{2+}\ Si^{4+} = Na^{1+}P^{5+}$, etc.), this being dictated by the requirement that the positive and negative charges in a crystall structure be equal.

As far as the quantitative ratio between the substituting and substituted ions is concerned, their numbers are, as a rule, equal too. It will be shown later, however, in descriptions of individual minerals, that there exist fully justified exceptions to this. For instance, $3Mg^{2+}$ are replaced by $2Al^{3+}$, $3Fe^{2+}$ by $2Fe^{3+}$, etc., the total cationic valence remaining the same (there are no changes whatever in the anionic radical). It should be emphasised that such substitution is confined to definite types of crystal structure, the most favourable conditions being found in the sheet structures.

As in other classes, among the silicates there are instances of restricted miscibility of mineral species, as well as phenomena of disintegration of solid solutions.

The restricted miscibility of isostructural, or structurally similar, compounds is due to the considerable difference in size of the substituting and substituted ions. Thus, the silicates of Ca and Mg, which are of the same type, have long been known to yield binary compounds (monticellite, diopside, etc.) which have restricted miscibility with their components (end members of the series), and even that at high temperatures only.

Only between $Mg_2[SiO_3]_2$ and $MgCa[SiO_3]_2$ (clinoenstatite—diopside) there exist continuous isomorphous mixtures formed in natural conditions at high temperatures.

8. Highly important structural characteristics of the silicates are the coordination numbers, since they control isomorphous substitutions. Some of the cations have two or even three coordination numbers. Listed below are the elements commonly occurring in the silicates, and their coordination numbers established for crystal structures that have been studied to-date:

B — 4	Al — 4, (5), and 6	$Mn^{\cdot\cdot}$ — 6 and 8	Ti — 6	
Si — 4	$Fe^{\cdots}$ — 4 and 6	Na — 6 and 8	Zr — 6 and 8	
Be — 4	Mg — 6 and 8	Ca — 6, 7 and 8	K — 6 and 10	
Zn — 4	$Fe^{\cdot\cdot}$ — 6 and 8	Li — 6	Ba — 12	

Coordination numbers, as it is to be expected, increase with the growth of the ionic radii. It is also seen from the above list that Ti^{4+} and Zr^{4+} are never surrounded by four oxygen ions, and hence cannot replace Si^{4+} in the silicon-oxygen tetrahedra. Therefore the former concepts of "titanosilicates" and "zirconosilicates" had to be discarded as erroneous. These elements participate in mineral structures as common cations, occurring in the lattices between the anionic radicals. It has been demonstrated, however, that Ti^{4+} could replace Si^{4+} to a considerable degree in pyroxenes, but only at relatively high temperatures.

As for Fe^{3+}, this element in a number of cases enters into the complex anion as a substitute for Si^{4+}, similarly to Al^{3+}, and with exactly the same effects. Such substitution has been proved for a number of strongly ferruginous silicates.

Classification of silicates. At present, with the great progress in X-ray methods of investigation of minerals, the silicates naturally must be classified not only on the basis of their chemical composition, but also according to the types of crystal structures.

Different methods of linkage of the silicon-oxygen tetrahedra leave a direct impress both on the chemical formulas of the minerals and on the morphological features of the crystals, as well as on their physical properties (refractive index, birefringence, specific gravity, and so forth).

The types of structures may be classified in different orders. Some authors classify silicates in the order we have adopted in the above review: starting with structures with independent silicon-oxygen tetrahedra and ending with continuous three-dimensional framework. Others adopt the reverse order, beginning with quartz which has a typical framework crystal structure.

We shall adhere to the former classification, i.e., start with those groups of silicates which correspond to typical salts and are the simplest and closest in constitution to the minerals reviewed earlier in the oxygen-salt class. As different from the latter, we shall divide the class of silicates into subclasses, as follows:

Subclass A. Silicates with isolated SiO_4 tetrahedra in crystal structures.

Subclass B. Silicates with isolated groups of SiO_4 tetrahedra in crystal structures.
- Type 1. With isolated Si_2O_7 groups.
- Type 2. With Si_nO_{3n} anionic rings.

Subclass C. Silicates with continuous chains of SiO_4 tetrahedra in crystal structures.
- Type 1. With single chains.
- Type 2. With double chains.

Subclass D. Silicates with continuous sheets of SiO_4 tetrahedra in crystal structures.

Subclass E. Silicates with continuous three-dimensional frameworks of $(Si, Al)O_4$ tetrahedra in crystal structures.

SILICATES WITH ISOLATED SiO_4 TETRAHEDRA IN CRYSTAL STRUCTURES

The salient feature of crystal structures of the silicates in this subclass is the occurrence of their unit cells as detached tetrahedral $[SiO_4]^{4-}$ anions. As has been stated in the introduction, these tetrahedra stand isolated in the crystal structure, i.e., none of the oxygen ions surrounding the Si ion are shared by the adjacent silicon-oxygen tetrahedra.

From the chemical standpoint, these silicates were regarded as orthosilicates, i.e., as salts of a hypothetical H_4SiO_4 acid. The most important cations in the silicates of this type are Mg^{2+}, Fe^{2+}, Ca^{2+}, partly Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, and also Al^{3+}, Fe^{3+}, partly Mn^{3+}, Cr^{3+}, sometimes Pb^{2+}, Be^{2+}, Ti^{4+}, Zr^{4+}, Th^{4+}, and occasionally Nb^{5+}. Na^{1+} and K^{1+} alkalis occur as a rare exception. Rare earths may also take part in the structure of crystal lattices, along with calcium, sodium, and partly thorium. Aluminium, in distinction from the other types of silicates, is never present in crystal structure as complex anions with fourfold coordination, i.e., does not replace Si in its tetrahedral groups. Presumably phosphorus alone is capable of replacing silicon ions (see "Apatite group").

The physical properties of silicates of this type are rather peculiar and are determined by the specific features of the compact crystal lattices. Crystal forms are usually isometric. The minerals possess high hardness and relatively high specific gravity, owing to the close packing of ions. This also explains their relatively high refractive indices. Intense colouring is characteristic only of the varieties containing chromophores.

1. ZIRCON GROUP

Included in this group are the orthosilicates of tetravalent Zr and Th, crystallising in the tetragonal system.

ZIRCON, $ZrSiO_4$. From corrupted Persian "tsar" meaning gold and "gun" colour. Synonym: hyacinth. Often present as an accessory mineral (in minor quantities) in acid and alkaline igneous rocks (granites, syenites, and nepheline-syenites).

Chemical composition. According to formula: ZrO_2 67.1%; (Zr 49.5%), SiO_2 32.9%. Practically always has a slight admixture of Fe_2O_3 (up to 0.35% and more), often CaO (0.05 to 4%), and sometimes Al_2O_3. Always contains hafnium oxide (sometimes up to 4% of HfO_2) and in *alvite* from Kragerö (Norway) even 16%. May contain Y_2O_3 and rare earths, chiefly Ce_2O_3 (hagatalite) sometimes up to 16% with P_2O_5 content of 4 to 5% (amagutilite). Certain varieties may contain Nb and Ta (naegite), ThO_2, up to 7% and even 12% (högtveitite), and also U_3O_8, up to 1.5% and more. Occasionally contains negligible Sn and Be (in alvite, the content of $BeO + Al_2O_3$ may reach 15%), etc.

Finally, varieties are known containing much P_2O_5 (oyamalite). *Malacons* and cyrtolites* rich in radioactive substances and hence metamict contain considerable H_2O (2 to 12%).

System, tetragonal; symmetry, ditetragonal dipyramidal $L^4 4L^2 5PC$. Space group $I4/amd(D_{4h}^{19})$. $a_0 = 6.58$; $c_0 = 5.93$. Mostly in crystals, more seldom in irregular grains. **Crystal structure.** X-ray investigation shows a typical radical-ionic structure comprised of anionic SiO_4 groups and Zr^{4+} cations surrounded by eight oxygen ions (Fig.275). The SiO_4 tetrahedra alternate parallel to L^4 with the Zr ions. Thus, zircon sharply differs in structure from rutile whose crystals externally

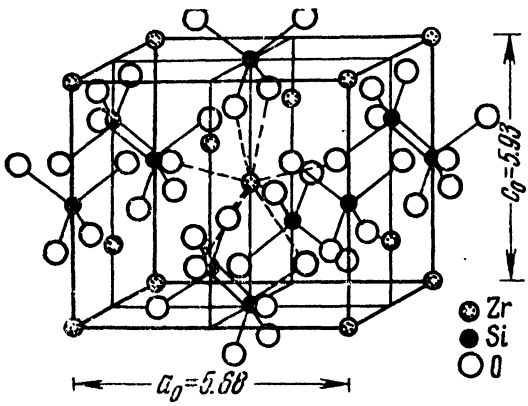


Fig. 275. Crystal structure of zircon. Centre—eight linkages between Zr^{4+} ion and oxygen ions of $[SiO_4]^{4-}$ groups.

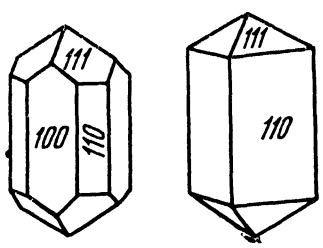


Fig. 276. Most common zircon crystals.

resemble very closely those of zircon, but whose structure is analogous to that of anhydride, $Ca[SO_4]$. **Habit**, short-columnar, isometric, less often dipyramidal. Common forms: tetragonal prisms {100} and {110} and a tetragonal dipyramid {111} (Fig. 276). Twins are geniculate, like those of rutile, but occur far less often.

Colour. Colourless, but mostly yellow, orange, red, and less often green. **Lustre**, adamantine, sometimes greasy. Malacons are usually dark brown. $n_x = 1.968$ to 2.015 and $n_y = 1.923$ to 1.960.

Hardness, 7 to 8. For varieties that underwent metamict decay it diminishes to 6; moreover, they are remarkably tenacious while common zircons are brittle. **Cleavage**, relatively rare parallel to {110}. Fracture uneven; for altered varieties, conchoidal. **Specific gravity**, 4.68 to 4.70; for altered varieties such as cyrtolites declines to 4.7 and even 3.8 (alteration causes increase of volume and slight distortion of the external crystal form). **Other properties.** Malacons and cyrtolites are, as a rule, radioactive.

Diagnostic features. Zircon crystals have characteristic tetragonal short-columnar and less often dipyramidal habit. May be mistaken for: (1) rutile (distinguished by hardness and refractive indices), (2) cassiterite (distinguished by specific gravity, paragenesis, chemical reactions, and lower birefringence under the microscope), (3) thorite

* From the Greek "cyrtos" meaning curved, convex (reference to curved crystal faces).

(distinguished by hardness, chemical reactions, and much higher birefringence), and (4) monazite which occurs in analogous conditions (distinguished by hardness and by habit, monazite usually being tabular).

Infusible before the blowpipe. Insoluble in acids. Decomposes when fused in a powdered state with soda; the flux, when dissolved in dilute HCl, colours the lithmus paper orange (reaction for Zr).

Genesis and occurrence. Zircon occurs as small, rare disseminated crystals in magmatic intrusive rocks; nepheline-syenites, granites, diorites, gneisses, but more often and in larger crystals in syenitic and granitic *pegmatites*. In metamorphosed sedimentary rocks (crystalline schists and paragneisses) it is found as rounded relict grains.

Because of the idiomorphism of zircon crystals with regard to all the accompanying minerals, it is thought to be one of the first minerals to crystallise from magma. This concept does not agree, however, with a number of facts observed in nature: (1) zircon is rather often closely associated with later minerals containing volatiles (apatite, fluorite, micas, etc.); (2) according to Lacroix, in the Madagascar nephelines where its content may reach 7 per cent, zircon often occurs in cracks in partly solidified parent rock; (3) in effusive rocks (trachytes, basalts) it occurs as tiny crystals in druse-lined cavities; (4) it occurs pseudomorphous after minerals of magmatic origin such as alkaline hornblende (riebeckite), and others. The idiomorphism of zircon in many instances may be due to the fact that, despite its relatively late formation, similar to metacrystals (pyrite, magnetite, apatite, etc.), it is capable of forming perfect crystals.

As a chemically inert mineral, zircon is easily liberated from its accessories in the course of weathering and passes into placers, and hence as rounded grains, into sedimentary rocks.

Zircon predominantly occurs in miaskite and syenite pegmatites together with black mica, nepheline, albite, apatite as well as with various minerals containing TR, Nb, Ta, Th and U (pyrochlore, aschinite, samarskite, etc.). Crystals are usually not large, up to 1 cm across, though occasionally large individuals are found. The largest specimen ever found (in 1837), about 3.5 kg in weight, consisted of several individuals. A study was made of oriented intergrowths of zircon with pyrochlore along (111) planes, the face of the pyrochlore octahedron coinciding with that of the zircon tetragonal dipyramid. It transpired that the ordered nature of this intergrowth was explained by the isometricity of the [110] and [112] edges of zircon and pyrochlore respectively. It should be noted that when the intergrowths were broken, no idiomorphism was observed in minerals in relation to each other: their fractured composite planes were uneven and irregular. This suggests a simultaneous development of both.

In a number of localities, zircon is widely distributed in placers from which it is recovered by sluicing. In certain areas, the accessory zircon of granites has predominantly a barrel-shaped habit and pointed ends, is always transparent and usually colourless. The zircons of

granitoid veins are also transparent but practically always coloured pink or violet. The zircons of pegmatite dikes are usually isometric, dipyramidal prismatic in habit, and are mostly coloured various shades of intense brown.

Outside the U.S.S.R., large zircon deposits occur in southern Norway in nepheline-syenites, sometimes in enormous quantities: Hiterö, Kragerö, Telemarken, etc. Zircon also occurs in placers in Ceylon, Brazil, Australia, and Madagascar.

Uses. Transparent beautifully coloured varieties are used as gemstones. Usually the mineral is a source of ZrO_2 used because of its low heat conductivity and expansion factor in the manufacture of acid-resistant and refractory crucibles (melting point about 3000°). It is added to quartz glass (up to 2.5 per cent) for refractory and acid-resistant laboratory utensils, and is used in refractory bricks and cement for lining electrical furnaces, as well as for the manufacture of white enamels and very stable pigments.

Metallic zirconium alloyed with magnesium (40 per cent) is used in smokeless flash powders (for signalling and photography). Pure zirconium, owing to its malleability, is used as a substitute for platinum in the manufacture of scientific instruments. It can also be used in spark plugs and in thermoelements in pyrometers.

Being added in certain proportions, in the form of ferrozirconium and other alloys, to steel, copper, and brass it improves the quality of castings, increases the hardness and chemical stability of the alloys. In steel making, zirconium is the best deoxidiser. Thanks to its ability to combine with nitrogen, zirconium completely removes undesirable nitrides from steel.

Hafnium, extracted from zircon as a by-product is added in the form of oxide to alloys used for electronic tube filaments. Its high melting point and electronic-emission factor enable the use of hafnium in radio valves, coatings of X-ray cathodes, etc.

THORITE, $ThSiO_4$. Varieties: orangite (transparent orange-coloured varieties): uranothorite with 10 to 16% of UO_2; mackintoshite and thorogummite also with UO_2 but with a higher H_2O content; auerlite, a phosphorus-bearing variety rich in water. Also contains rare earths, CaO, up to 13% of Fe_2O_3 (ferrithorite), etc.

System, tetragonal. Crystals extremely rare, in habit do not differ from those of zircon (Fig. 277). Usually occurs as impregnated grains, less often massive.

Colour, black, brown, yellow, and orange. **Streak,** dark brown, light orange (for orangite). **Lustre,** vitreous, greasy. $n = 1.68$ to 1.82.

Hardness, 4.5 to 5 (lower for altered varieties). Brittle. **Cleavage,** none. Fracture, conchoidal. **Specific gravity,** 5.4 (for altered varieties 4.8 and even 4.0). All varieties are highly radioactive.

Diagnostic features. Infusible before the blowpipe. In the glass tube gives water. Dissolves in hydrochloric acid with separation of gelatin-

ous silica. On addition of oxalic acid the solution yields a precipitate, which is soluble in ammonium oxalate. With borax gives an orange bead which fades on cooling.

Genesis and occurrence. Thorite is usually formed in the latest stages of crystallisation of certain acidic and alkaline magmatic rocks. Mostly occurs in pegmatitic formations and in the aureoles of contact alteration of the host rocks penetrated by the intrusives. Occasionally

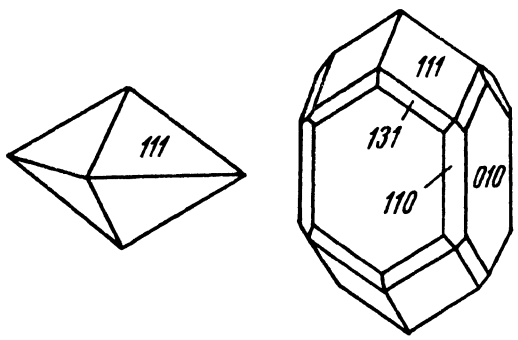


Fig. 277. Thorite crystals.

found in high-temperature hydrothermal formations. Orangite and thorite occur in a number of localities at Langesundfjord (Norway) in granites and syenites, in association with hornblende, black mica, zircon; Löven and Lanbo islands (as large black crystals), and elsewhere. In small amounts also occurs in Sweden near Lindenes, in Madagascar (ferrithorite), and elsewhere.

2. OLIVINE GROUP

This group includes silicates of $A_2^{\cdot\cdot}[SiO_4]$ type where A = Mg, Fe, Mn, Ni, Co, Zn, Ca, and Pb. All of them, except Ca and Pb, isomorphously replace one another in crystal structures. The last two elements, owing to their large ionic radii, form binary compounds.

FORSTERITE, Mg_2SiO_4. A purely magnesial member of the $MgSiO_4$-Fe_2SiO_4 isomorphous series (Fig. 278). Theoretical composition: MgO 57.1%, SiO_2 42.9%.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. **Crystal structure.** See below under "Olivine". **Habit,** isometric or slightly flattened, representing a combination of the following forms: {110}, {010}, {111}, and {001}.

Colour. Colourless; in aggregates light grey. Transparent. **Lustre,** vitreous, strong. $n_x = 1.670$, $n_y = 1.651$, and $n_z = 1.635$.

Hardness, 7. **Cleavage,** {010} distinct. **Specific gravity,** 3.217.

Diagnostic features. Positively identifiable in polished sections under the microscope, by optical constants (refractive indices, birefringence,

and the angle of optical axes). In the forsterite-fayalite isomorphous series has the lowest specific gravity.

Infusible before the blowpipe. Insoluble in hydrochloric acid. In concentrated sulphuric acid, its powder yields gelatinous SiO_2.

Genesis and occurrence. Mostly occurs in contact-metamorphic rocks (dolomites and limestones). Thus, it is found in the vicinity of

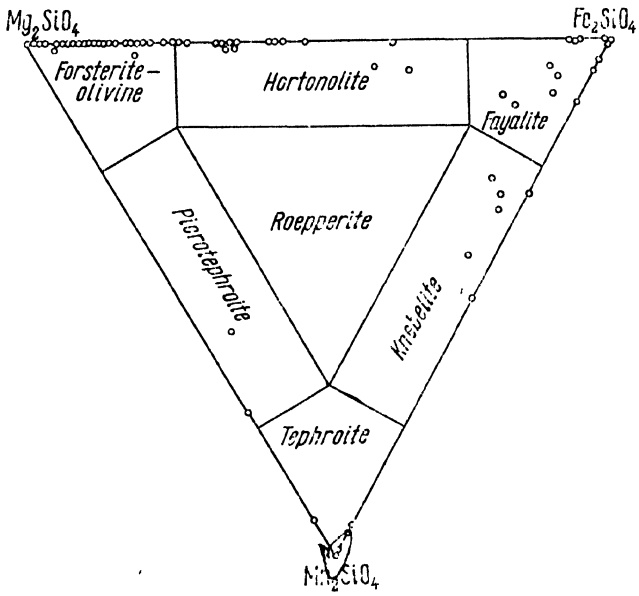


Fig. 278. Chemical composition of principal minerals of the olivine group.

Slyudyanka Station (Trans-Baikal Region) where it is associated with chondrodite and phlogopite; in the Nikolae-Maximilianovskoye mine of the Nazyam range (Zlatoust district, Southern Urals) associated with clinohumite, brucite, etc., in bluish coarse-grained marble. Instances are known of forsterite deriving from serpentinised ultrabasic rocks, e.g., at Snarum (Norway) where it is associated with magnesite, phlogopite, hematite, and spinel, probably through reworking by pneumatolytic agents in oxidising conditions. Also reported to be present together with olivine in the ancient volcanic products of Vesuvius on Monte Somma where it is accompanied by spinel and augite.

OLIVINE, $(Mg,Fe)_2SiO_4$. Named for its olive-green colour. Synonyms: chrysolite, peridot. "Chrysos" is the Greek for gold. Olivine, essentially a ferruginous variety of forsterite (Fig. 278), is very widely distributed in nature as a rock-forming mineral in ultrabasic igneous rocks.

Chemical composition, usually varies within the following limits (per cent): MgO 50 to 45; FeO 8 to 12, rarely up to 20; NiO 0.1 to 0.3; CoO up to 0.01. May contain manganese. Iron is partly present as oxides (in incompletely serpentinised olivines).

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Pbnm$ (D_{2h}^{16}). $a_0 = 4.77$; $b_0 = 10.28$; $c_0 = 6.00$. With increasing iron content, the unit cell increases in size, because the Fe^{2+} cation is larger than Mg^{2+}.

Crystal structure. The olivine structure, according to Bragg and Brown, projected on the (100) plane, is shown in Figs. 279 and 280.

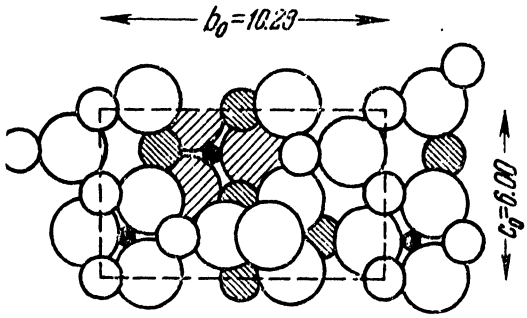


Fig. 279. Crystal structure of olivine projected on (100).

Black circles—silicon ions; large circles—oxygen ions; medium circles—magnesium ions.

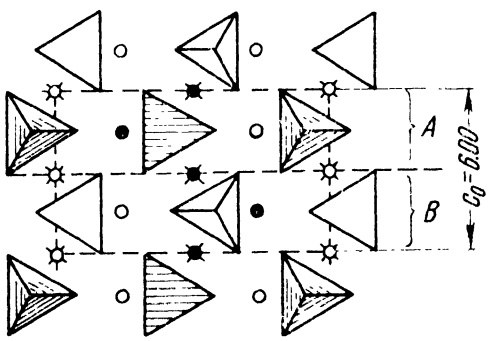


Fig. 280. Crystal structure of olivine projected on plane (diagrammatically).

The structure is composed of several sets (*A* and *B*). The tetrahedra apexes alternately point upward and downward, the different sets being arranged at different levels (the hatched tetrahedra occupy a relatively higher position). Small circles stand for magnesium ions.

Its specific features may be summarised as follows: (1) all the oxygen ions are arranged in the almost hexagonal closest packing, and within a unit cell occur in two sheets parallel to (100); one of the sheets is shown in Fig. 279 as hatchured circles; (2) each Si ion is surrounded by four oxygen ions (isolated tetrahedral groupings are outlined in Fig. 280); (3) each Mg ion is surrounded by six oxygen ions. **Habit.** Olivine commonly occurs in granular aggregates. Well-developed crystals in cavities (or ingrown in metamorphic rocks) are comparatively rare. The most common forms are (Fig. 281): {100}, {110}, {010}, {111}, {001}, etc. Twins are rare, mostly along (011).

Colour of olivine is yellow with a greenish tinge; sometimes colourless and absolutely transparent; in partly serpentinised olivine rocks (dunites) has a false green tint, which is caused by serpentine, metasomatically developing along cracks in olivine. **Lustre**, vitreous, greasy. $n_x = 1.68$, $n_y = 1.66$, and $n_z = 1.64$.

Hardness, 6.5 to 7. Brittle. **Cleavage**, {010} distinct or imperfect, more seldom along {100}. Fracture commonly conchoidal. **Specific gravity**, 3.3 to 3.5 (increases with FeO content).

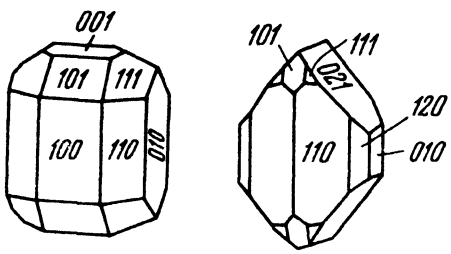


Fig. 281. Olivine crystals.

Diagnostic features. In olivine basalts, large impregnated olivine grains are identifiable visually by dark greenish-yellow colour, vitreous lustre, and uneven fracture. In intrusive olivine rocks is characteristically in paragenesis with magnesial silicates (serpentine, pyroxenes), as well as with chrome-spinellids.

Infusible before the blowpipe. Almost insoluble in hydrochloric acid. In the powdered state dissolves briskly in concentrated sulphuric acid with evolution of gelatinous SiO_2.

Genesis and occurrence. Chiefly of *magmatic* origin. In mountainous regions whole massifs are composed of igneous silica-poor olivine rocks: (1) dunite which almost entirely consists of olivine with negligible admixture of chrome-spinellids, and (2) peridotites, which besides olivine contain pyroxenes. It is true that in such rocks the olivine is mostly serpentinised (later hydrothermal alteration).

Olivine is often a constituent of such rocks as gabbro, diabase, basalt, and tuffs of basic effusives. As a rule, it is not found in quartz-bearing, i.e., silica-enriched rocks.

Fairly large crystals and rounded pebbles of transparent olivine, of a beautifully, green or yellowish-green colour (the so-called chrysolite), occur in placers in Upper Egypt (east of Esna), India, Brazil, and elsewhere.

When exposed to weathering, the ferrous oxide of the olivine is further oxidised, and its grains become brown.

Large masses of olivine and olivine-pyroxene rocks, often strongly serpentinised, are found in the Soviet Union in the Urals, North Caucasus, Transcaucasia, and Southern Siberia. Many of them are associated with deposits of chromite and sometimes platinum (the middle and northern Urals). In the old crusts of weathering (southern and middle Urals), there have developed exogenous deposits of iron oxide ores and hydrosilicate nickel ores.

Uses. Weakly ferruginous pure olivine rocks, either unaltered or partly serpentinised, provide a high-grade material for refractory forsterite bricks. Since the bricks are fired in oxidising conditions, and all the iron separates in the form of magnetite, it is important that the ini-

tial raw material contain minimum of iron and that the $MgO : SiO_2$ ratio be close to 2 (in molecular terms). Otherwise, in the process of firing, less refractory pyroxene, a mineral richer in silica, will be formed along with forsterite. To make up for the ferrous oxide removed from the silicate portion, a corresponding amount of magnesite is added to the mix.

Transparent, beautifully coloured crystals of olivine untouched by metamorphism (chrysolites) are used as gemstones.

FAYALITE, Fe_2SiO_4. Fayal is an island of the Azores, where the mineral was discovered as inclusions in boulders on the seashore. This is the end member of the forsterite-fayalite isomorphous series and also of the tephroite-fayalite series (Fig. 278).

Chemical composition is characterised by a sharp predominance of FeO. In the purely ferruginous mineral species the FeO content is as high as 76%. The MgO content does not usually exceed several per cent. Often contains larger amounts of MnO and sometimes of ZnO. Besides FeO, may contain Fe_2O_3, probably as a product of partial oxidation.

System, orthorhombic; symmetry, rhombic dipyramidal. **Habit.** Rare crystals resemble those of olivine, sometimes are tabular and short-prismatic.

Colour, dark yellow to greenish black; oxidised varieties brownish. **Lustre**, vitreous, strong, close to adamantine. $n_x = 1.886$, $n_y = 1.877$, and $n_z = 1.835$.

Hardness, 6 to 6.5. **Cleavage**, {010} distinct, {100} imperfect. **Specific gravity**, 4.0 to 4.35.

Before the blowpipe fuses into black magnetic glass. Decomposes in hydrochloric acid with evolution of gelatinous silica.

Genesis and occurrence. Crystals occur in cavities in obsidian (volcanic glass) in the Yellowstone Park (U.S.A.), the Lipari Islands, and elsewhere. As a rare exception, fayalite (talaskite) — the poorest in silica olivine-group mineral—has been found in a vein of granitic pegmatite as large crystals, surrounded by biotite, together with microcline-pertite, albite, quartz, and other minerals on the banks of the Jashi River, a tributary of the Talas (Kirghiz ridge). Was found granular massive in the Mysovskoye deposit on the southern shore of Lake Baikal.

3. WILLEMITE GROUP

This group includes orthosilicates of Zn, and partly of Mn, crystallising in the trigonal system. We shall also review here an orthosilicate of Be known as phenacite.

WILLEMITE, Zn_2SiO_4. A relatively rare mineral, only occasionally forming considerable masses in the oxidised zones of lead-zinc deposits.

Chemical composition. ZnO 73.0%, SiO_2 27.0%. Usually contains some MnO and FeO. **System,** trigonal; symmetry, rhombohedral L_6^3C. Space group $R\bar{3}(C_{3i}^2)$. $a_0 = 12.49$; $c_0 = 8.26$. **Crystal structure,** absolutely identical with that of phenacite. The Be ions are replaced by Zn ions. **Habit.** Crystals are rare (Fig. 282) and usually bounded by prismatic $\{11\bar{2}0\}$ and rhombohedral $\{10\bar{1}1\}$ faces. Often occurs as druses of acicular crystals or radially fibrous aggregates and also as stalactitic forms in leaching cavities.

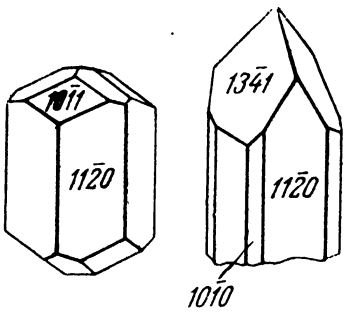


Fig. 282. Willemite crystals.

Colour. Colourless or yellowish brown, sometimes with greenish or reddish tinges (MnO admixture). **Lustre,** vitreous, greasy. $n_x = 1.719$ to 1.723, and $n_y = 1.691$ to 1.694.

Hardness, 5 to 6. Brittle. **Cleavage,** sometimes distinct parallel to {0001}. Fracture, conchoidal. **Specific gravity,** 3.89 to 4.18. Some of the varieties show green luminiscence in ultraviolet radiation.

Diagnostic features. Willemite differs from similar calamine, $(Zn_4[Si_2O_7][OH]_2 \cdot H_2O)$, occurring in identical conditions and often in similar aggregates, by optical constants, higher hardness and greater specific gravity.

Almost infusible before the blowpipe. After prolonged ignition in the reducing flame on charcoal, gives a ZnO coating, yellow when hot, white on cooling, and green when moistened with nitric cobalt solution and subsequently ignited in the oxidising flame. In the closed glass tube, in distinction from calamine, yields little or no water. The powdered mineral gelatinises with hydrochloric acid.

Genesis and occurrence. Occurs chiefly in the *oxidised zones* of lead-zinc sulphide deposits, sometimes pseudomorphous after calamine.

As an anhydrous compound it is very probably formed as a product of weathering in the conditions of hot climate.

An exceptional case of *endogenous* formation of manganous willemite has been reported in the well-known contact-metasomatic (?) deposit at Franklin, New Jersey (U.S.A.) in association with zincite, franklinite, and other zinc minerals.

So far willemite has been discovered in very few deposits (12 or 15). It has been found in quantity in the oxidised zones of lead-zinc deposits at *Broken Hill* (Northern Rhodesia), and at *Kumysh-Tag* in the Kirghiz ridge (Central Asia).

Uses. Willemite is rarely of economic importance as a zinc ore. It is also used in fluorescent screens in cathode-ray tubes and other instruments.

PHENACITE, Be_2SiO_4. "Phenacis" is the Greek for liar; its colourless varieties in fragments being almost indistinguishable from quartz. A comparatively rare mineral.

Chemical composition. BeO 45.5%, SiO_2 54.5%. Chemical analyses show the presence of negligible MgO, CaO, Al_2O_3, and Na_2O.

System, trigonal; symmetry, rhombohedral L_6^3C. Space group $R\bar{3}(C_{3i}^2)$. $a_0 = 12.43$; $b_0 = 8.22$. **Habit**, rhombohedral, short-columnar. Common forms are prism $\{11\bar{2}0\}$ with rhombohedra $\{10\bar{1}1\}$, $\{13\bar{4}1\}$, etc. (Fig. 283). Penetration twins on $\{10\bar{1}0\}$ are frequent. Usually occurs as crystals ingrown in rock, sometimes as druses in cavities.

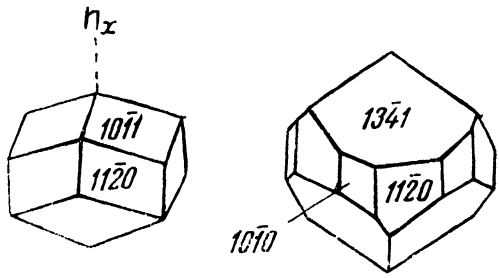


Fig. 283. Phenacite crystals.

Colour. Transparent, colourless or slightly wine-yellow, sometimes pink, rarely brown. **Lustre**, vitreous, greasy. $n_x = 1.670$ and $n_y = 1.654$.

Hardness, 7.5. **Cleavage**, $\{11\bar{2}0\}$ imperfect. Fracture, conchoidal. **Specific gravity**, 2.96 to 3.0.

Diagnostic features. Crystals are distinguished by rhombohedral or short-columnar habit from the prismatic crystals of beryl. Also differs from beryl by somewhat higher specific gravity. From chrysoberyl, on the contrary, it is distinguished by somewhat lower hardness and specific gravity, lower refractive index, and different crystal form (phenacite has no pinacoids).

Infusible before the blowpipe. Insoluble in acids. In the salt of phosphorus flux dissolves slowly, leaving a silica skeleton.

Genesis and occurrence. The occurrence and paragenesis of minerals indicate that phenacite is formed by pneumatolytic processes. Mostly occurs in *pegmatitic* formations genetically related to acidic plutonic rocks. Associates: beryl (emerald), chrysoberyl, topaz, feldspars, micas, quartz, etc.

Phenacite was discovered in the Urals early in the last century. Its crystals are often an accessory and, therefore, a guide to emeralds. They are found in mica schists, being sometimes as large as 10 cm across. Often associates with beryl being distributed in sporadic pockets. Small crystals occur in granitic pegmatites, associated with amazonite, topaz, and other minerals.

Notable foreign localities are *Kragerö*, Telemarken (Norway), where large prismatic crystals and twins have been found together with quartz and albite.

Uses. Not very important due to occurrence in small accumulations, but together with beryl may be mined as a beryl ore. Transparent beau-

tifully coloured varieties are used as gemstones. It should be noted that the colour of phenacite is extremely unstable; thus, beautifully coloured specimens, when freshly mined, are in a few months completely discoloured on exposure to sunlight.

4. TOPAZ GROUP

Topaz is the sole representative of the transitional crystal structure between the hexagonal type of closest packing (olivine) and cubic type (disthene). Its structure is characterised by the quadruple-layer closest packing, (according to the classification suggested by N.V. Belov).

TOPAZ, $Al_2[SiO_4][F, OH]_2$. The name comes from Topazos Island in the Red Sea.

Chemical composition. Al_2O_3 62.0 to 48.2%, SiO_2 39 to 28.2%, F 13 to 20.4%, H_2O up to 2.45%. For topaz containing no OH it is (per cent): Al_2O_3 55.4, SiO_2 32.6, F 20.7; the total being 108.7 and, on subtracting $O(=F_2)$ 8.7 the total will be 100%. The F : OH ratio in topazes richest in OH is usually about 3 : 1. Often contains gas and liquid inclusions.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Pbnm$ (D_{2h}^{16}). $a_0 = 4.641$, $b_0 = 8.783$; $c_0 = 8.378$. **Habit.** In well-formed crystals occurs exclusively in cavities. The crystals are usually characterised by variety and perfection of faces and sometimes huge dimensions (up to 25 to 32 kg in weight). Most common forms are prisms {110}, {120}, {021}, {041}; pinacoids {001}; dipyramids {111}, {223}, etc. (Fig. 284).

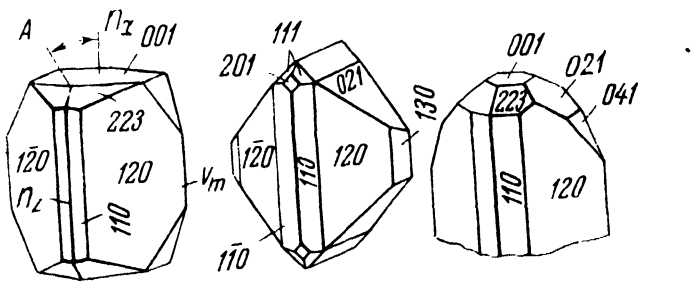


Fig. 284. Topaz crystals.

Colour. Colourless, water-transparent varieties are comparatively rare. Mostly coloured light yellow, wine-yellow, straw-yellow, blue, violet, green, pink, and rarely red. On prolonged exposure to sunlight the colouring often fades. **Lustre,** vitreous. $n_x = 1.618$ to 1.638, $n_y = 1.610$ to 1.631, and $n_z = 1.607$ to 1.629.

Hardness, 8. **Cleavage,** {001} perfect. Fracture, not parallel to cleavage, conchoidal. **Specific gravity,** 3.52 to 3.57.

Diagnostic features. Rather easily identifiable by crystal habit, differing from similar minerals by high hardness. Occurs in compact

granular masses similar to quartz, from which it differs by cleavage and greater hardness.

Infusible before the blowpipe, but on thorough ignition becomes turbid. Only turbid or opaque varieties carrying abundant occlusions of gas and liquid swell upon heating. In the closed tube gives the reaction for F with salt of phosphorus. Powdered ignited topaz on moistening with nitric cobalt and subsequent thorough ignition turns blue (Al reaction). With salt of phosphorus decomposes leaving a SiO_2 skeleton.

Genesis and occurrence. Occurs in miarolitic cavities, chiefly in acidic igneous rocks, such as granites and rhyolites, particularly in *pegmatite* dikes. As tiny inclusions, it is found in contact aureoles round intrusive masses, rarely in the wall rocks of ore deposits. Often associates with fluorite, tourmaline, smoky quartz, beryl, cassiterite, feldspars, and, in *greisens*, with such minerals as micas, cassiterite, wolframite, sulphides, etc. May be pseudomorphous after feldspars, quartz, etc. Subsequent hydrothermal processes may alter topaz to thin-scaly aggregates of muscovite.

Also occurs in *hydrothermal* veins in schists, gneisses, and other rocks. It should be noted that topazes of hydrothermal origin are richer in hydroxyl, which replaces fluorine. Crystals have a long-prismatic habit and are often pink.

On weathering topaz is almost impervious to chemical alteration and therefore is found in well-preserved crystals together with quartz and beryl, among minerals completely decomposed and altered to argillaceous products. This also explains why it passes into placers as rounded pebbles (near the primary deposits).

In the U.S.S.R., topazes mostly occur in pegmatite dikes associated with granite intrusives in the Urals, Volhynia, eastern and northeastern Siberia.

In the Urals, the mines *Murzinka*, *Alabashka*, *Yuzhakova*, etc., were once famed for excellent crystal druses of orthoclase, morion, smoky rock crystal, bluish and light-blue topaz, lepidolite, albite, and other semi-precious stones found in miarolitic cavities in pegmatite dikes.

In the 18th century and early in the 19th century several mines were started in the *Ilmen mountains* (Southern Urals) in the pegmatite dikes of a granite-gneiss band for the recovery of topaz crystals that were then considered the best.

In the basins of the *Kamenka* and *Sanarka* rivers (Kochkar district, Southern Urals) topaz pebbles of pink, violet, and wine-yellow colour were extracted together with placer gold and other gemstones.

There were recently opened up pegmatite dikes *Volhynia* (the Ukraine) containing unique smoky or pale wine-yellow topazes, some as large as 12 × 12 cm in cross section.

Famous foreign localities are *Minas Geraes* and *Minas Novas* (Brazil), where the zone of weathering and placers have long since been mined for yellowish-red, wine-yellow and colourless transparent topazes.

Uses. Transparent and beautifully coloured crystals or pebbles of topaz are used as gemstones. Highly valued were yellow, bluish, pinkish, and colourless topazes from the Urals and Siberia.

ALUMINIUN SILICATES

5. DISTHENE GROUP

This group comprises three modifications of a substance of one and the same composition having the general empirical formula $Al_2O_3 \cdot SiO_2$, or Al_2SiO_5. The modifications are disthene (kyanite), andalusite, and sillimanite.

The distinguishing feature of the crystal structure of these compounds is that there are two kinds of Al ions in each lattice: half of these ions in the structure have a coordination number of 6, while the other half have different coordination numbers: 6 (disthene), 5 (andalusite), and 4 (sillimanite).

DISTHENE, $Al_2[SiO_4]O$, or $Al_2O_3 \cdot SiO_2$. In Greek "di" means dual, "sthenos"—resisting; a name derived from its variable hardness in two directions. Synonym: kyanite; "kyanos" is the Greek for dark blue.

Chemical composition. Al_2O_3 63.1%, SiO_2 36.9%. Common isomorphous admixtures: Fe_2O_3 1 to 2%, sometimes up to 7%; Cr_2O_3 up to 1.8%, and negligible amounts of CaO, MgO, FeO, TiO_2. Spectral analyses also indicate the presence of Ga, K, and other elements. Tiny inclusions of foreign minerals are commonly revealed in thin polished sections under the microscope.

System, triclinic; symmetry, pinacoidal. Space group $P1(C_1^i)$. $a_0 = 7.09$; $b_0 = 7.72$; $c_0 = 5.56$; $\alpha = 90°05'$; $\beta = 101°02'$; $\gamma = 106°44'$.

Habit. Usually long columnar crystals, parallel to the c axis, frequently flattened, bladed masses (Fig. 285). The principal forms are pinacoids {100}, {010}, and {110}. Twins are very frequent. The twinning plane is usually (100), the twinning axis being perpendicular to it. Twins are readily identifiable by re-entrant angles (Fig. 286). In some twins the individuals cross at an angle close to 60°. Stellate intergrowths of crystals have been recorded.

Colour, light blue, blue (of varying intensity), sometimes green, yellow, less often colourless, rarely black. **Lustre**, vitreous, sometimes pearly on cleavage surfaces. $n_x = 1.728$, $n_y = 1.722$, $n_z = 1.713$.

Hardness varies with direction, which is very characteristic of disthene: 4 to 5 on the face (100) parallel to the long direction; 6 across it; 7 on the faces (010) and (110). Brittle. **Cleavage**, {100} perfect, {010} less perfect, parting on {001}. **Specific gravity**, 3.56 to 3.68 (depending on the number of inclusions), much higher than that of andalusite and sillimanite, which agrees well with the closeness of ionic packing in the crystal structure.

Diagnostic features. Readily identifiable by light-blue or blue colour, nonuniform hardness, and occurrence in crystalline, mostly micaceous schists.

Infusible before the blowpipe. Insoluble in hydrochloric acid. Pre-ignited white powder turns dark blue in nitric cobalt solution after repeated strong ignition.

Genesis and occurrence. Disthene, as evident from a comparative study of its occurrences in crystalline schists, is chiefly the product of metamorphism of alumina-rich rocks under very high pressures, i.e., at a great depth in the earth's crust.

In addition to micas, disthene is frequently associated with corundum (sometimes in considerable quantities), tourmaline, rutile, staurolite, andalusite, and other minerals forming in metamorphic rocks.

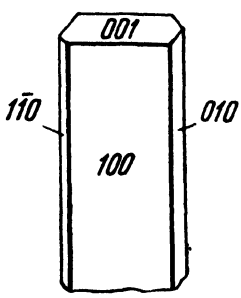


Fig. 285. Disthene crystal.

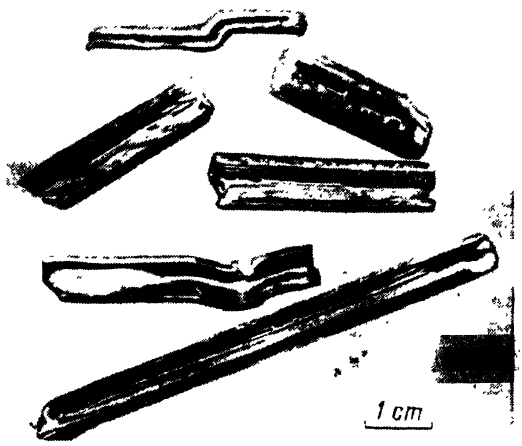


Fig. 286. Disthene twins.

Disthene crystals are frequently replaced by mica and pyrophyllite, probably through the action of silicic alkaline solutions. May be paramorphous after andalusite. It is noteworthy that disthene forms ordered intergrowths with staurolite.

Being chemically inert, disthene passes into placers.

A number of major deposits of disthene-bearing crystalline schists occur in the north-western part of the U.S.S.R. There are several varieties of disthene differing in colour, form and mineral associations. Light-blue disthene in large columnar crystals (up to 20 to 30 cm long) occurs disseminated in disthene-staurolite schists. These rocks in places are enriched in sillimanite and cordierite.

In the U.S.S.R., well known is the *Borisovskoye* deposit (Kochkar district, Southern Urals) in mica schists (in a granite mass) intersected by veins of granite, aplite, and pegmatites. In the contact zone of the schists with granite, disthene is absent (because of high temperatures). Sometimes is found associated with tourmaline. Lenses of disthene-bearing schists gradually pass into lenses without disthene. Some placers in this locality contain up to 7 per cent of disthene, which is recovered by slucing.

Outside the Soviet Union, large deposits of solid disthene rocks occur in Northern India, particularly at *Lapsa Buru;* in North Carolina (U.S.A.) where the disthene deposits are found in a thick series of met-

amorphic rocks intruded by gabbro, diorites, granites, pegmatites, and quartz veins. The disthene is believed to have been formed by the action of the pneumatolytic agents of the magma on the host rocks.

Uses. Rocks containing disthene, andalusite and sillimanite are an important source of alumina-rich mullite for the manufacture of mullite refractories. These minerals when subjected to high-temperature roasting will decompose yielding mullite ($Al_6Si_2O_{13}$) with a felted structure and cristobalite glass. Mullite is mechanically strong, highly refractory, and highly resistive to acids, including hydrofluoric acid, and alkalis. Hence the uses of disthene, andalusite, and sillimanite rocks and their concentrates in the production of high-quality porcelain-like refractory and acid-resistant articles, which are vastly superior to quartz and other refractories; and also in the manufacture of special-purpose insulators, spark plugs, crucibles for steel, pyrometer tubes, etc. An iron-oxide content in excess of 2% is undesirable. Silumine, a silicon-aluminium alloy, is produced directly from the disthene minerals by an electrothermal process.

ANDALUSITE, $Al_2[SiO_4]O$. The name derives from the province of Andalusia in Spain.

Chemical composition is the same as for disthene; often contains negligible Fe_2O_3. A manganiferous variety, *viridine*, contains up to 7 per cent of Mn_2O_3.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group *Pnnm* (D_{2h}^{12}). $a_0 = 7.76$; $b_0 = 7.90$; $c_0 = 5.56$. **Habit.** Large prismatic, of almost square section, columnar. Principal forms: rhombic prisms {110}, {101}; pinacoid {001}, etc. A typical crystal is shown in Fig. 287. Carbonaceous shales and slates sometimes contain crystals with a peculiar internal structure known as *chiastolite*. The argillaceous or carbonaceous matter occluded during crystal growth is arranged along definite crystallographic directions, appearing in cross section as a black cross (Fig. 288) while longitudinal sections show lengthwise-oriented bands against a white or grey background (colours in the picture are reversed). No twins have been observed. May also occur in radiate rod-like and granular aggregates.

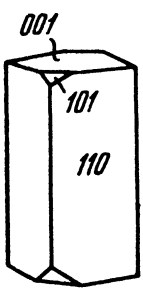


Fig. 287. Andalusite crystal.

Colour. Rarely colourless; usually grey, yellow, brown, pink, red, and dark green (manganous variety). **Lustre**, vitreous. $n_x = 1.639$ to 1.647, $n_y = 1.633$ to 1.644, and $n_z = 1.629$ to 1.640.

Hardness, 7 to 7.5. **Cleavage**, {110} distinct. Fracture, uneven and splintery. **Specific gravity**, 3.1 to 3.2.

Diagnostic features. Crystals characterised by almost rectangular prismatic forms with prismatic cleavage. Andalusite is distinguished from many other silicates of similar colour by greater hardness, and also by optical constants under the microscope.

Infusible before the blowpipe. At temperatures over 1380° decomposes forming mullite. Insoluble in acids. With nitric cobalt gives the aluminium reaction.

Genesis and occurrence. Often occurs as a contact-metamorphic mineral in shales and slates, and also in altered effusive rocks, especially in genetic association with granite intrusives. Less often occurs in gneisses and mica schists associated with garnet, corundum, disthene, etc.

In Soviet Kazakhstan, there are widespread numerous andalusite-bearing "secondary quartzites" formed through contact-pneumatolytic metamorphism of acidic effusive rocks. The largest deposit is *Semiz-Bugu* (145 km east of Nurinsk station of the Omsk railway).

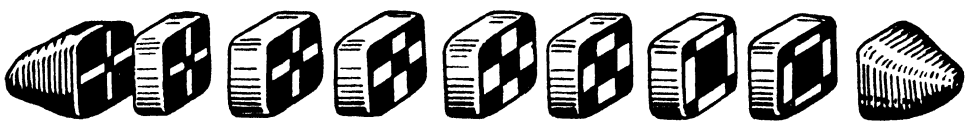


Fig. 288. Cross sections of chiastolite.

The central parts of the deposit are composed of pure corundum and muscovite-corundum masses, grading over towards the periphery into andalusite rock with rutile, muscovite, diaspore, pyrophyllite, and topaz which, in turn, grade over into andalusite-bearing quartzites. In the vicinity of the corundum bodies, the andalusite content is 90 to 95 per cent, while in the quartzites it is as low as 18 per cent.

Mineralogically important red-brown chiastolite has been recorded from mica schists in the area of the Aleksandrovsk deposit, near Mankovo village (Nerchinsk district, Trans-Baikal province), and yellow-grey chiastolite from the shores of the Argun River. Excellent chiastolite crystals are found at Mount Howden (southern Australia).

A huge andalusite deposit is known at White Mountain (California). There a rock, very rich (85%) in andalusite, occurs as lenses and pockets in andalusite-bearing quartzites and quartz-sericite-tourmaline schists. The andalusite is believed to have derived from effusive porphyrys reworked by granitic magmas.

For uses see "Disthene".

SILLIMANITE, $Al[AlSiO_5]$. **Chemical composition,** the same as for disthene. Usually contains up to 2-3 per cent of Fe_2O_3.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Pbnm(D_{2h}^{16})$. $a_0 = 7.43$; $b_0 = 7.58$; $c_0 = 5.74$. **Crystal structure,** according to N. V. Belov, is characterised by the fact that the anionic $[AlSiO_5]$ complex constitutes a ribbon comprised of two rows of tetrahedra whose apexes are joined at an angle of 180°, the apexes being shared by each pair of $(Al, Si)O_4$ tetrahedra. **Habit,** acicular, not terminated by faces. The prism faces of the [001] zone are strongly striated. Occurs in compact radial masses, fibrous aggregates,

and in microscopic capillary, often bent inclusions in other minerals, such as quartz and feldspars.

Colour, grey, light brown, pale green. **Lustre**, vitreous. $n_x = 1.677$, $n_y = 1.658$, and $n_z = 1.657$.

Hardness, 7. **Cleavage**, along the {010} pinacoid perfect. **Specific gravity**, 3.23 to 3.25.

Diagnostic features. Sillimanite is characterised by acicular, rod-like and capillary crystal forms. Distinguished from its associate andalusite by optical constants.

Infusible before the blowpipe. At about 1545°C decomposes to mullite. Insoluble in acids. Gives the aluminium reaction.

Genesis and occurrence. As a high-temperature contact-metamorphic mineral, sillimanite often occurs directly at the contact with igneous rocks, or even in igneous rocks themselves as a product of reaction with clastic alumina-rich rocks entrapped in the process of intrusion. Also occurs in crystalline schists as an earlier mineral, sometimes with andalusite, spinel, cordierite, corundum, etc.

Large deposits of massive sillimanite (up to 85%) occur in the form of lenses and pockets in crystalline schists at *Khazi Hills* and *Pipra* (India). They were formed through the action on the schists of pneumatolytic agents, genetically associated with the intrusion of tourmaline-muscovite granite.

For uses see "Disthene".

6. STAUROLITE GROUP

Of the minerals of this group, only staurolite has been studied in detail. In properties and mode of occurrence it closely resembles the minerals of the preceding group.

STAUROLITE, $Fe^{\cdot\cdot}Al_4[SiO_4]_2O_2[OH]_2$ or $Fe[OH]_2 \cdot 2Al_2SiO_5$. Named after its commonly occurring cruciform twins: "stauros" is the Greek for cross.

Chemical composition. FeO 15.8%, Al_2O_3 55.9%, SiO_2 26.3%, H_2O 2.0%. $Fe^{\cdot\cdot}$ is replaced by $Mn^{\cdot\cdot}$, sometimes to a considerable degree.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Ccmm(D_{2h}^{19})$. $a_0 = 7.81$; $b_0 = 16.59$; $c_0 = 5.64$. **Habit.** Crystals are usually in the form of short and thick prisms. Most common forms: prisms {110}, sometimes {101}; pinacoids {001} and {010} (Fig. 289). Very characteristic twins (Fig. 289), twin plane (032) giving a rectangular cross and twin plane (232) giving an oblique cross. Rarely occurs in irregular grains.

Colour, red-brown to brownish black. Seldom transparent. **Lustre**, vitreous. $n_x = 1.746$, $n_y = 1.741$, and $n_z = 1.736$.

Hardness, 7 to 7.5. **Cleavage**, {010} distinct. Fracture, uneven. **Specific gravity**, 3.65 to 3.77 (varies depending upon foreign inclusions).

Diagnostic features. Readily identifiable by colour and crystal form, especially in twins.

Infusible before the blowpipe, except for manganese-rich varieties which easily fuse into black magnetic glass. Insoluble in acids. Only sulphuric acid partly decomposes it.

Genesis and occurrence. As a relatively high-temperature mineral, staurolite occurs characteristically in crystalline schists derived from

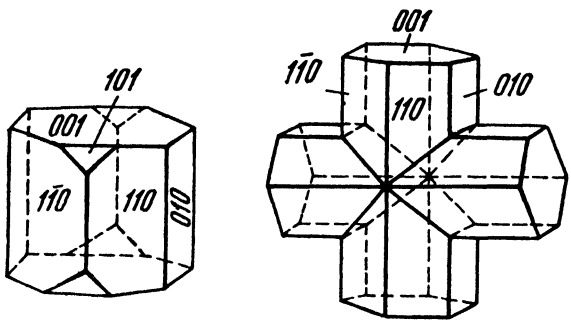


Fig. 289. Staurolite crystal and twin on (032).

regional, less often from contact metamorphism. Frequently found in rocks rich in silica and iron, associated with garnets, andalusite, cordierite, micas, magnetite, brookite, etc.

The mineral is rather inert chemically. Sometimes alters to green mica and chlorites, probably through the action of subsequent hydrothermal processes. Occurs in placers.

Occurrences of staurolite are too numerous to be listed. In the U.S.S.R., it is found in the schists of Mount Taganai (Southern Urals), in placers along the *Sanarka* and *Kamenka* rivers (Kochkar district), and in disthene-muscovite-staurolite schists in the north-western part of the U.S.S.R., in the vicinity of Lake Baikal, and elsewhere.

Staurolite has no economic importance.

7. GARNET GROUP

The group comprises numerous minerals with a general formula $A_3B_2[SiO_4]_3$ where A may be Mg, $Fe^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, or Ca, and B may be Al, $Fe^{\cdot\cdot\cdot}$, or Cr. Especially numerous among them are the mineral species of two isomorphous series:

Almandite series, $(Mg, Fe, Mn)_3Al_2[SiO_4]_3$
Pyrope ..... $Mg_3Al_2[SiO_4]_3$
Almandite ..... $Fe_3Al_2[SiO_4]_3$
Spessartite..... $Mn_3Al_2[SiO_4]_3$
Andradite series, $Ca_3(Al, Fe, Cr)_2[SiO_4]_3$
Grossularite ..... $Ca_3Al_2[SiO_4]_3$
Andradite ..... $Ca_3Fe_2[SiO_4]_3$
Uvarovite ..... $Ca_3Cr_2[SiO_4]_3$

Since all of them crystallise in the same system and have many properties in common we shall describe them together.

GARNETS (for formulas see above). From corrupted "granatus", which is the Latin for grain-like. Named because of similarity in colour of the first studied garnet crystals to the pulp enveloping pomegranate seeds. The names of the individual members of the group have different origin.

Pyrope, comes from the Greek "pyropos", fire-like. Named for its dark-red colour.

Almandite, named after the place Alabanda once famed for its stone-cutters; Pliny called it "venisa alabandine".

Spessartite, named after the locality Spessart in Bavaria.

Grossularite, the name of the pale-green variety (after the botanical name for gooseberry) discovered by Academician Laxman along the Vilui river (Eastern Siberia) in 1790.

Essonite, brown ferruginous grossularite from Ceylon.

Andradite, named after the Portuguese mineralogist d'Andrada who described manganous-ferruginous garnet in 1800. *Demantoid*, a transparent green variety of andradite found in placers of the Bobrovka river (the Urals).

Uvarovite, named after Minister Uvarov; discovered in the Urals and analysed by Academician Hess in 1832.

Schorlomite, a titanium-rich andradite variety.

Chemical composition. The theoretical composition of the principal mineral species is given below in Table 14.

Table 14

Chemical Composition of Garnets

(per cent by weight)

Mineral	MgO	FeO	MnO	CaO	Al_2O_3	Fe_2O_3	Cr_2O_3	SiO_2
Pyrope	29.8	—	—	—	25.4	—	—	44.8
Almandite	—	43.3	—	—	20.5	—	—	36.2
Spessartite	—	—	43.0	—	20.6	—	—	36.4
Grossularite	—	—	—	37.3	22.7	—	—	40.0
Andradite	—	—	—	33.0	—	31.5	—	36.5
Uvarovite	—	—	—	33.5	—	—	30.6	35.9

Mg and $Fe^{\cdot\cdot}$ and also $Fe^{\cdot\cdot}$ and $Mn^{\cdot\cdot}$ in this group freely substitute each other virtually in any ratio, but the magnesian-manganous garnet is rare. As for the trivalent elements, they widely substitute each other, though chrome-bearing garnets occur very seldom.

Negligible quantities of K_2O, Na_2O as well as P_2O_5, V_2O_5, ZrO_2, BeO, etc., are sometimes present as impurities.

System, cubic; symmetry, hexoctahedral $3L^44L_6^36L^29PC$. Space group $Ia3d(O_h^{10})$. $a_0 = 11.51$ for almandite; 11.59 for grossularite; 11.83 for andradite. Crystals are generally very characteristic of all garnets. **Habit.** The most common form is rhombic dodecahedron {110} (Fig. 290), less often in combination with a tetragon-trioctahedron

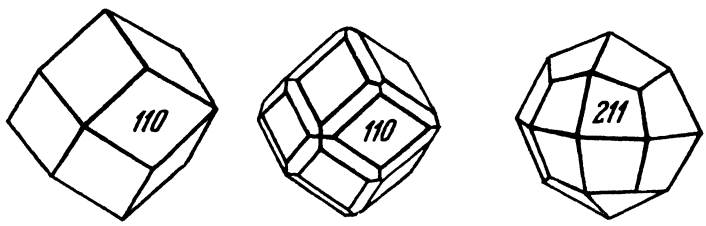


Fig. 290. Garnet crystals (most common).

{211}. The latter form may also occur independently, the crystal faces being striated parallel to the longer diagonal. Cubic and octahedral faces extremely rare. Penetration twins along (210) are also very rare. Often in massive granular aggregates.

Colour varies very widely. Colourless transparent varieties are rare. The most common colours of the individual minerals are given in Table 15. Blue garnets do not occur.

Table 15

Physical Properties of Garnets

Mineral and composition	Sp. gr.	Colour	n
Pyrope, $Mg_3Al_2[SiO_4]_3$	3.51	Dark red, pink-red, black	1.705
Almandite, $Fe_3Al_2[SiO_4]_3$	4.25	Red, brown-red, black	1.830
Spessartite, $Mn_3Al_2[SiO_4]_3$	4.18	Dark red, orange-yellow, brown	1.800
Grossularite, $Ca_3Al_2[SiO_4]_3$	3.53	Honey-yellow, pale green, brown, red	1.735
Andradite, $Ca_3Fe_2[SiO_4]_3$	3.75	Yellow, greenish, brown-red, black	1.895
Uvarovite, $Ca_3Cr_2[SiO_4]_3$	3.52	Emerald-green	1.870
Schorlomite, $Ca_3(Al, Fe, Ti)_2[(Si, Ti)O_4]_3$	3.88	Black, brownish black	2.0

Chrome-bearing garnets are usually bright green and those, poor in chromium, red. The green colour is also characteristic of certain transparent varieties of andradite such as demantoid. Generally speaking, no strict dependence of the colouring of garnets on their composition has been established. **Lustre**, greasy, vitreous, sometimes nearly adamantine (andradite), or adamantine (schorlomite). The refractive

indices for the principal minerals are given in Table 15. They increase with increasing FeO, Fe_2O_3, and TiO_2 content.

Hardness, 6.5 to 7.5. Almandite, pyrope, and spessartite are the hardest (7 to 7.5). **Cleavage,** {110} indistinct, usually none. Fracture, uneven. **Specific gravity,** 3.5 to 4.2 (see Table 15).

Diagnostic features. Garnets are readily identifiable by crystal habit, greasy lustre, high hardness, and comparatively high specific gravity.

Rather readily fusible before the blowpipe, except for chrome garnets, especially andradite and the varieties that closely resemble andradite in composition: on fusion give globules of various colours; the ferruginous varieties become magnetic. With borax and salt of phosphorus many of the minerals give characteristic reactions for Fe, Mn, and Cr. Andradite alone gelatinises with difficulty in hydrochloric acid. The other minerals decompose in acids only after fusion.

Genesis and occurrence. Most widespread are garnets of *contact-metasomatic* origin deriving from the reactions of predominantly acidic magmas with carbonate rocks (limestones and dolomites), at rather high temperatures. Garnets often occur massive (grossularite and andradite) or as constituents of skarns composed predominantly of calcareous silicates: diopside, hedenbergite, epidote, vesuvianite, sometimes wollastonite, actinolite, chlorites, helvite, etc. Andradite skarns usually accompany magnetite deposits of contact origin, such as Mount *Magnitnaya*, Mount *Vysokaya*, Mount *Blagodat* (the Urals), *Dashkesan* (Transcaucasia), etc. Deposits of scheelite may also be associated with garnet skarns.

Spessartite often occurs in pegmatites. Sometimes contains yttrium, which may be a guide to the possible occurrence of yttrium-bearing minerals such as xenotime, fergussonite, yttrialite, etc. Pyrope is found in diamond-bearing kimberlites.

Less often are deposits of garnets (mostly almandite) formed through the action of acidic magmas on basic metamorphic rocks (amphibolites, hornblende gneisses, hornblende chlorites), especially if the latter occur in igneous rocks as xenoliths.

Garnets of recent formation widely occur in mica, chlorite, talc, amphibole, and other crystalline *schists*. The composition of the garnets depends on that of the parent rocks. Metamorphism of Al- and Fe-rich rocks produces almandite; of calcareous rocks, grossularite; of magnesium-alumina rocks, pyrope, etc. Garnet crystals, which are sometimes as large as 1 cm across, often contain inclusions of foreign minerals formed in schists. The common paragenetic associates of garnets are muscovite, biotite, quartz, disthene, sillimanite, graphite, rutile, magnetite, etc. Czechoslovakia is famed for her deposits of dark-red garnet (pyrope) of gem quality.

Uvarovite and other chrome-rich garnets often occur as well-developed crystals associated with chrome-spinellids and chrome-

chlorites in cavities (mostly in fissures) in deposits of chromite and in ultrabasic igneous rocks (Saranovskoye deposit in the Urals).

In the course of weathering, the garnets as relatively inert minerals pass into placers. Ferruginous garnets, however, are decomposed by intensive weathering into brown iron ore in the form of iron hats. Manganous garnets decompose even more readily to manganese hydroxides.

Uses. Transparent, beautifully coloured garnets are used as semi-precious stones. At the present they are not much valued.

Very hard garnets (almandite, pyrope, and spessartite) make good abrasives. Large single crystals are more suitable for this purpose than those found as granular masses. About 90 per cent of garnets go into the so-called garnet paper or cloth for polishing hard wood (oak, walnut, maple, mahogany, etc.) and plate glass and for finishing leather, hard rubber, celluloid, and other articles.

Garnets are obtained from their rocks by concentration. Commercially important rocks contain over 10 per cent of well-developed crystals (over 1 cm in diameter).

8. VESUVIANITE GROUP

The name vesuvianite in point of fact covers several, as yet poorly studied, minerals of variable composition. The chemical formula has been suggested tentatively. However, according to X-ray data obtained by Warren and Model, the crystal structure of vesuvianite has much in common with that of the garnets.

VESUVIANITE, $Ca_3Al_2[SiO_4]_2[OH]_4$. The formula is approximate. The mineral was first discovered on Mount Vesuvius, but was not identified correctly. Synonym: *viluite* (after the Vilui River in Yakutia). The latter name antedates that of vesuvianite.

Chemical composition is variable. The content of individual constituents is as follows (per cent): CaO 33 to 37, Al_2O_3 13 to 16, SiO_2 35 to 39, H_2O 2 to 3. Alkalis are also present: K_2O, Na_2O, Li_2O (up to 1.5%), MgO, FeO, MnO, sometimes ZnO (up to a few per cent), SrO, Fe_2O_3 (4 to 9%), Cr_2O_3 (up to 4.3%), TiO_2 (up to 4.7%), occasionally (in beryllium vesuvianite) BeO (up to 9.2%). OH is often replaced by F (up to 2%). Practically always present is B_2O_3.

System, tetragonal; symmetry, ditetragonal dipyramidal L^44L^25PC. Space group $P4/nnc(D_{4h}^4)$. $a_0 = 15.63$; $c_0 = 11.83$. **Habit.** Characteristic crystals are prismatic (Fig. 291), less often pyramidal, usually occurring in cavities. Sometimes tabular forms occur. The most common combinations of prism faces are {110}, {100}, with dipyramid {111}, and pinacoid {001}. The prism faces commonly bear vertical broken striations, and the pinacoid faces, prominent square figures. Twins are unknown. **Aggregates.** Vesuvianite when massive is of granular or rod-like structure.

Colour, yellow, grey, green, various shades of brown, black, seldom light blue, red, and pink. Chrome-vesuvianite is intensely emerald-green. **Lustre**, vitreous, greasy. $n_y = 1.705$ to 1.732, and $n_z = 1.701$ to 1.726.

Hardness, 6.5. Brittle. **Cleavage**, {100}, {110} imperfect. Fracture, uneven or conchoidal. **Specific gravity**, 3.34 to 3.44.

Diagnostic features. Crystals are rather readily identified by their forms. When massive, is almost indistinguishable externally from the aggregates of garnet and epidote, but easily distinguished in thin polished sections under the microscope by optical constants and association with calcium-bearing minerals.

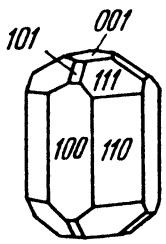
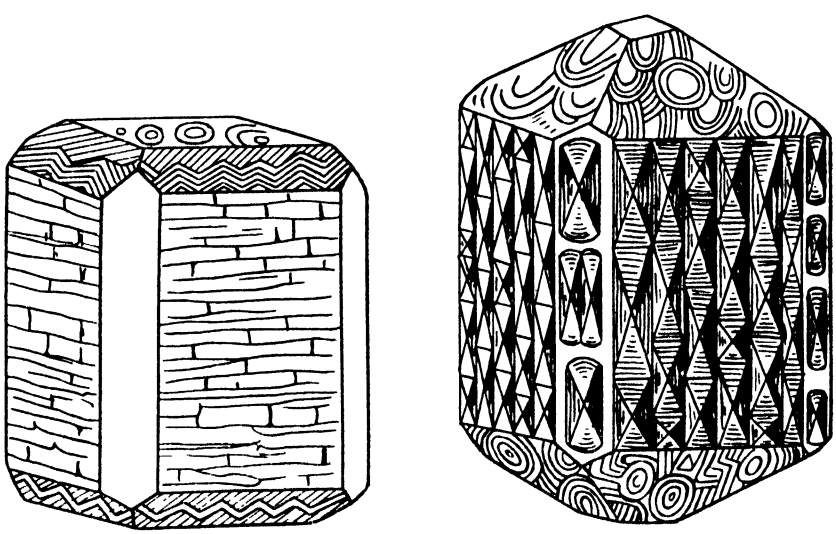


Fig. 291. Vesuvianite crystal. Vesuvius.

Before the blowpipe readily fuses with swelling due to the evolution of volatiles giving greenish or brown glass. Partly decomposes in hydrochloric acid. After preliminary ignition gelatinises completely.

Genesis. Not as common as garnets, vesuvianite is nevertheless a typical mineral of certain *contact-metasomatic* formations deriving from limestones or dolomites. Occurs in association with garnets (grossularite), diopside, epidote, calcite, chlorites, scapolites, etc.

Less often it occurs in *metamorphic* rocks: serpentinites, chlorite slates, gneisses, etc., having been formed through the action of volatile components on primary calcium-rich minerals, viz., basic feldspars, diopside, hornblendes, etc.


Fig. 292. Viluite crystals.

In the course of later hydrothermal action, vesuvianite, like garnets, is replaced by secondary minerals, such as chlorites, mica, and talc. Epidote may occur pseudomorphous after vesuvianite.

The following are the most important of the numerous vesuvianite localities. On *Vesuvius* it is found in ejectamenta in crystalline limestones associated with mica, augite, chlorite, scapolite, magnetite,

etc. In the Urals, well-developed crystals and granular masses of vesuvianite occur in chlorite schists in the *Nazyam* ridge (Zlatoust), in the *Shishim* ridge at the Akhmatovskaya, Nikolae-Maximilianovskaya and Yeremeyevskaya mines (also near Zlatoust), in the vicinity of *Medvedevka* station and *Polyakovka* village (Southern Urals) where they occur in serpentinites, and on the banks of the *Borzovka* River, Kyshtym district (Middle Urals) in the form of boulders of solid apple-green obsidian associated with corundum.

Viluite discovered by Academician Laxman in 1790 occurs on the banks of the *Vilui* River at the mouth of its tributary Akhtaragda (Yakutia) as well-developed crystals up to 2 cm long (Fig. 292), of dark-green or green-brown colour in semi-weathered metamorphosed rocks. Their crystal faces are very peculiar. Sometimes (Fig. 292, left), when the (001) face is well-developed, the prism faces are covered, as it were, with horizontally oriented plates of a brickwork pattern; in other cases they have envelope-like elevations (Fig. 292, right). The pyramidal faces bear finer and more intricate patterns.

Vesuvianite has no economic importance.

9. SPHENE GROUP

SPHENE, $CaTi[SiO_4]O$. "Sphenos" is the Greek for wedge. Named after the wedge-like crystals. Synonym: *titanite*. First described in Russia by G. Rose in the Ilmen mountains in 1842. As an accessory mineral, it occurs rather frequently in acidic and basic intrusive igneous rocks (granites, syenites, nepheline-syenites, diorites, etc.).

Chemical composition. CaO 28.6%, TiO_2 40.8%, SiO_2 30.6%. Often contains FeO (up to 6%), MnO (up to 3%), MgO, Fe_2O_3, Al_2O_3(Y, Ce)$_2O_3$ up to 12% (yttrotitanite), more seldom Cr_2O_3, ZrO_2 (up to 0.18%), Nb_2O_5, F, OH, Th, etc.

System, monoclinic; symmetry, rhombic prismatic L^2PC. Space group $C2/c(C_{2h}^6)$. $a_0 = 6.55$; $b_0 = 8.70$; $c_0 = 7.43$; $\beta = 119°43'$.

Habit. Generally occurs as disseminated crystals that present a large variety of form combinations. Most commonly in flattened envelope-like prisms of wedge-shaped cross section (Fig. 293). When the {001} faces are predominant, the crystals have a tabular form. Much more seldom, when the prismatic {110} and pinacoidal faces are best developed, prismatic crystals are formed (Fig. 294). Fairly frequent are penetration twins (100), and less often (001).

Colour, yellow, green, grey, sometimes black, pink, or red. **Lustre**, either subadamantine or adamantine, greasy. $n_x = 1.979$ to 2.054, $n_y = 1.894$ to 1.935, and $n_z = 1.888$ to 1.918.

Hardness, 5 to 6. **Cleavage**, {110} distinct or imperfect. **Specific gravity**, 3.29 to 3.56.

Diagnostic features. Sphene often occurs in characteristic wedge-shaped crystals with acute and obtuse interfacial angles, which distinguishes it from minerals of similar yellowish-brown colour.

Before the blowpipe fuses on the edges into dark glass. With salt of phosphorus in the reducing flame shows reaction for Ti (a violet bead) upon addition of tin. Decomposes partly in hydrochloric acid, and completely in sulphuric acid, forming calcium sulphate. When boiled with metallic tin in concentrated hydrochloric acid, colours the solution violet as a result of formation of $TiCl_3$.

Genesis and occurrence. In small amounts, as an accessory constituent, sphene occurs fairly often in *magmatic* rocks (granites, syenites, trachytes, andesites, etc.), associated with feldspars, nepheline, aegirine, zircon, apatite, and other minerals. Larger crystals

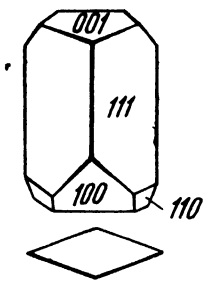


Fig. 293. Sphene crystal.

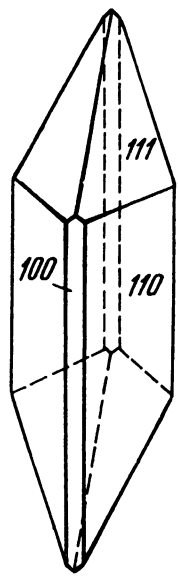


Fig. 294. Prismatic sphene crystal.

occur in *pegmatites*, mostly of the syenite type. Less often it is formed in contact-metasomatic formations, through the action of less acid magmas on limestones; also observed in paragenesis with diopside, garnet, epidote, chlorites, magnetite, etc.

Sometimes sphene is rather characteristic of certain *metamorphic* rocks (gneisses, mica and chlorite schists, amphibolites, etc.). In well-developed crystals may be found in Alpine-cleft veins with calcite, chlorite, epidote, albite, amular, etc.

Under the action of subsequent hydrothermal carbonate solutions, decomposes into calcite, quartz, and cryptocrystalline rutile or anatase; sometimes alters to brookite or perovskite. Garnet pseudomorphs after sphene have been recorded.

In zones of weathering sphene accumulates in placers, as a chemically inert mineral, though instances are known when it altered to the so-called xanthitane which appears as pale-yellow coatings or pulverulent, finely-dispersed matter, probably rutile or anatase, with hydroxides of other elements.

Occurs in apatite deposits in nepheline-apatitesphene rocks on the Kola Peninsula, as irregular grains up to 1 cm in diameter and as prismatic crystals elongated parallel to the *c* axis with the prevalent development of the prism {110} (Fig. 294). Very peculiar are

also acicular radial or fibrous aggregates tinted pink or yellow which are disseminated as more recent formations between the grains of other minerals.

In the *Ilmen mountains* (the Urals), sphene of diverse generations occurs chiefly in syenite and nepheline-syenite pegmatites in association with apatite, aegirine, magnetite, ilmenite (which it often replaces), black mica, hornblende, aegirine-augite, and other minerals. Often contains inclusions of these minerals. Is found in well-developed crystals (Fig. 295) sometimes as large as 10 to 15 cm. Some varieties contain admixtures of Sr and V.

In the *Nazyam* and *Shishim mountains*, Zlatoust district (Southern Urals) sphene is present in contact formations at the contact of gabbro and amphibolites with limestones. It also occurs as pale-yellow,

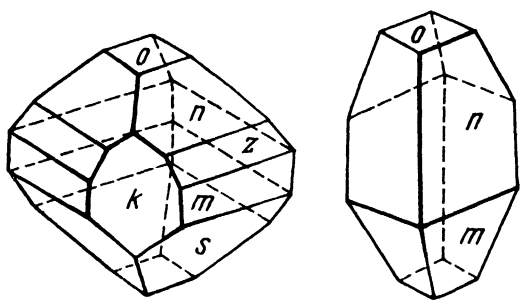


Fig. 295. Sphene crystals from the Ilmen mountains.
o {001}, *n* {111}, *m* {110}, *s* {021}, *k* {100}.

brownish-yellow, rarely as transparent colourless crystals in marbled limestones. Some crystals weigh up to 300 g (specimens in the Museum of the Mining Institute in Leningrad) both as simple and intricate combinations. Peculiar penetration twins along (100) of tabular form have been recorded. Accompanied by varying (mostly calcium- and magnesium-bearing) minerals: diopside, garnet, epidote, vesuvianite, perovskite, chlorites, apatite, calcite, spinel, forsterite, etc.

Outside the Soviet Union, occurs in Alpine-cleft veins in a number of localities in Switzerland: Saint Gotthard, Binnenthal, Zermatt, etc., where excellent multifaceted pale-green crystals have been found; also in Piedmont (Italy) as reddish or yellowish crystals, in San Marcello as manganous variety (greenovite), etc.

Uses. When found in quantity, sphene is a raw material for titanium oxide and other compounds.

10. OTHER ORTHOSILICATES

Included in this group are silicates which, though of different composition, due to a variety of causes may contain detached SiO_4 tetrahedra in the crystal lattice.

AXINITE, $Ca_2(Mn, Fe)Al_2BSi_4O_{15}$ [OH]. From the Greek "axine" for axe. Crystals are often wedge-shaped and considerably flattened, with acute dihedral angles.

Chemical composition is variable. CaO content fairly constant. Most variable are the contents of MnO (sometimes very considerable), FeO (up to 8%), and MgO. Also contains Fe_2O_3 (up to a few per cent), K_2O and Na_2O.

System, triclinic; symmetry, pinacoidal. Space group $P\bar{1}(C_i^1)$. $a_0 = 7.15$; $b_0 = 9.16$; $c_0 = 8.96$; $\alpha = 88°04'$; $\beta = 91°36'$; $\gamma = 77°42'$.

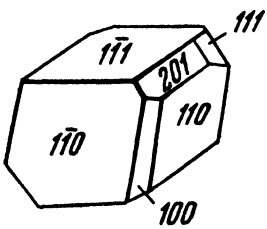


Fig. 296. Axinite crystal.

Habit. Most common forms are {1$\bar{1}$0}, {110}, {111} (Fig. 296). Crystals are generally multifaceted. The faces mentioned above usually are striated. **Aggregates.** Often in druses in cavities. Also forms veinlets and masses of foliated or platy aggregates.

Colour, brown, red, pink, violet, blue, white, grey, yellow (manganaxinite). Chlorite inclusions may give it a greenish-grey tinge. **Lustre**, vitreous.

Hardness. 6.5 to 7. **Cleavage**, {010} distinct, along other planes imperfect. **Specific gravity**, 3.25 to 3.30.

Diagnostic features. Wedge-shaped forms give it a resemblance to sphene, from which it differs by greater hardness. Axinite crystals are mostly found in cavities.

Before the blowpipe swells and fuses readily to green glass, which turns black in the reducing flame (oxidation of manganese). With soda gives the manganese reaction. When fused in a platinum wire loop with a mixture of three parts of $KHSO_4$ and one part of CaF_2, colours the flame green (boron). Insoluble in hydrochloric acid, but after ignition dissolves with separation of gelatinous silica.

Genesis and occurrence. As a hydrothermal mineral, axinite is observed sometimes in cavities in granite or diorite, in contact zones, and as a rare accessory in hydrothermal vein ore deposits. It occurs fairly frequently in metamorphic rocks as veinlets, ingrown crystals in cracks, especially in Alpine-cleft veins in alumina-enriched schists. Associates are quartz, feldspars, epidote, chlorite, amphibole-asbestos; and in ore deposits—magnetite and sulphides, (sphalerite, chalcopyrite, arsenopyrite, etc.).

Occurrences of axinite, sometimes considerable, are known in the Urals, and elsewhere in the U.S.S.R.

An important foreign locality is Bourg d'Oisans, Dauphiné (France) where large axinite crystals have been found on the walls of cracks in diorite, and axinite veins in crystalline schists in Switzerland.

DATOLITE, $Ca_2B_2[SiO_4]_2[OH]_2$. **Chemical composition.** CaO 35.0%, B_2O_3 21.8%, SiO_2 37.6%, H_2O 5.6%. **System**, monoclinic; symmetry, prismatic. Space group $P2_1/a(C_{2h}^5)$. $a_0 = 9.66$; $b_0 = 7.64$; $c_0 = 4.83$; $\beta = 90°09'$. **Habit.** Occurs in multifaceted crystals of most diverse

habit. The most common forms are {110}, {011}, and {201}. Often occurs in granular aggregates.

Colour, white, sometimes greyish, pale green, yellow, red, violet, and olive-green. **Lustre**, vitreous. $n_x = 1.670$, $n_y = 1.653$ and $n_z = 1.625$.

Hardness, 5 to 5.5. **Cleavage**, none. Fracture, conchoidal. **Specific gravity**, 2.9 to 3.0.

Diagnostic features. Vitreous lustre, conchoidal fracture, and blowpipe behaviour. Easily recognised by optical constants under the microscope.

Swells and readily fuses in the blowpipe flame giving transparent glass. Colours the flame green. Gelatinises with hydrochloric acid.

Genesis and occurrence. Occurs in ore veins, often in cavities in amygdaloidal igneous rocks associated with calcite, prehnite, zeolites, and also in skarns.

In the U.S.S.R., datolite has been recorded from the Crimea, Caucasus, Northern Urals, Far-Eastern Coast, etc.

Worth mentioning among foreign localities are those in Harz (Germany) in veins with calcite and sulphides; in native copper deposits with zeolites in the Quinnesec district in Michigan (U.S.A.), and in magnetite deposits at Arendal (Norway).

Uses. Large bodies are an economic source of boron. In contrast to many borosilicates, readily dissolves in acids. For uses of boron see "Ascharite".

RINKOLITE, $(Ca, Na, Ce)_3 (Ti, Nb) [SiO_4]_2[F, OH]_2$? Named by E. M. Bonshtedt-Kupletskaya because of its similarity in properties with rinkite.

Chemical composition (per cent): CaO 24.7-27.3, Na_2O 6.3-9.2, TiO_2 8.4-10.7, Nb_2O_5-Ta_2O_5 2.2-2.6, Ce_2O_3 5.4-8.8, La_2O_3 5.4-7.3, Y_2O_3 1.3-3.1, SiO_2 27.3-29.8, F 5.1-6, H_2O 0.5-2.4, etc.

System, monoclinic. **Habit**, prismatic. Crystals often poorly developed, elongated parallel to the *c* axis, and flattened (Fig. 297). They may be 7 to 8 cm long. Rinkolite also occurs massive in granular and sheaf-like aggregates. A glassy or cryptocrystalline variety, externally resembling jointer's glue, is known as *lovchorrite*. Lovchorrite occurs in compact masses filling spaces between other minerals.

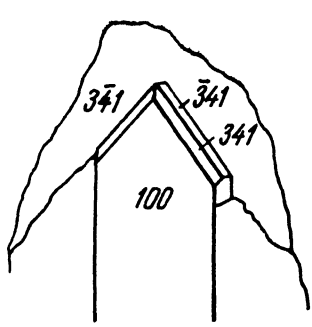


Fig. 297. Rinkolite crystal.

Colour, dark yellow, brownish yellow or greenish yellow. **Streak**, pale yellow. **Lustre**, vitreous on cleavage surfaces, and greasy or waxy on fracture surfaces (for lovchorrite). $n_x = 1.651$ to 1.681, $n_y = 1.645$ to 1.667, and $n_z = 1.643$ to 1.663.

Hardness, 5. Brittle. **Cleavage**, {100} perfect, and {010} distinct. Fracture, uneven; finely-conchoidal for lovchorrite. **Specific gravity**, 3.40, for lovchorrite 3.2 to 3.36.

Diagnostic features. Characterised by colour, poorly developed elongated crystals, sheaf-like aggregates. From rinkite differs materially in optical constants. Lovchorrite is recognised by external features.

Fuses with difficulty before the blowpipe. Soluble in acids. Amorphous lovchorrite when heated up to 750° crystallises into rinkolite. Melting point 1200 to 1400°C. Radioactive.

Genesis. Being a rare mineral of magmatic origin, rinkolite occurs mostly in pegmatites in intrusive igneous rocks abundant in alkalis, viz., nepheline-syenites and rocks of similar composition. Common associates: feldspars, nepheline, aegirine, hornblende, eudialyte, astrophyllite, etc.

On weathering rinkolite becomes dull and loose. Lovchorrite turns brown and changes to a light-coloured earthy mass; this is accompanied by leaching much of CaO, SrO, alkalis, fluorine, diminishing of the SiO_2 content and an increase in the H_2O and CO_2 content.

Uses. Rinkolite and lovchorrite are an important source of the rare earths. For uses of the latter see "Monazite".

LAMPROPHYLLITE, $Na_2SrFe^{\cdot\cdot}\ Ti_2[SiO_4]_3[F, O, OH]$? Also contains BaO (up to 2%), K_2O (up to 2.3%), MnO (up to 5.2%), F (up to 1.8%), etc.

System, orthorhombic. **Habit.** Crystals tabular parallel to (100), elongated parallel to the *c* axis (Fig. 298), often as long as 20 cm. Also occurs as rosettes of elongated crystals similar to astrophyllite and as stellate aggregates.

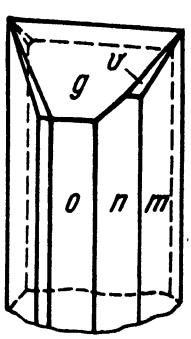


Fig. 298. Lamprophyllite crystal: *c* {100}, *n* {530}, *m* {110}, *g* {301}, *v* {851}.

Colour, golden-brown, and dark brown on cleavage surface. **Lustre**, vitreous. $n_y = 1.779$ and $n_z = 1.747$.

Hardness, 2 to 3. Brittle. **Cleavage**, {100} highly perfect; easily splits into fragile plates. **Specific gravity**, 3.44 to 3.53.

Before the blowpipe fuses readily into a dark-grey mass which, as different from astrophyllite, is nonmagnetic. Soluble in acids.

Occurrences. As an accessory mineral, occurs in nepheline-syenites, but chiefly in pegmatitic segregation. Lamprophyllite associates with aegirine, nepheline, eudialyte, etc. Being a characteristic mineral of lujaurites (alkaline rocks), it often occurs in large quantities in paragenesis with feldspar, nepheline, sodalite, aegirine, eudialyte, murmanite, etc.

ASTROPHYLLITE, $(K, Na)_2(Fe^{\cdot\cdot}, Mn)_4TiSi_4O_{14}[OH, F]_2$? The Mn-Fe ratio varies widely. Also contains ZrO_2, BaO, MgO, Al_2O_3, and Nb_2O_5.

System, triclinic. Astrophyllite is similar to lamprophyllite. Crystals rare and imperfect. **Habit**, either platy (Fig. 299) or acicular,

parallel to the *b* axis (Fig. 300). Occurs in lamellar, sometimes beautiful stellate aggregates.

Colour, bronze-brown, golden-yellow, and orange. **Lustre**, vitreous; pearly on cleavage surfaces. $n_x = 1.733$, $n_y = 1.703$, and $n_z = 1.678$.

Hardness, 3 to 3.5. Brittle. **Cleavage**, {100} perfect, and {001} indistinct. Easily splits along cleavage into fragile thin plates. **Specific gravity**, 3.28 to 3.30.

Before the blowpipe fuses readily into a black magnetic globule (in distinction from lamprophyllite). In the closed tube, gives a little water. Soluble in hydrochloric and sulphuric acids.

Genesis and occurrence. Occurs in alkaline intrusive igneous rocks, such as nepheline-syenites, associated with aegirine, black mica, feld-

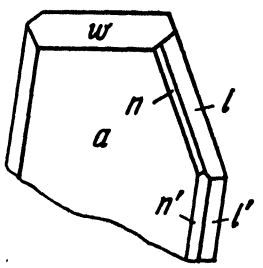


Fig. 299. Astrophyllite crystal.

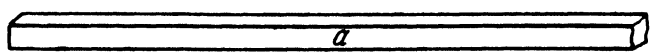


Fig. 300. Portion of acicular astrophyllite crystal.

spars, zircon, sphene, etc. Discovered on islands in the Langesundfjord (Norway) in zircon-syenite.

Widespread in pegmatites of basic igneous rocks, sometimes as large platy segregations of fibrous-platy aggregates, often as acicular individuals. Astrophyllite may also occur in stellate accumulations known as "suns".

Subclass B.

SILICATES WITH ISOLATED GROUPS OF SiO_4 TETRAHEDRA IN CRYSTAL STRUCTURES

a. *Silicates with Isolated Si_2O_7 Groups*

By the chemical criterion, this subclass comprises the so-called pyrosilicates whose crystal lattices on X-ray examination reveal the presence of isolated $[Si_2O_7]^{6-}$ groups, each consisting of two silicon-oxygen tetrahedra with one commonly shared oxygen ion (cf. Fig. 271).

A characteristic feature of this type of compounds is the predominance among cations of ions with large ionic radii, viz., Y, Ce, La, Se, Pb, Ba, K, Ca, Na, whereas in the binary compounds of the same type these occur in combination with Al, Mg, Be, and Zn. It is true, however, among the basic salts there are found simple silicates of Zn and Be (calamine and bertrandite).

Along with calamine, the minerals of the epidote group will be reviewed here (zoisite, epidote, orthite, ilvaite, prehnite, etc.) whose

crystal structures as demonstrated by N. V. Belov et al, likewise contain $[Si_2O_7]^{6-}$ radicals.

CALAMINE, $Zn_4[Si_2O_7][OH]_2 \cdot H_2O$. Synonym: hemimorphite, which is often used in literature, since the name of calamine is also used for smithsonite. The name of calamine was derived by Agricola from the Latin word "calamus" meaning reed, a reference to the occurrence of the mineral as long stalactitic formations. The second name has been suggested as a reference to its hemimorphic crystal forms.

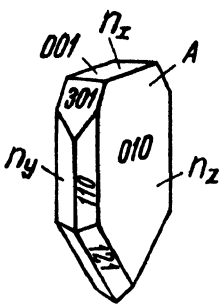


Fig. 301. Calamine crystal.

Chemical composition. ZnO 67.5%, SiO_2 25.0%, H_2O 7.5%. On heating to 500°, calamine loses half its water, the crystals remaining transparent. The other half represented by hydroxyl evaporates at higher temperatures, which results in the destruction of the crystal structure.

System, orthorhombic; symmetry, rhombic pyramidal L^22P. Space group $Imm(C_{2v}^{20})$. $a_0 = 8.38$; $b_0 = 10.70$; $c_0 = 5.11$. **Habit.** Crystals usually small and occur exclusively in cavities. Tabular (Fig. 301). They are obviously hemimorphic along the vertical axis, i.e., have no plane of symmetry parallel to (001); terminated by different faces at the top and at the bottom—only $\{12\bar{1}\}$ faces at the bottom, and by many other faces at the top. **Aggregates.** Mostly as crystalline crusts of radial structure, and also as reniform or stalactitic masses, occasionally as massive granular or earthy aggregates.

Colour. Crystals usually colourless. When massive, white or grey but more commonly yellow, brown, green or light blue. **Lustre,** vitreous; pearly on cleavage surfaces. $n_x = 1.636$, $n_y = 1.617$, and $n_z = 1.614$.

Hardness, 4 to 5. **Cleavage**, {110} perfect, and {101} imperfect. **Specific gravity**, 3.40 to 3.50. **Other properties.** When heated, crystals develop opposite electric charges, at the upper and lower terminations.

Diagnostic features. Differs from smithsonite, with which it is often associated, in that no CO_2 is separated on dissolution in acids.

Almost infusible before the blowpipe. Roasted with soda on charcoal gives a yellow coating which turns white on cooling (ZnO). Dissolves in acids with separation of gelatinous silica, in contrast to smithsonite. In the closed tube decrepitates, turns white and gives off water.

Genesis and occurrence. Together with smithsonite, cerussite, limonite, and other minerals, calamine forms in the zones of oxidation in the course of weathering of lead-zinc sulphide deposits. Apparently, silica passes into solutions in the course of decomposition of silicates containing Fe^{2+} which is capable of oxidising to Fe^{3+}. Calamine may also occur as a primary mineral in hydrothermal deposits formed near the surface. Pseudomorphs are known after smithsonite, calcite,

dolomite, fluorite, pyromorphite, galena, and other minerals. Willemite, malachite, quartz, etc., have been found pseudomorphous after calamine.

Calamine occurs in numerous deposits. Well known are the rich deposits in *Upper Silesia* (Poland). In the U.S.S.R., calamine occurs in the Eastern Trans-Baikal province: at *Klichkinskoye*, *Taininskoye*, *Tryokhsvyatitelskoye*, etc., where rather large crystals have been recorded. Also occurs in deposits in Central Kazakhstan, such as *Akjal*, *Kyzyl-Espe*, *Gulshad*. At *Reible* and *Bleiberg* in Carinthia (Eastern Alps) it occurs, possibly as an endogenous mineral, in association with smithsonite, sphalerite galena, calcite, dolomite, etc. Large masses of calamine have been found in the oxidised zones of many deposits.

Uses. Together with smithsonite, calamine is an important ore of zinc.

ZOISITE, $Ca_2Al_3[Si_2O_7][SiO_4]O[OH]$. Synonym: saussurite, a cryptocrystalline variety mixed with actinolite, chlorite, and other minerals deriving from basic calcium-rich plagioclases in the process of hydrothermal alteration.

Chemical composition. CaO 24.6%, Al_2O_3 33.9%, SiO_2 39.5%, H_2O 2.0%. Part of Al_2O_3 may occasionally be replaced by Fe_2O_3 (2 to 5%).

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Pnma(D_{2h}^{16})$. $a_0 = 16.20$; $b_0 = 5.50$; $c_0 = 10.14$. **Habit**, prismatic (Fig. 302). The prism faces usually strongly striated. Clearly terminated crystals are rare and usually ingrown in some altered rocks. **Aggregates**, mostly rod-like or granular.

Colour, grey, green, sometimes pink, red, brown. **Lustre**, vitreous. $n_x = 1.702$, $n_y = 1.696$, and $n_z = 1.696$.

Hardness, 6. **Cleavage**, {010} perfect, and {100} imperfect. Fracture, uneven. **Specific gravity**, 3.25 to 3.36.

Diagnostic features can be recognised positively only by optical constants in thin polished sections. Differs from epidote by much lower birefringence and the absence of colouring.

Before the blowpipe swells and fuses into a white blebby mass. Insoluble in acids. After ignition and fusion gives gelatinous silica with hydrochloric acid.

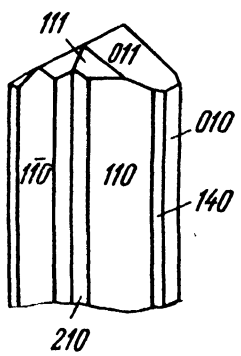


Fig. 302. Zoisite crystal.

Genesis and occurrence. Commonly occurs as a product of hydrothermal alteration of basic plagioclases associated with amphiboles in metamorphic rocks, crystalline schists, amphibolites, etc. Also found in hydrothermal deposits in paragenesis with sulphides (pyrrhotite, chalcopyrite, etc.) as transparent or translucent, often greenish, crystals.

Originally discovered in Saualpe mountains (Carinthia). In the U.S.S.R., has been recorded from Mount Urma (the Urals), in the Altai mountains, and elsewhere.

EPIDOTE, $Ca_2(Al, Fe)_3[Si_2O_7][SiO_4]O[OH]$. "Epidosis" is the Greek for increment. The name derives from the outline of prismatic crystals in cross section; epidote, in contrast to amphibole, has the form of a parallelogram, instead of a rhomb (one side being longer than the other). Epidote is widely distributed in nature, especially in metamorphic, hydrothermally altered, calcium-rich rocks.

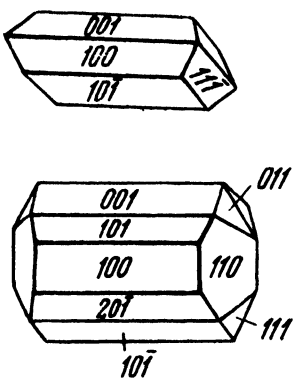


Fig. 303. Epidote crystals.

Chemical composition. As different from zoisite, epidote is rich in iron. The Fe_2O_3 content may be as high as 17%. The variety with Al : Fe = = 3 : 1 has the following composition (per cent): CaO 23.5, Al_2O_3 24.1, Fe_2O_3 12.6, SiO_2 37.9, H_2O 1.9.

System, monoclinic; symmetry, rhombic prismatic L^2PC. Space group $P2_1/m(C_{2h}^2)$. $a_0 =$ = 8.89; $b_0 = 5.62$; $c_0 = 10.23$; $\beta = 115°24'$. **Habit**, prismatic, the crystals being elongated parallel to the *b* axis (Fig. 303); sometimes rod-like (cf. Fig. 13 where the *b* axis is vertical), occasionally isometric. Well-developed crystals often show a great diversity of faces (over 290). The faces of the *b* axis zone are deeply striated (cf. Fig. 13). Twins common, with composition plane (100), occasionally (001). **Aggregates.** Besides druses of crystals in cavities, epidote often occurs massive as granular radial-fibrous or parallel-columnar aggregates.

Colour, usually green of various shades, yellow, black, or grey. Darker with increasing Fe_2O_3 content. **Lustre**, vitreous, strong. $n_x =$ = 1.74, $n_y = 1.73$, and $n_z = 1.72$.

Hardness, 6.5. **Cleavage**, {001} perfect, and {100} imperfect. **Specific gravity**, 3.35 to 3.45.

Diagnostic features. The most common varieties can be readily recognised without the aid of the microscope by pistachio-green colour and, when in crystals, by habit.

Swells and fuses before the blowpipe, the iron-rich varieties give magnetic slag. Decomposes in hydrochloric acid with separation of gelatinous silica only after fusion or strong ignition.

Genesis and occurrence. The mode of occurrence and paragenesis of the minerals accompanying epidote suggest its hydrothermal formation. It occurs fairly often (sometimes in large masses) in contact-metasomatic deposits in association with quartz, chlorites, calcite, sulphides, and other minerals. Epidote frequently replaces garnets, pyroxenes, amphiboles, and other earlier ferruginous calcium sil-

icates. If the environment becomes enriched with iron, epidote develops metasomatically also in basic plagioclases.

As a rock-forming mineral it is widely distributed in hydrothermally altered basic igneous rocks. It is especially characteristic of the so-called green schists which also contain chlorite and albite.

In the U.S.S.R., well-developed crystals occur at the *Akhmatovskaya* mine (Fig. 303), the *Nazyam* mountains near Zlatoust, at the *Polyakovsky* mine in the Kumachinskiye mountains (Southern Urals), etc. Epidote crystals known as *pushkinite* of green, yellow, and even

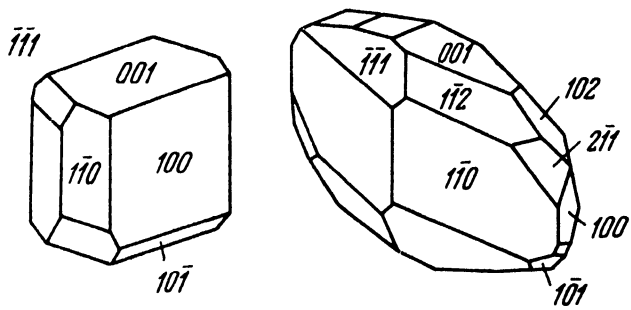


Fig. 304. Orthite crystals.

red colour, containing about 2 per cent of Na_2O and 1.5 per cent of Li_2O have been reported from the vicinity of the Verkh-Neyvinsky and Kyshtym mines (the Urals). Moreover, epidote is widely distributed as a rock-forming mineral in metamorphic rocks in mountain regions.

ORTHITE, $(Ca, Ce)_2(Al, Fe)_3[Si_2O_7]\,[SiO_4]O[O, OH]$. "Orthos" is the Greek for straight. The name derives from the straight external forms of its crystals. Synonym: allanite, adopted in American literature.

Chemical composition varies widely in oxide content. Ce_2O_3 up to 6 per cent $(La. . .)_2O_3$ up to 7 per cent. In addition to the constituents given by the formula, may also contain Na_2O, FeO, sometimes MgO, MnO, Y_2O_3 up to 8 per cent (*yttrorthite*), Sc_2O_3, ThO_2, sometimes BeO up to 3.8 per cent.

System, monoclinic; symmetry, rhombic prismatic L^2PC. **Habit**, thick tabular (Fig. 304), sometimes rod-like. Often found disseminated, more rarely massive.

Colour, brown, pitch-black, occasionally yellow. Translucent to opaque. **Lustre**, vitreous (resinous), greasy. $n_x = 1.66$ to 1.80, $n_y = 1.65$ to 1.78, and $n_z = 1.64$ to 1.77.

Hardness, 6. Brittle. **Cleavage**, practically none. Fracture, subconchoidal. **Specific gravity**, 4.1 (for altered varieties as low as 2.7). Radioactive.

Diagnostic features. Recognised approximately by black or brown colour, resinous lustre, and uneven or conchoidal fracture. Distinguished from similar radioactive minerals by relatively low specific gravity.

Before the blowpipe fuses readily with swelling into a brown or black vesicular glass. Strongly altered varieties give off much water. Usually decomposes in hydrochloric acid with separation of gelatinous silica, but after ignition becomes insoluble in acids.

Genesis and occurrence. Disseminated orthite occurs chiefly in acidic intrusive igneous rocks, such as granites, syenites, also in pegmatites, sometimes in gneisses, less often in schists; has been also found in effusive igneous rocks and in contact-metasomatic deposits (in crystalline limestones).

Like most radioactive minerals, is capable of altering to an isotropic or nearly isotropic matter enriched with water.

Has been described as uralorthite occurring in pegmatite dikes as irregular grains and crystals in reddish feldspar associated with zircon, corundum, black mica, etc. Russian Academician N. I. Koksharov has described it under the name of *bagrationite* occurring in multifaceted crystals (Fig. 304, right).

The best known foreign localities are in Scandinavia where it occurs in a magnetite deposit near Arendal, in Kragerö (Norway), near Falun (Sweden), and elsewhere.

ILVAITE, $CaFe_2^{\cdot\cdot}Fe^{\cdot\cdot}[Si_2O_7]O[OH]$. The name derives from the Latin name of the Elba Island (Italy). Synonym: lievrite.

Chemical composition not constant; especially variable are the FeO and MnO contents. For the purely ferruginous variety the following percentages are observed: CaO 13.7, FeO 35.2, Fe_2O_3 19.6, SiO_2 29.3, H_2O 2.2. The MnO content may be up to 9 per cent.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Pcmn(D_{2h}^{16})$. $a_0 = 8.82$, $b_0 = 5.86$; $c_0 = 13.07$. **Habit**, mostly prismatic. The prism faces are vertically striated. Crystals are confined to cavities. Commonly in irregular grains or granular massive, sometimes in radiate rod-like or veined aggregates.

Colour, black with a brownish or greenish tinge. **Lustre**, submetallic, greasy. In thin polished sections slightly translucent. $n_x = 1.91$ and $n_y = 1.89$.

Hardness, 5.5 to 6. Brittle. **Cleavage**, {001} and {010} perfect. Fracture, uneven, partly conchoidal. **Specific gravity**, 3.8 to 4.1.

Diagnostic features. Characterised by black colour, uneven or conchoidal fracture and relatively high hardness, and also by blowpipe behaviour.

Before the blowpipe fuses quietly into a black strongly magnetic globule. With salt of phosphorus gives the iron reaction. In some cases displays a positive reaction for manganese. Readily gelatinises with hydrochloric acid.

Genesis and occurrence. Commonly occurs in contact-metasomatic iron deposits, especially in the zone of skarns associated with garnets (andradite), hedenbergite, magnetite, sulphides of iron and copper, etc. Has been recorded from alkali-rich igneous rocks (nepheline-syenites).

Decomposes on weathering, forming limonite, (sometimes manganese hydroxides).

Originally discovered on the *Island of Elba*, at the Marina River as large crystals and segregations at the contact of pyroxene masses (probably hedenbergite) with marble.

In the U.S.S.R., ilvaite occurs at the *Turya* copper mines (Northern Urals), mostly at the contacts of hedenbergite skarns with marbled limestones, and also in certain lead-zinc deposits associated with silicates of Fe and Ca, for instance at *Tetyukhe* (Far-Eastern territory), in pyrrhotite deposits associated with basic rocks, and elsewhere.

PREHNITE, $Ca_2Al_2Si_3O_{10}[OH]_2$. Named after Captain Prehn who brought the mineral from the Cape of Good Hope.

Chemical composition. CaO 27.1%, Al_2O_3 24.8%, SiO_2 43.7%, H_2O 4.4%. Also contains a minor amount of Fe_2O_3.

System, orthorhombic; symmetry, rhombic pyramidal L^22P. Space group $P2cm(C_{2v}^4)$. $a_0 = 4.65$; $b_0 = 5.52$; $c_0 = 18.53$. **Habit.** Well-developed crystals are extremely rare. Usually short-columnar or tabular. Occurs mostly massive as reniform aggregates of radially fibrous structure in cavities in altered igneous basic rocks.

Colour, white, grey, greenish grey, yellow-green. Translucent. **Lustre**, vitreous. $n_x = 1.642$, $n_y = 1.618$, and $n_z = 1.612$.

Hardness, 6.5. **Cleavage**, {001} distinct. Fracture, uneven. **Specific gravity**, 2.8 to 3.0.

Diagnostic features. Massive ilvaite is usually characterised by pale greenish tints. Differs from externally similar zeolite by higher hardness, and optical properties, and from chalcedony, by blowpipe behaviour.

Before the blowpipe fuses rapidly with swelling into a blebby glass. As different from zeolites, in the closed tube gives off water at high temperatures. Dissolves slowly in hydrochloric acid without gelatinising.

Genesis and occurrence. Prehnite occurs fairly often in hydrothermally altered basic rocks (gabbro, diabases) deriving chiefly from basic plagioclases. Occurs also in amygdules and fissures in the same rocks as sinter and radially fibrous aggregates, sometimes associated with zeolites, calcite, epidote. May be paragenetically associated with native copper, as in deposits in the Lake Superior district (U.S.A.).

In the U.S.S.R., prehnite has been reported in many localities of the Urals, the Caucasus, Transcaucasia, in the Crimea, and elsewhere.

b. *Silicates with Ring-shaped Anionic Radicals*

As has been stated in the introduction to the silicates, this type of crystal structures possesses specific features: the crystal lattices contain isolated groups of SiO_4 tetrahedra which are linked into rings, i.e., anionic radicals, viz., $[Si_3O_9]^{6-}$, $[Si_6O_{18}]^{12-}$, etc.

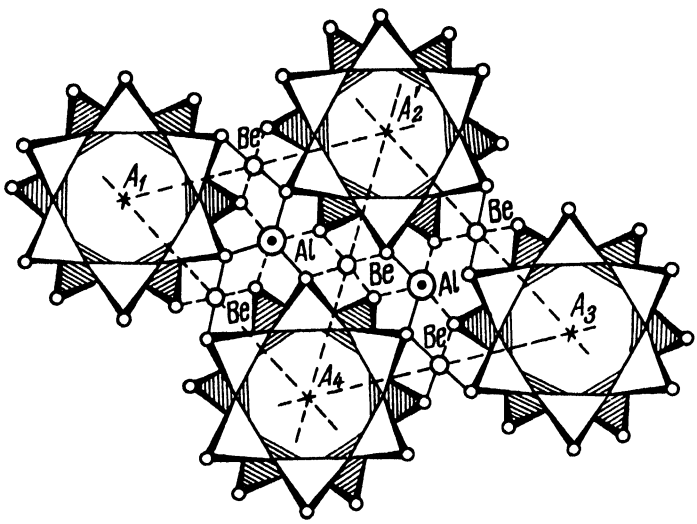


Fig. 305. Crystal structure of beryl projected on (0001).

Besides the minerals with ring-shaped anionic radicals, eudialyte also comes under discussion here. Also included here, after dioptase (copper silicate), is chrysocolla, a colloform variety of the copper silicate.

BERYL, $Be_3Al_2[Si_6O_{18}]$. This mineral is the most common beryllium mineral in the earth's crust.

Chemical composition. BeO 14.1%, Al_2O_3 19.0%, SiO_2 66.9%. May have as admixtures the following alkalis (up to 7%): Na_2O, K_2O, Li_2O, sometimes Rb_2O, Cs_2O (*vorobyevite* contains up to 3 per cent)*. Occasionally contains helium, and H_2O (up to 3 per cent).

System, hexagonal; symmetry, dihexagonal dipyramidal L^66L^27PC. Space group $P6/mcc(D^2_{6h})$. $a_0 = 9.21$; $c_0 = 9.17$. **Crystal structure** is exceptionally interesting. It is shown in Fig. 305 projected on the (0001) plane. At the corners of the rhomb there are shown pairs of the ring radicals (one beneath the other) which are somewhat turned in relation to each other. The Al and Be ions occur in the plane between ring radicals, however not on the same level, but, as shown in the vertical projection (Fig. 306), between the sheets of rings. Thus, the crystal structure as a whole is held together both by the lateral

* The formula of vorobyevite, which contains a large caesium cation, may be written as follows: $Cs(Be_2Li)Al_2[Si_6O_{18}]$.

and vertical linkages. The Al ions are surrounded by six, and the Be ions by four oxygen ions each. The Be^{2+} ions closely connect the ring radicals into a strong common framework. It should be noted that in each link the ring radicals occurring one beneath the other have

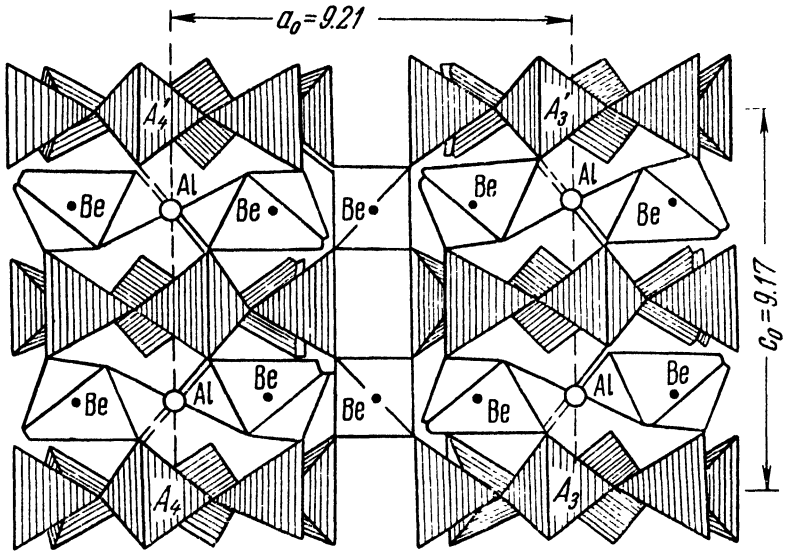


Fig. 306. Vertical projection of beryl crystal structure.

large voids inside. It is in these voids that are located the larger ions, such as Na^{1+}, K^{1+}, Cs^{1+}, and also H_2O, which are sometimes present in beryls.

Habit. Crystals columnar or prismatic and usually well-developed (Fig. 307). The most developed are commonly prism $\{10\bar{1}0\}$ and pinacoid $\{0001\}$. Much less so are the faces of dipyramids $(11\bar{2}1)$, $(10\bar{1}1)$, and prism $(11\bar{2}0)$. The prism faces are often vertically striated.

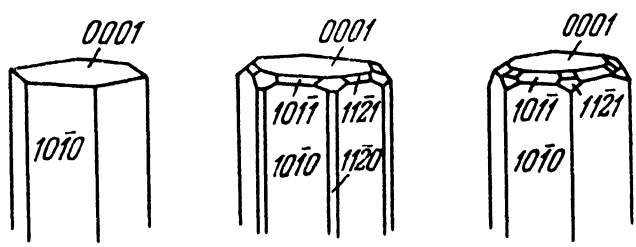


Fig. 307. Beryl crystals.

Twins have not been established; or to be more precise, the dependences governing occasional intergrowths of individual crystals have not been studied as yet. **Aggregates.** Beryl occurs usually as single disseminated crystals, sometimes in druses, sometimes massive. Rod-like aggregates are encountered.

Colour most often greenish white, yellow, yellowish green, light blue, bright green, and sometimes pink. The causes of coloration have not been fully established. Colourless transparent varieties have also been described. The following varieties are distinguished according to colour: (1) *emerald*, pleasant deep bright green (hence the term "emerald-green"); transparent flawless individuals, are highly valued precious stones; the colour is due to a trace of chromium; (2) *aquamarine*, a transparent sea-blue variety; the name derives from two Latin words: "aqua" (water) and "mare" (sea); (3) *vorobyevite*, a pink variety (contains cesium); named after the Russian mineralogist V. I. Vorobyev; (4) *heliodor*, a yellow transparent variety (contains a trace of iron oxide). **Lustre**, vitreous. $n_y = 1.568$ to 1.602, and $n_z = 1.564$ to 1.595.

Hardness, 7.5 to 8. Brittle. **Cleavage**, parallel to prism $\{10\bar{1}0\}$, and to pinacoid {0001} indistinct. Fracture, uneven to conchoidal. **Specific gravity**, 2.63 to 2.91.

Diagnostic features. Beryl is recognised readily by crystal habit and high hardness, distinguishing it from morphologically similar columnar minerals crystallising in the hexagonal system. As compared with chrysoberyl and phenacite, beryl has lower specific gravity and different optical properties.

Infusible before the blowpipe but the edges of fragments become rounded. The transparent varieties become turbid (at high temperatures). With borax gives a transparent, colourless glass; only emerald yields a pale-green bead. Insoluble in acids.

Genesis and occurrence. Beryl occurs most often in *pegmatite* dikes in acid intrusive rocks or in wall rocks among reaction-metasomatic formations, genetically associated with pegmatites. Also occurs in pneumatolytically altered granites known as *greisens*, less often in cavities in the granites themselves paragenetically associated with minerals having volatile constituents.

Associates, besides feldspars, micas, and quartz, are topaz, tourmaline, fluorite, sometimes phenacite, chrysoberyl, wolframite, cassiterite, sulphides (arsenopyrite, molybdenite), etc.

As a chemically inert mineral, upon weathering and denudation of primary deposits, beryl passes into placers as rounded crystals or pebbles. Mention should be made of occasional etch figures on crystal faces. There are also cases of replacement of beryl by kaolinite (apparently through a hydrothermal process).

Long famous localities in the U.S.S.R. are the *Izumrud* (Emerald) *Mines* in the Urals, the *Tigeretskiye Belki*, in the Altai mountains, etc. Aquamarine deposits occur in the Trans-Baikal province: at *Sherlovaya Gora*, *Adun-Chilong*, *Borshchovochny ridge*, and elsewhere.

Beryl occurs in some localities in the U.S.A., Colombia, Brazil, India, and South Africa (Transvaal).

A notable occurrence is at *Albany* (Maine), where some gigantic crystals have been found (up to 5 m in length, 1.5 m in width, and

16 tons in weight); also at *Branchville* (Connecticut), and elsewhere in the United States. A large emerald deposit is known at *Muso* (Colombia) in limestones and schists rich in carbonaceous and bituminous matter, genetically related to pegmatite dikes, and associated with quartz, calcite, pyrite, parisite and some other minerals.

Uses. Beautifully coloured transparent emeralds and aquamarines are valued as gemstones.

Of late beryl ores have been used increasingly as a source of metallic beryllium—one of the lightest metals (specific gravity 1.5 times lower than that of aluminium). Forms alloys with aluminium and magnesium which because of their light weight and high strength are particularly important for the aircraft industry. It is also a source of important alloys with other metals. Beryllium salts are used in various industries and in pharmaceutics.

CORDIERITE, $Al_3(Mg, Fe)_2[Si_5AlO_{18}]$. Synonyms: *iolite* ("iol" is the Greek for violet) and *dichroite* (from "dichros", double-coloured). Discovered by Academician Koksharov in the Urals in 1856.

Chemical composition. SiO_2 about 50%; MgO and FeO widely variable. Varieties which contain FeO only, are referred to as *ferruginous cordierite.* May have admixtures of CaO, Na_2O, and H_2O. Unaltered varieties contain no Fe_2O_3.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Cccm(D_{2h}^{20})$. $a_0 = 17.03$; $b_0 = 9.67$; $c_0 = 9.35$. **Crystal structure** similar to that of beryl except that the places of the Be ions are taken by Al ions. In the anionic radical, one Si^{4+} ion is replaced by Al^{3+} balancing the extra charge of the cations (cf. the formula). The unit cell has a pseudohexagonal shape. **Habit.** Crystals are rare and mostly in poorly-developed prismatic forms (Fig. 308) which are pseudohexagonal because of twinning (similarly to aragonite); much more commonly massive or impregnated irregular grains.

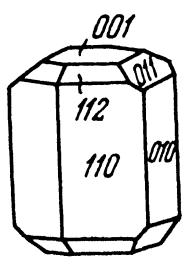


Fig. 308. Cordierite crystal.

Colour. Sometimes colourless, but more often tinted various shades of blue and violet; less often yellowish white or brown (evidently oxidised varieties). **Lustre**, vitreous. $n_x = 1.541$, $n_y = 1.539$, and $n_z = 1.534$.

Hardness, 7 to 7.5. Brittle. **Cleavage**, {010} distinct, and {100} and {001} imperfect. Fracture, conchoidal. **Specific gravity**, 2.60 to 2.66.

Diagnostic features. Cordierite may be distinguished from externally similar quartz by conchoidal fracture, bluish shades, and vitreous lustre; from sapphire, by lower hardness; positively distinguished from quartz by optical properties (biaxiality and lemon-yellow pleochroic zones around inclusions).

Either infusible or fusible with difficulty before the blowpipe. Insoluble in acids. With cobalt nitrate gives the aluminium reaction.

Genesis and occurrence. Cordierite occurs chiefly in gneisses, schists, and altered igneous rocks associated with magnesial and aluminous minerals (hypersthene, rhombic amphiboles, biotite, sillimanite, basic plagioclases, talc, etc.). Cordierite also occurs in lavas, in which case it contains inclusions of volcanic glass, an indication of its high-temperature origin. Is found in placers as pebbles.

Frequently is semi-decomposed, and shows lamellar structure and pearly chatoyancy. In the course of later hydrothermal processes cordierite readily alters to talc, thin lamellar aggregates of mica, chlorites, etc.

In the U.S.S.R., occurs at Murzinka (*Maslyanka* village), in the Trans-Baikal province (Tsipikansk district), and elsewhere.

ACHIRITE, $Cu_6[Si_6O_{18}]\cdot 6H_2O$, or $CuSiO_3\cdot H_2O$. Synonym; *dioptase* ("dia" is the Greek for through, "optasia", seeing; so named because its cleavage is often visible through the crystals). A rather rare mineral found in copper deposits.

Chemical composition. CuO 50.5%, SiO_2 38.1%, H_2O 11.4%. Usually without admixtures. Contains negligible Fe_2O_3 (up to 0.2%).

System, trigonal; symmetry, rhombohedral L_6^3C. Space group $R3(C_{3i}^2)$. $a_0 = 14.61$; $c_0 = 7.80$. **Crystal structure**, studied in detail by N. V. Belov, consists of anionic $[Si_6O_{18}]^{12-}$ hexagonal rings. The water molecules occur in the tabular channels of the rings. **Habit.** Usually as short acutely terminated columns (Fig. 309), less often rhombohedral. Druses are common in fissures and irregularly-shaped cavities.

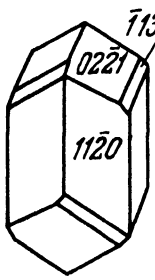


Fig. 309. Dioptase crystal.

Colour, emerald-green. **Streak**, green. **Lustre**, vitreous. Transparent or translucent. $n_x = 1.697$, and $n_y = 1.644$.

Hardness, 5. Brittle. **Cleavage**, parallel to the rhombohedron $\{10\bar{1}1\}$ perfect. **Specific gravity**, 3.28 to 3.35.

Diagnostic features. Characterised by crystal habit, emerald-green colour, and relatively high hardness.

Infusible before the blowpipe. When strongly ignited in the oxidising flame, becomes black, in the reducing flame red, giving the flame a green coloration. Gives a copper globule with soda. Gelatinises with hydrochloric and nitric acids.

Genesis and occurrence. Judging by paragenetic association, achirite forms in the course of weathering of copper deposits. Associated with achirite are malachite, calcite, sometimes wulfenite, calamine, and other minerals.

As a chemically inert and hard mineral, occurs in gold placers.

In the U.S.S.R., very large achirite crystals have been found at *Altyn-Tyube* (Central Kazakhstan) in cracks in limestone. It is from these that in 1780 a Kazakh merchant Achir brought crystals, which

were for a long time mistaken for emerald, then named achirite, and more recently dioptase. In the U.S.S.R., the former name has been retained.

Outside the U.S.S.R., dioptase finds have been recorded from the basin of the *Niari River* (Congo), in *Katanga* (Congo), at *Copiapon*, Atacama (Chile), etc.

CHRYSOCOLLA, $CuSiO_3 \cdot nH_2O$; n about 2. "Chrysos" is the Greek for gold, "colla", glue.

Chemical composition variable. Often contains impurities: Al_2O_3 (pilarite) up to 17%, Fe_2O_3 up to 7%, P_2O_3 (demidovite) 7 to 9%.

System, not determined. Usually chrysocolla occurs as a typical colloid. Is also found in opal-like masses as crusts with a sinter, sometimes vesicular surface, also as earthy masses.

Colour, light blue, bluish green or blue, brown (due to admixture of iron hydroxides), and even black.

Streak, for purer varieties, greenish white. **Lustre,** vitreous, waxy; dull for opal-like varieties.

Hardness, about 2, sometimes 4. Brittle. Fracture, uneven, conchoidal. **Specific gravity,** 2.0 to 2.3. Part of the water is lost when the mineral is heated to 110°, and the remainder at higher temperatures.

Diagnostic features. Identifiable by occurrence in colloform masses, bluish-green shades, and relatively low hardness.

Infusible before the blowpipe, which it colours green. In the glass tube gives off water readily and turns black. Decomposes in acids yielding pulverulent silica.

Genesis and occurrence. Chrysocolla is a mineral typical of the oxidised zones of copper deposits and occurs predominantly in regions of a hot arid climate.

Associated with it are most diverse oxygen copper compounds. Chrysocolla may be pseudomorphous after malachite, azurite, atacamite, libethenite, cerussite, calcite, etc. Gradual alteration to less hydrous copper silicates (plancheite) have been observed. Forms on the walls of workings in abandoned mines from neutral solutions.

Chrysocolla has been recorded from numerous deposits. In the Urals it has been reported from the *Turya mines*, *Mednorudyansk* (demidovite). In Central Kazakhstan it is found in the *Jezkazgan* copper deposit, also at the *Koktas-Jartas*, *Uspensky* mine, and elsewhere.

The most interesting chrysocolla formations outside the Soviet Union occur in Chile, in western United States, in Africa (Congo), and elsewhere.

EUDIALYTE, $(Na, Ca)_6ZrSi_6O_{18}[OH, Cl]$? "Eu" is the Greek for easy, "dialitos" decomposed (reference to its behaviour before the blowpipe and in acids). *Eucolite* is a FeO-rich variety; *mesodialyte*, an intermediate variety in respect to FeO content.

Chemical composition (per cent): Na_2O 11.6 to 17.3, CaO 8.9 to 11.3, ZrO_2 12.0 to 14.5, $(Ce, La, Y)_2O_3$ 0.3 to 2.9, FeO 3.1 to 7.1, MnO 0.3 to 3.1, SiO_2 47.2 to 51.2, H_2O 0.03 to 2.9, Cl 0.7 to 1.6.

System, trigonal; symmetry, ditrigonal scalenohedral $L_6^3 3L^2 3PC$. Space group $R\bar{3}m(D_{3d}^5)$. $a_0 = 13.01$ (for rhombohedral cell). **Habit**, thick tabular, platy, less often prismatic (Fig. 310). Most common

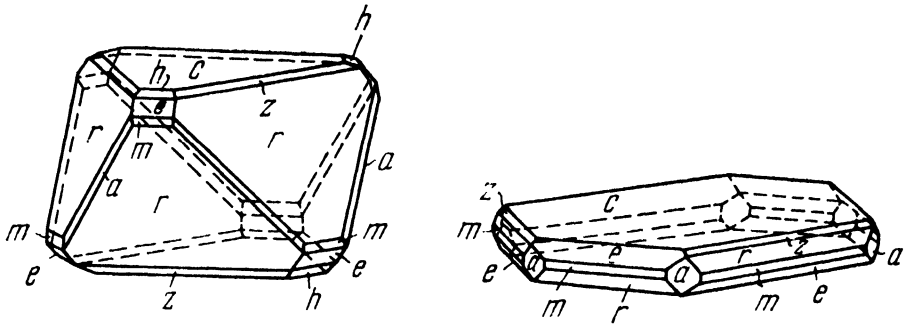


Fig. 310. Eucolite crystals: *r* {10$\bar{1}$1}, *c* {0001}, *m* {10$\bar{1}$0}, *a* {11$\bar{2}$0}, *z* {10$\bar{1}$4}, *e* {00$\bar{1}$2}.

forms: pinacoid {0001}, rhombohedra {10$\bar{1}$1}, {10$\bar{1}$3}, prisms {10$\bar{1}$0}, {11$\bar{2}$0}, etc. Occurs also as irregular grains, more seldom as vein-shaped masses.

Colour, pink, pink-red of varying shades, reddish brown, brown, yellow-brown, and light yellow. **Lustre**, vitreous. For eudialyte: $n_x = 1.610$ and $n_y = 1.608$; for eucolite: $n_y = 1.620$ and $n_z = 1.618$.

Hardness, 5 to 5.5. Brittle. **Cleavage**, {0001} imperfect. **Specific gravity**, 2.84 to 2.98 (increasing from eudialyte to eucolite).

Diagnostic features. Eudialyte is usually pink or red (crimson) of varying shades, by which it is easily detected in basic igneous rocks, especially when associated with zirconium-bearing silicates. In polished sections is recognised at once by optical properties, such as pleochroism and very low birefringence.

Before the blowpipe fuses readily to a green vesicular glass; colours the flame yellow. In the closed tube gives off water. Easily soluble in acids. A solution in hydrochloric acid gives a Zr reaction (litmus paper becomes orange).

Genesis and occurrence. Eudialyte is confined exclusively to *magmatic* alkaline rocks (nepheline-syenites) and to *pegmatitic* offshoots in paragenesis with nepheline, feldspars, aegirine, etc. In some rocks (eudialytic lujaurite) eudialyte is distributed so widely that it is rock-forming mineral.

Eudialyte is evidently altered easily in the course of hydrothermal processes since there have been observed its replacement by catapleite and sometimes by fine pyramidal crystals of zircon disseminated in the semi-decomposed mass in association with zeolites, fluorite, and other minerals of hydrothermal origin.

On weathering eudialyte losses alkalis and silica, turning into a brown porous mass of ZrO_2 and Fe_2O_3 (probably in the form of hydroxides).

Uses. Eudialyte-rich varieties of alkaline igneous rocl s are a source of eudialyte concentrates for obtaining zirconium. The a verage eudialyte content in such rocks (eudialytic lujaurites) is 6-8 per cent and sometimes (in vein varieties) up to 30 per cent or more.

TOURMALINE, $(Na, \overline{Ca})\,(Mg, Al)_6\,[B_3Al_3Si_6(O, \overline{OH})_{30}]$. The formula is for the most common species. The name is derived from the Sinhalese word "Turmali". Under this name it was brought to Holland along with other precious stones from Ceylon in 1703.

Chemical composition is variable due to numerous isomorphous replacements. The percentage of the principal constituents varies as follows: SiO_2 30 to 44, B_2O_3 8 to 12, Al_2O_3 18 to 44, $FeO + Fe_2O_3$ 0 to 38, MgO 0 to 25, Na_2O 0 to 6, CaO 0 to 4, H_2O 1 to 4. Tourmaline may also contain the following isomorphous admixtures: K (K_2O up to 2.5%), Li (Li_2O up to 1.3%), $Mn^{\cdot\cdot}$ (MnO up to 3.5%), Cr (Cr_2O_3 up to 10.7%), as well as F (up to 1.2%) and Cl.

Magnesium-rich tourmalines are known as *dravite*; ferruginous varieties as *schorlite;* those enriched in lith ium as *elbaite.* The alumina-rich varieties have no special designation.

System, trigonal; symmetry, ditrigonal pyramidal L^33P. Space group $R3m(C_{3v}^5)$. $a_0 = 15.51$ to 16.01; $c_0 = 7.10$ to 7.22. **Crystal structure.** The structure of tourmaline has been investigated by Y. N. Belova and N. V. Belov who disproved the data given by Burger. According to the latest findings, the characteristic structural units of tourmaline, in distinction from beryl, are double-tier anionic rings (Fig. 311) with the formula $A_{12}O_{30}$, where half the A ions are Si^{4+}, and the other half Al^{3+} and B^{3+} ions. The silicon ions, surrounded by four oxygen ions each, occupy one tier (sheet) of the anionic radical, forming six-membered rings of ditrigonal configuration. The rings possess a threefold axis intersected by three mirror planes of symmetry. The other layer of each double ring consists of the Al^{3+} and B^{3+} ions which are tetrahedrally surrounded by oxygen ions and together with them produce a roughly triangular form. These isolated double-tier rings occur at the apexes of the rhombohedral unit cell and are linked by shared Mg and Al ions (this time in sixfold oxygen coordination). These ions linked by the shared oxygen ions form screw-type chains in the crystal structure parallel to the right- and left-hand threefold screw axes of the unit rhombohedron. The Ca and Na ions, being in sixfold oxygen coordination, occur on the same threefold axes that carry the double anionic rings, and thus serve as the connecting link parallel to the c axis. All these specific features of tourmaline crystal structure fully agree with the physical and chemical properties of the mineral, primarily with crystal form, the difference between their terminating faces, as well as with pyro- and

piezoelectrical and optical properties (optical sign, light absorption), etc. The increased hardness of tourmaline is attributed to the higher coordination of boron (4 instead of 3) similarly to aluminium silicates (coordination number 6). **Habit.** Crystals are usually columnar and elongated parallel to the threefold axis of symmetry. Occasionally

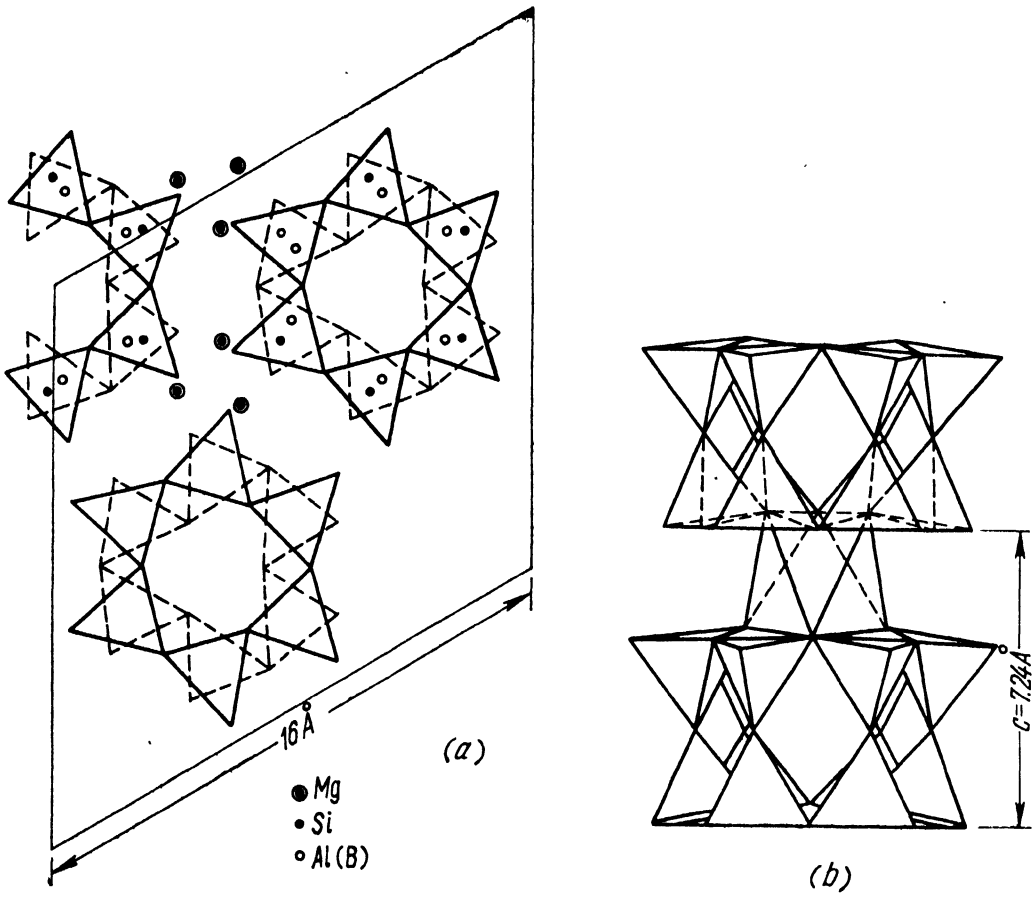


Fig. 311. Crystal structure of tourmaline.
a – view of two-level rings along *c* axis; *b* – their vertical projection.

occurs in short-prismatic crystals. Small, often microscopic crystals sometimes alternate with larger individuals up to 20 cm and more long and several centimetres across. The most common forms are prisms $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$, trigonal pyramids $\{10\bar{1}1\}$, $\{02\bar{2}1\}$, etc., (Fig. 312). About 180 simple forms have been recognised for tourmaline. The crystal terminations frequently show unequal development. Very often the prism faces are vertically striated and the crystals show a spherical triangular outline in cross section (Fig. 313). This is explained by the combination of the numerous faces of the prismatic zone. Twins are very rare, with the composition plane $(10\bar{1}1)$. **Aggregates.** Tourmaline often occurs in rod-like, radially-divergent

(tourmaline suns), fibrous-acicular or fibrous aggregates. More seldom as granular, sometimes cryptocrystalline, masses.

Colour, depends on chemical composition. The varieties with none or little iron are green, pink, and red. They are usually poor in MgO and FeO, but often rich in Li_2O and Al_2O_3. The pink colour depends on the presence of Mn, Li, and Cs. Dark-red tourmalines are called *rubellite*. MgO-rich tourmalines are mostly brown and yellow. The ferruginous varieties are intensely dark-coloured: black (schorl),

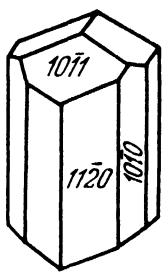


Fig. 312. Prismatic tourmaline crystal.

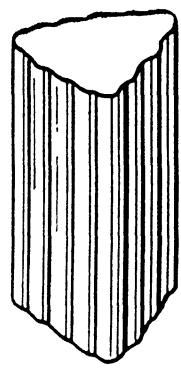


Fig. 313. Striations and cross section of tourmaline crystals.

dark green, dark blue (indicolite), and dark brown. Less often it is colourless and transparent. Chromium-bearing tourmalines are intensely dark green. Sometimes crystal terminations may have a different colouring, e.g., the colourless crystals from Elba, which have deep black terminations. There are varieties with zonal distribution of colour. Thus in cross fracture the centre may be red, and on the periphery one or more sharply outlined polygonal zones may have varying shades of green or some other colour. **Lustre**, vitreous. For dravite: $n_y = 1.635$, and $n_z = 1.614$. For schorlite: $n_y = 1.698$, and $n_z = 1.658$.

Hardness, 7 to 7.5, increasing in a direction perpendicular to the c axis and decreasing parallel to it. **Cleavage**, practically absent or highly imperfect parallel to the $\{11\bar{2}0\}$ prism and $\{10\bar{1}1\}$ pyramid. Fracture, uneven. **Specific gravity**, 2.90 to 3.25.

Other properties. Electrifies on heating, friction, pressure, the ends developing opposite charges.

Diagnostic features. Tourmaline crystals are readily identifiable by spherical triangular cross section, sharply defined vertical striation, and high hardness. It differs from externally similar pyroxenes, amphiboles, and epidote by the absence of cleavage and greater hardness; from rutile by hardness, streak, and cross section.

Behaviour before the blowpipe varies with composition. The colourless or pale-coloured lithium-rich varieties do not fuse but become turbid, sometimes with swelling. The varieties more abundant in

iron fuse with difficulty, while ferro-magnesian species fuse rather readily to blebby glass. All the tourmalines, when mixed with CaF_2 and $KHSO_4$, show a boron reaction (green flame). Insoluble in acids.

Genesis and occurrence. Tourmalines are fairly often associated with minerals containing volatile and rare constituents. Pink, red (rubellite), and polychromatic tourmalines generally occur in *pegmatites* and are associated with minerals containing lithium, cesium, rhubidium, and other rare elements. Blue and green tourmalines (indicolite and verdelite) according to the findings of A. I. Ginzburg are widely distributed in pegmatites albitised in the process of tantaloniobium and tin mineralisation.

Often occur in *hydrothermal* ore deposits and in various altered rocks, including crystalline schists, gneisses, and phyllites subjected to pneumatolytic action.

Microscopic crystals of tourmalines occur in granites or in their contact aureoles mostly associated with quartz, sometimes with topaz, cassiterite, and other minerals, especially in *greisens*.

On weathering tourmaline behaves as a chemically inert mineral, passing, as a residual product into placers. Is found in many sedimentary rocks. The solution pits sometimes observed on tourmaline crystals are probably due to hydrothermal processes.

Deposits in which tourmaline, especially the black varieties, appear in varying amounts are very numerous. We shall mention but a few, most important mineralogically.

Deservedly famous are the deposits in pegmatite dikes at *Shaitanka*, *Murzinka*, *Yuzhakovaya*, *Sarapulka* and *Lipovka* (north-east of Sverdlovsk in the Urals) where variously coloured tourmalines have been found in radiate rod-like aggregates. Especially remarkable are the carmine-red tourmalines of Sarapulka; excellent crimson crystals have been found with lepidolite on the northern slope of *Borshchovochny ridge* (Trans-Baikal province). At the Shabry village, *Nizhne-Iset* district (the Urals) in cracks in chromite deposits and at their contact with talc schists, large crystals (several centimetres long and 1 cm across) of dark-green or almost black chromium tourmalines have been found.

We shall mention of foreign localities. Widely famous are tourmalines from pegmatite dikes in *Madagascar*, remarkable both for size and colour. Beautiful variously coloured (red, pink, green, blue, violet, etc.) tourmalines occur in the pegmatites of *San Diego* and elsewhere in California. The placers of *Ceylon* have long been famous for intensely coloured transparent tourmalines, which were exported to Europe to be cut as gems. Rare blue tourmalines (indicolite) are often found in that locality.

Uses. Beautifully coloured transparent tourmalines are cut as gemstones, while larger crystals with piezoelectric properties are cut into sections for frequency control in radio transmitters.

Subclass C.

SILICATES WITH CONTINUOUS CHAINS OF SiO_4 TETRAHEDRA IN CRYSTAL SRUCTURE

The principal representatives of this subclass are pyroxenes and amphiboles, considered to be typical metasilicates. Although fundamentally differing in the quantitative ratio of constituents, they have a number of characteristic external features in common: similar habit, closely similar crystal structure, cleavage, optical properties, specific gravity, hardness, etc. The following cations are predominant in pyroxenes and amphiboles: Mg^{2+}, Fe^{2+}, Ca^{2+}, Na^{1+}, Li^{1+}, Al^{3+}, Fe^{3+}, and the following anions: $[SiO_4]^{4-}$, sometimes $[AlO_4]^{5-}$, and also $[OH]^{1-}$, and Cl^{1-} (in amphiboles). The most common are ferromagnesian pyroxenes and amphiboles which are the principal rock-forming minerals of many igneous rocks. Their total quantity in the earth's crust is as much as 16 per cent by weight.

Pyroxenes and amphiboles differ from iron-magnesium rock-forming orthosilicates (minerals of the olivine group) in the following chemical properties:

(1) they contain more SiO_2 (SiO_2-deficient melts give rise to olivines);

(2) along with Mg and Fe, an essential constituent is Ca (in the orthosilicates its role is negligible), in view of which, binary compounds, such as diopside and tremolite are widely represented among them;

(3) many pyroxenes and amphiboles, especially those constituting binary compounds, often contain as impurities Al_2O_3, Na_2O, sometimes Fe_2O_3, etc. (the orthosilicates are relatively pure in composition).

The physical properties of these minerals fully agree with their crystal structure, which differs materially from that of the orthosilicates by the presence of continuous anionic chains comprised of silicon-oxygen tetrahedra extending in one direction (parallel to the *c* axis). The minerals of this subclass have the following principal features:

1. Unlike the isometric olivine minerals, the crystal individuals are usually elongated in one direction, because the Si—O—Si bond is predominantly apolar in nature and therefore more stable than that of the metallic Ca^{2+} and Mg^{2+} cations occurring between the chains and carrying a small charge; that is why the crystals are much more likely to split parallel to the *c* axis than across the chains.

2. In distinction from the orthosilicates, the pyroxenes and amphiboles have more pronounced cleavage, which is characteristically parallel to the prism, i.e., to the elongation of the individuals.

3. The refractive indices and birefringence are generally lower than those of the minerals of the olivine group.

4. Owing to the relatively loose packing of ions, the pyroxenes and amphiboles have somewhat lower specific gravity than the respective minerals of the olivine group.

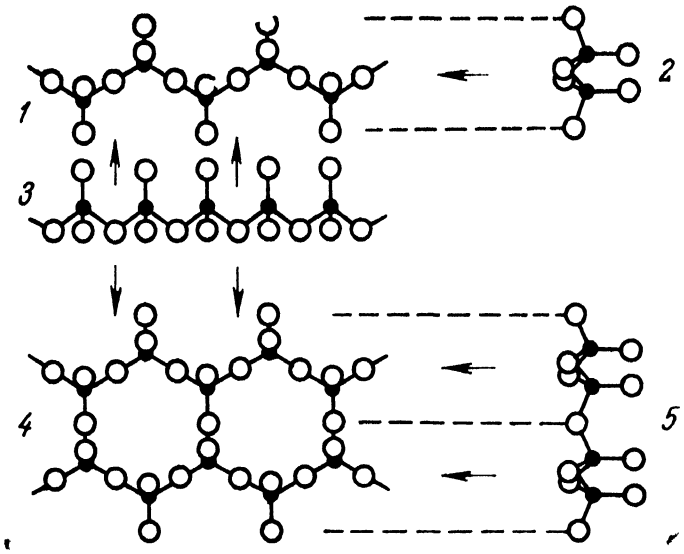


Fig. 314. Silicon-oxygen chains in three projections (*1*, *2*, *3* – in pyroxenes; *4*, *5*, and *3* – in amphiboles).

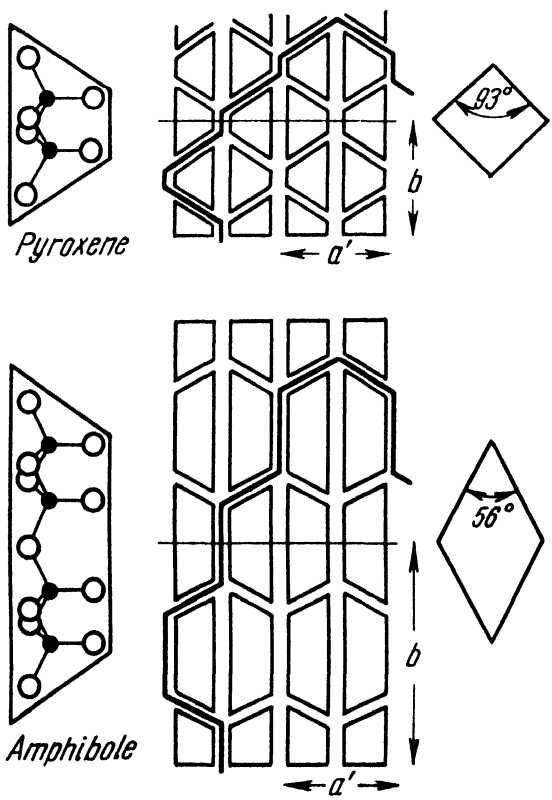


Fig. 315. Projections of diagrammatic representations of crystal structures of pyroxene and amphibole parallel to *c* axis. Left: silicon-oxygen chains in the same projection.

Although the *pyroxenes* and *amphiboles* have much in common, they substantially *differ from each other* in some features. The principal differences between them are given below.

(a) According to X-ray examination, in the crystal structure of pyroxenes the anionic radicals are single anionic chains of silicon-oxygen tetrahedra, with the formula $[SiO_3]_\infty$, and in the amphibole structures they are double chains with the formula $[Si_4O_{11}]_\infty$ (cf. Fig. 272). For better understanding see projections *2* and *5* parallel to the *c* axis (Fig. 314).

(b) The above explains the difference in the angles of prismatic cleavage between pyroxenes and amphiboles, parallel to the elongation

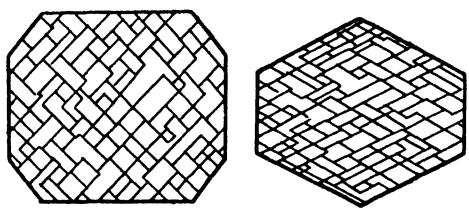


Fig. 316. Cross section of pyroxene crystals (*a*) and amphibole (*b*) with cleavage directions (at different angles on each).

of the chains. Figure 315 shows diagrammatically the structures of diopside and tremolite comprised of four unit cells projected on (001). The chains of silicon-oxygen tetrahedra as shown by the heavy lines, are trapezoidal blocks. It will be seen that the amphibole blocks parallel to the *b* axis are twice as large as those of pyroxenes. In both cases as shown by the heavy lines, the cleavage planes pass diagonally between the chains without breaking them, i.e., parallel to the {110} prism. Thus, the broken lines generally form a squaroid with an angle of 87° for the pyroxenes and a rhomboid with an angle of 124° for the amphiboles.

(c) The habit of the two groups of minerals fully conforms to the above, the crystals of pyroxenes showing pseudotetragonal, and those of amphiboles pseudohexagonal outlines in cross section (Fig. 316).

As stated earlier, it has been demonstrated recently that the minerals of the group contain a new type of anionic radical with the formula $[Si_3O_9]_\infty$, representing the next natural member in the silicate series of this subclass.

According to the above the subclass may be divided into the following types.

1. Silicates with single $[SiO_3]_\infty$ chains (group of pyroxenes).
2. Silicates with double $[Si_4O_{11}]_\infty$ chains (group of amphiboles).
3. Silicates with single $[Si_3O_9]_\infty$ chains (wollastonite group).

a. *Silicates with Single* $[SiO_3]_\infty$ *Anionic Chains*

GROUP OF PYROXENES

This rather extensive group of minerals has long been divided according to crystallographic features into two subgroups: monoclinic and orthorhombic pyroxenes.

We shall describe the following minerals of the group:

Monoclinic pyroxenes

Diopside ..... $CaMg[Si_2O_6]$
Hedenbergite ..... $CaFe[Si_2O_6]$
Augite ..... $Ca(Mg, Fe, Al)[(Si, Al)_2O_6]$
Jadeite ..... $NaAl[Si_2O_6]$
Aegirine ..... $NaFe^{\cdots}[Si_2O_6]$
Spodumene ..... $LiAl[Si_2O_6]$

Orthorhombic pyroxenes

Enstatite ..... $Mg_2[Si_2O_6]$
Hypersthene ..... $(Mg, Fe)_2[Si_2O_6]$

The monoclinic pyroxenes occur for the most part as binary and more complex compounds in whose structure in some cases there are cations Mg^{2+} and Fe^{2+} that can substitute for one another and also Ca^{2+}, while in other cases the cations are $Na^{1+}(Li^{1+})$ with Fe^{3+} and Al^{3+}. There is also a pyroxene called augite which besides (Mg, Fe) and Ca, also contains Al, Fe^{3+} and sometimes Ti, apparently with partial substitution of Al for Si in the silicon-oxygen chains (which means that in point of fact we are dealing here with an alumosilicate). When a part of the Si^{4+} ions are replaced by Al^{3+} ions, the total negative charge of the chains correspondingly increases and it is but natural that it must be balanced by inclusion of cations of higher valency in the crystal structure.

The orthorhombic pyroxenes are metasilicates of Mg and Fe and, just as in the case of the olivine group, form a continuous series of isomorphous mixtures: $Mg_2[Si_2O_6]$—$Fe_2[Si_2O_6]$. Magnesian and ferromagnesian varieties of pyroxenes of this series are very widespread in nature.

DIOPSIDE, $CaMg[Si_2O_6]$. From the Greek "dis" meaning twice and "opsis" appearance. Diopside is a typical binary compound and the end member of the important $CaMg[Si_2O_6]$ — $CaFe^{\cdot\cdot}[Si_2O_6]$ (diopside-hedenbergite) isomorphous series; a mineral species of intermediate composition is called *salite.* Diopside is widely distributed as a rock-forming mineral in many igneous rocks and also in contact-metasomatic formations.

Chemical composition. CaO 25.9%, MgO 18.5%, SiO_2 55.6%. May contain as impurities FeO, MnO, sometimes Al_2O_3, Fe_2O_3, Cr_2O_3 up

to a few per cent (*chrome-diopside*), V_2O_3 2 to 4% (*lavrovite*), N_2O, occasionally TiO_2.

System, monoclinic; symmetry, prismatic L^2PC. Space group $C2/c(C_{2h}^6)$. $a_0 = 9.71$; $b_0 = 8.89$; $c_0 = 5.24$; $\beta = 105°51'$. **Habit.** Well-formed crystals are relatively rare. Usually short-columnar (Fig. 317) with predominant {101} and {010} pinacoids. Twins are

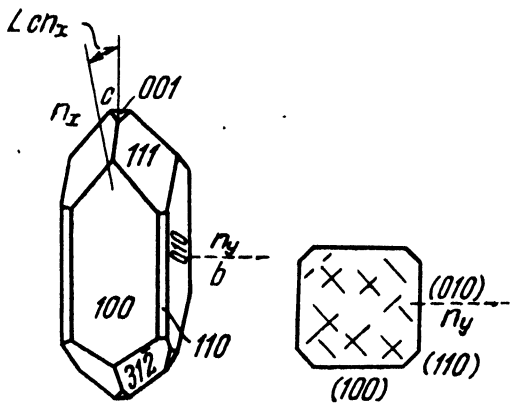


Fig. 317. Diopside crystal. Right: cross section and cleavage.

common, along (100) and (102) planes. **Aggregates.** Diopside occurs mostly as massive granular aggregates, but in contact-metasomatic formations rod-like and radial crystal aggregates are found.

Colour. Rarely colourless. Usually tinted various, mostly pale, shades of dirty green or grey. **Lustre**, vitreous. Refractive indices vary with the content of the hedenbergite molecule. For pure diopside: $n_x = 1.694$, $n_y = 1.671$, and $n_z = 1.664$.

Hardness, 5.5. to 6. Brittle. **Cleavage**, parallel to the {110} prism distinct at an angle of 87°. Sometimes has a parting parallel to {010}. **Specific gravity**, 3.27 to 3.38.

Diagnostic features. Well-formed crystals of diopside differ from those of augite by predominance of vertical pinacoids and grey or light-green shades of colour. Since diopside may form isomorphous mixtures with various other pyroxenes, positive identification requires determination of optical constants, and in some cases chemical analyses.

Fusible with difficulty before the blowpipe. Practically insoluble in acids.

Genesis and occurrence. As a mineral of *magmatic* origin, diopside is a common constituent of basic and ultrabasic igneous rocks (e.g., pyroxenites, peridotites, gabbro, diabases), sometimes pyroxene-diorites, syenites, and also basalts, dolerites, etc.

Often makes up a substantial part of *contact-metasomatic* formations, as a constituent of skarns and contact hornfelses together with wollastonite, garnets, and other minerals in the numerous deposits

of magnetite and other ores in the Urals, Central Asia, Siberia, Transcaucasia, and elsewhere.

Well-developed diopside crystals of similar origin occur in the Nazyam mountains, Zlatoust district (the Urals) in the *Akhmatovskoye mine* among chlorite schists with garnet, clinochlore, etc. Large diopside crystals have been found in marbled limestones on Vesuvius. Very large well-developed crystals were described by Russian Academician V. M. Severgin under the name of "baikalite" (they were found in phlogopite deposits in the *Slyudyanka* district in the south-western part of the Trans-Baikal province).

HEDENBERGITE, $CaFe^{\cdot\cdot}[Si_2O_6]$. Named after L. Hedenberg, the Swedish chemist who was the first to analyse the mineral.

Chemical composition. CaO 22.2%, FeO 29.4%, SiO_2 48.4%. A magnesia-rich variety is called *salite*. Contains negligible amounts of alkalis and alumina.

System, monoclinic; symmetry, prismatic. Hedenbergite occurs mostly in radial and coarse rod-like aggregates.

Colour, dark green to black-green. **Streak**, light grey with a greenish tint. **Lustre**, vitreous. For pure hedenbergite: $n_x = 1.757$, $n_y = 1.745$, and $n_z = 1.739$.

Hardness, 5.5 to 6. **Cleavage**, parallel to the {110} prism, with an intersection angle of 87°. **Specific gravity**, 3.5 to 3.6.

Diagnostic features. Readily identifiable by rod-like aggregates, dark-green or greenish-black colour. Like salite, generally occurs at the contact of intrusive rocks with marbled limestones.

Before the blowpipe fuses to a black magnetic glass.

Genesis and occurrence. Along with salite, hedenbergite is a common mineral in many *contact-metasomatic* deposits of magnetite, sometimes of copper sulphide ores, and in certain high-temperature hydrothermal deposits of metasomatic origin in limestones. Paragenetically associated with hedenbergite are ilvaite, magnetite, ferruginous garnets, sulphides (pyrrhotite, chalcopyrite, black sphalerite), calcite, epidote, etc.

In such deposits hedenbergite develops clearly, by replacing limestone or marble. In turn, hedenbergite, as well as salite, may be metasomatically replaced by iron and copper sulphides, ilvaite, sometimes by epidote, chlorites, and other minerals.

In the U.S.S.R., occurs in the *Turya copper mines* (in the skarn zone); at the Chokpak deposits (Kazakhstan), *Troitsky mine* (the Altai), at *Jimara* (Osetia), and elsewhere.

AUGITE, $Ca(Mg, Fe, Al)[(Si, Al)_2O_6]$. Aluminiferous pyroxene. From the Greek "auge" for lustre (crystal faces are often lustrous). An important rock-forming mineral of certain igneous rocks.

Chemical composition is much more complex than that of other pyroxenes. Contains almost invariably an excess of MgO and FeO and,

what is most important, augite is enriched in Al_2O_3 (4 to 9%), Fe_2O_3, and also Na_2O. MgO is partially replaced by FeO and MnO.

Aegirine-augite, a variety rich in Na_2O and Fe_2O_3, differs from common augite in optical properties; is common in basic igneous rocks. A variety intermediate in composition between augite and aegirine-augite is called *fedorovite* after the Russian crystallographer Y. S. Fyodorov.

Titanaugite, a variety rich in TiO_2, Fe_2O_3, and Al_2O_3(TiO_2 4 to 5% as compared with 0.1 to 0.7% for common augite).

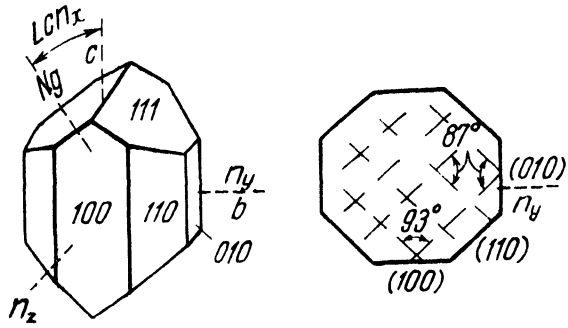


Fig. 318. Augite crystal. Right: cross section and cleavage.

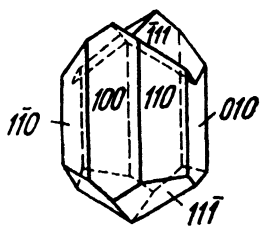


Fig. 319. Augite twin parallel to (100).

System, monoclinic; symmetry, prismatic. **Habit**, short-columnar, tabular, more seldom isometric. In distinction from diopside, the {110} prism faces are generally better developed than those of the pinacoids. The most common crystal form and cross section are shown in Fig. 318. The most typical cross section is octagonal with more or less equally developed sides. Twins common, twin plane (100) (Fig. 319). **Aggregates**, massive granular.

Colour, black, greenish- and brownish-black, more seldom dark green or brown. **Lustre**, vitreous. $n_x = 1.710$ to 1.724, $n_y = 1.692$ to 1.706, and $n_z = 1.685$ to 1.700.

Hardness, 5 to 6. **Cleavage**, parallel to the {110} prism distinct. Sometimes a parting parallel to {100}. The augites and other monoclinic pyroxenes with such sharply pronounced parting are called *diallage*. **Specific gravity**, 3.2 to 3.6.

Diagnostic features. Individual augite crystals which are readily liberated from volcanic tuffs and basic rock ashes are rather simply recognised by characteristic form (cf. Fig. 318) and black colour. In other cases positive identification is impossible without careful microscopic examination and chemical analyses.

Fuses with difficulty before the blowpipe. Insoluble in acids. Titanaugite dissolves completely in hot hydrochloric acid.

Genesis and occurrence. Augite most commonly occurs in certain *magmatic* effusive rocks of basic composition: andesites, phonolites, basalts, in their tuffs and volcanic ashes. These rocks sometimes yield

rather large crystals of characteristic form (cf. Figs. 318 and 319). Common associates are basic plagioclases, magnetite, sometimes olivine, etc.

Aegirine-augite is found in basic igneous rocks, such as nepheline-syenites in the *Ilmen mountains* (Southern Urals), and also in their effusive analogues such as phonolites, leucitophyres, etc.

During the post-magmatic stage augite and other monoclinic pyroxenes may be replaced by the amphibole minerals. Under the microscope one frequently observes the development of hornblende at this stage as a single whole, the pyroxene form being preserved. Such pseudomorphs are known as *uralite* (they were first recognised in the Urals).

In the course of hydrothermal alteration of igneous rocks, augite decomposes and is often replaced by epidote, chlorites, calcite, and other minerals.

JADEITE, $NaAl[Si_2O_6]$. The jadeite molecule enters into the composition of diopside and aegirine, which explains their increased Na_2O and Al_2O_3 content.

System, monoclinic. Crystals are rare; jadeite occurs mostly in compact granular aggregates of apple-green, greenish-blue, and white colour. **Lustre**, vitreous. $n_x = 1.667$, $n_y = 1.659$, and $n_z = 1.654$.

Hardness, 6.5 to 7. Extremely tough. **Cleavage**, {110} distinct, {010} and {100} imperfect. Fracture of cryptocrystalline varieties is uneven and splintery. The mineral strongly resembles nephrite (amphibole group). **Specific gravity**, 3.3 to 3.4. Before the blowpipe readily fuses to a translucent glass. Soluble in acids only upon fusion.

Occurs in metamorphic alkaline rocks, more seldom in contact-metasomatic formations.

AEGIRINE, $NaFe'''[Si_2O_6]$. From Aegir, the Icelandic god of the sea. Synonym: acmite. An extremely important rock-forming mineral of many alkali-rich igneous rocks.

Chemical composition. Na_2O 13.4%, Fe_2O_3 34.6%, SiO_2 52%. Impurities: K_2O, often CaO, FeO, MnO, MgO, Al_2O_3, TiO_2, sometimes V_2O_3, occasionally traces of rare earths, BeO, ZrO_2 and ThO_2. Aegirine and augite, aegirine and diopside, and also aegirine and hedenbergite form isomorphous mixtures. The intermediate varieties are called respectively aegirine-augite, aegirine-diopside, and aegirine-hedenbergite.

System, monoclinic; symmetry, prismatic. **Habit**, usually long-prismatic columnar or acicular (Fig. 320). Faces are vertically striated or furrowed. The (100) face is almost always well-developed. Twins common, twin plane (100); often polysynthetic. **Aggregates.** Massive, rod-like, radial-fibrous, and stellate.

Colour, commonly greenish black, dark green, sometimes brown or reddish brown (acmite). **Streak**, light green. **Lustre**, vitreous. $n_x = 1.787$, $n_y = 1.768$, and $n_z = 1.742$.

Hardness, 5.5 to 6. **Cleavage**, parallel to the prism, distinct with an angle of 87°; a parting parallel to {010} and {001}. **Specific gravity**, 3.43 to 3.60.

Diagnostic features. Readily identifiable by columnar habit, dark-green or greenish-black colour, and association with alkaline silicates (nepheline, feldspars, alkaline amphiboles). From similar dark-green tourmaline differs by lower hardness and distinct cleavage.

Readily fuses before the blowpipe to a black lustrous magnetic bead. Colours the flame yellow. Poorly soluble in acids.

Genesis and occurrence. Aegirine is a typical rock-forming mineral of alkali-rich igneous intrusive and effusive rocks (nepheline-syenites, phonolites, leucitophyres, etc.). Occasionally is found in contact-metasomatic formations as a product of reaction between basic magmas and host rocks.

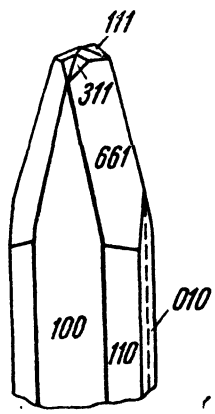


Fig. 320. Aegirine crystal.

Large crystals occur in nepheline-syenite pegmatites in the *Vishneviye* and *Ilmen mountains* (the Urals). Its associates, apart from nepheline, feldspars, and hornblende, are black micas, which sometimes replace aegirine crystals, and also sodalite, cancrinite, and other rare silicates.

SPODUMENE, $LiAl[Si_2O_6]$. Occupies a somewhat special position among the pyroxenes. Forms no isomorphous mixtures with other pyroxenes.

Chemical composition. Li_2O 8.1%, Al_2O_3 27.4%, SiO_2 64.5%. Admixtures may be Na_2O and negligible quantities of CaO, MgO, and occasionally Cr_2O_3. Certain varieties also contain rare earths, sometimes caesium.

System, monoclinic; symmetry, prismatic L^2PC. Space group $C2/c(C^6_{2h})$. $a_0 = 9.50$, $b_0 = 8.30$, $c_0 = 5.24$, $\beta = 110°20'$. **Habit**, prismatic. Vertical faces striated. Occurs often in very large crystals (sometimes up to 16 m long). Twins parallel to (100). **Aggregates**, platy rod-like. Also occurs in compact cryptocrystalline masses.

Colour, greyish white, often with a greenish tinge, yellowish green, violet (kunzite). **Lustre**, vitreous; slightly pearly on cleavage surfaces. $n_x = 1.675$, $n_y = 1.66$, and $n_z = 1.65$.

Hardness, 6.5 to 7 (lower for altered varieties). **Cleavage**, parallel to the prism, perfect or distinct; parting on {100}. **Specific gravity**, 3.13 to 3.20.

Diagnostic features. May be positively recognised by optical constants under the microscope. Spodumene has the smallest angle of extinction of the monoclinic pyroxenes.

Swells in the blowpipe flame, sometimes colouring the flame slightly red (Li). Fuses to a transparent glass. On fusing with CaF_2 + + $KHSO_4$ colours the flame bright red (Li). Insoluble in hydrochloric acid.

Genesis and occurrence. Occurs in granite *pegmatites* in association with quartz, feldspars, lithium micas, tourmaline, etc.

Very susceptible to later alterations. Decomposes in solutions containing Na_2O, giving eucryptite ($LiAlSiO_4$), albite ($NaAlSi_3O_8$), and sericite (potash mica).

We shall mention here but a few of the many spodumene deposits. A very well-known locality is at *Key-stone*, South Dacota (U.S.A.) where enormous crystals of altered spodumene up to 16 m long, about 1 m wide, and 90 tons in weight, have been recorded. The pegmatite deposits of *Madagascar* contain unaltered transparent variously tinted varieties: yellowish green, yellow, pink. At *Branchville*, Connecticut (U.S.A.) large altered spodumene crystals are associated with lithiophylite, uraninite, various manganese phosphates, and other minerals.

Uses. Together with lithium micas, spodumene is a source of lithium for medical preparations, fireworks, photography, glass making, X-ray photography, etc. Transparent beautifully coloured spodumenes have been cut as gemstones. Of late, metallic lithium finds uses in thermonuclear reactions.

ENSTATITE, $Mg_2[Si_2O_6]$. From the Greek "enstates" for resistant (reference to its refractoriness). Varieties with up to 5 per cent of FeO are classified as enstatites, and those with 5 to 14 per cent of FeO ($FeSiO_3$ 25%) are referred to as *bronzite* (although bronze chatoyancy is characteristic of weathered varieties and those containing oriented inclusions). Enstatite is an important rock-forming mineral of magnesian igneous rocks.

Chemical composition. Enstatite contains more SiO_2 than olivine — the purely magnesian variety contains SiO_2 60.0%; MgO 40.0%. Often contains NiO, (usually up to 0.2%). May contain as impurities CaO, MnO, Al_2O_3, and Fe_2O_3.

System, orthorhombic; symmetry, rhombic dipyramidal $3L^23PC$. Space group $Pbca(D_{2h}^{15})$. $a_0 = 18.2$; $b_0 = 8.86$; $c_0 = 5.20$. **Habit.** Rare enstatite crystals are either prismatic (Fig. 321), or more seldom tabular. Irregular grains widely distributed in rocks are frequently elongated. Ordered intergrowths with monoclinic pyroxenes have been observed.

Colour. Colourless, greyish white with a greenish tinge, less often brownish green. **Lustre**, vitreous. $n_x = 1.665$, $n_y = 1.659$, and $n_z = 1.656$.

Hardness, 5.5. **Cleavage,** {110} distinct; cleavage planes intersect at an angle of 85°. **Specific gravity,** 3.1 to 3.3 (increasing with FeO content).

Diagnostic features. In irregular grains, enstatite can be identified positively only by optical constants determined in thin polished sections under the microscope. Differs from the monoclinic pyroxenes by rectangular angle of extinction, sometimes by slight pleochroism, and from hypersthene by optical sign and the angle of optic axes.

Almost infusible before the blowpipe flame. Insoluble in acids.

Genesis and occurrence. A typical mineral of many magnesia-rich magmatic rocks. In association with olivine commonly forms the so-called peridotites, such as harzburgites, and is also an essential constituent of gabbro-norites, sometimes of diorites. Also occurs in effusive rocks (basalts, andesites). Much more seldom found in contact-metasomatic formations, but then often in large well-developed crystals.

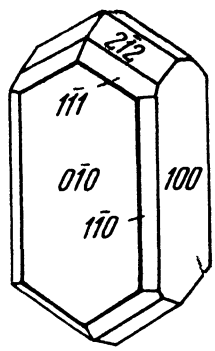


Fig. 321. Enstatite crystal.

When hydrothermal processes are superimposed on the post-magmatic stage, enstatite, more readily than olivine and the monoclinic pyroxenes, turns into a serpentine known as *bastite*, whose pseudomorphs after enstatite grains constitute crystal individuals with a characteristic well-pronounced parting (cleavage). This parting has a definite crystallographic orientation in relation to the replaced pyroxene. Bastite may be easily recognised in altered enstatite-bearing rocks by its golden-yellow or bronze chatoyancy on cleavage surfaces.

As a rock-forming mineral, enstatite frequently occurs in many igneous, especially intrusive, rocks (e.g., harzburgites, lherzolites, etc.) rich in magnesia but poor in calcium oxide. Such rocks are widespread in the Urals, Northern Caucasus, Trans-Caucasia, in Siberia, and elsewhere.

HYPERSTHENE, $(Mg, Fe)_2[Si_2O_6]$. From the Greek words "hyper" and "sthenos" meaning very strong. Orthorhombic pyroxenes containing over 14 per cent of FeO are usually classed with hypersthene.

Hypersthene has many physical properties in common with enstatite. Owing to the greater FeO content, refractive indices are higher for hypersthene than for enstatite: $n_x = 1.69$ to 1.73 and $n_z = 1.68$ to 1.71.

Colour, green to greenish- or brownish-black. **Specific gravity,** 3.3 to 3.5. Before the blowpipe fuses to a greenish-black enamel, magnetic for more ferruginous varieties. Partly soluble in hydrochloric acid.

Occurs in iron-enriched basic igneous rocks (gabbro-norites, certain varieties of trachyte and andesite).

Strongly ferruginous hypersthenes are found in large masses in the Slyudyanka district (South-Western Baikal province) in pyroxene-amphibole, biotite, and garnet gneisses. Also has been found in meteorites.

b. *Silicates with Double* $[Si_4O_{11}]$- *Anionic Chains*

GROUP OF AMPHIBOLES

The constitution of amphiboles is much more complex than that of pyroxenes, although both have much in common in qualitative composition.

According to X-ray data, a characteristic feature of the amphiboles, as stated earlier, is the presence in their crystal structure of the double chains (ribbons) of silicon-oxygen tetrahedra, conforming to the formula $[Si_4O_{11}]^{6-}$ (instead of Si_4O_{12} as could be expected from the chemical standpoint for a metasilicate). The remaining oxygen ion enters into the composition of the independent $[OH]^{1-}$ univalent anion. Thus, the total negative charge of the anionic complex is 7. This explains the chemical formula of so simple amphibole as anthophyllite: $Mg_7[Si_4O_{11}]_2[OH]_2$. The replacement of two oxygen ions, not bonded with Si, by two univalent $[OH]^{1-}$ ions causes a decrease in the number of cations: the number of the Mg ions is 7, not 8, as it was assumed according to the formula $MgSiO_3$ for anthophyllite.

Similarly, for binary compounds of the amphibole group, such as tremolite we have the formula: $Ca_2Mg_5[Si_4O_{11}]_2[OH]_2$, whereas prior to X-ray studies it was written $Ca_2Mg_8Si_8O_{24}$. This is further corroborated by recalculation of the data of chemical analyses when the $[OH]^{1-}$ anion is introduced into the formula. The ratio Ca : Mg(Fe) = = 2 : 5, whereas for pyroxenes of corresponding composition, e.g., for diopside, the same ratio is 1 : 1. This is another essential difference between the amphiboles and the pyroxenes.

Finally, for those binary compounds which are rich in trivalent (Al and $Fe^{\cdot\cdot\cdot}$) and univalent (Na and K) metals, we have the following relationship between the different metal groups: (Ca, Na) : :(Mg, $Fe^{\cdot\cdot}$, Al, $Fe^{\cdot\cdot\cdot}$) = 3 : 5. This is due to the extensive substitution of the Al^{3+} ions for the Si^{4+} ions in the chains of silicon-oxygen tetrahedra. As a result, the total negative charge of the chain increases, and therefore, must be neutralised by additional cations (mostly by Na^{1+} and K^{1+}). The amphiboles, as different from the pyroxenes, have corresponding spaces in their crystal structure to accommodate the additional ions of alkaline metals, which need be introduced when silicon is replaced by aluminium as follows $Si^{4+} \rightarrow Al^{3+} \cdot Na^{1+}$. That is why the number of positively charged ions in the structure increases from 7 to 8 (approximately). The Al : Si ratio in the silicon-oxygen chains, according to the data of chemical analyses, does not normally

exceed 1 : 3. The general formula of hornblende is as follows:

$$(Ca,Na)_{2-3}\,(Mg,Fe,Al)_5\,[(Si,Al)Si_3O_{11}]_2\,[OH]_2.$$

When a Si ion in the radical is completely replaced by an Al ion, the number (Ca, Na) should be 3, which is actually the case (provided the calculated remaining quantity of Al^{3+} or Fe^{3+} ions being linked to Mg and $Fe^{\cdot\cdot}$, is small). Otherwise, there may be an additional compensation of the negative charge by replacement of Mg by Al. According to chemical analysis data such cases do occur, though rarely (koksharovite, hastingsite).

Another chemical characteristic of the amphiboles is the frequent replacement of OH by F and Cl. The total number of these ions according to the formula should be 2, but it may be less (apparently they are replaced in part by oxygen ions).

Although the composition of the amphiboles varies within broad limits, all of them have much in common both in physical and chemical properties. The mode of formation of amphiboles in nature is somewhat different from that of pyroxenes. The presence of hydroxyl, fluorine, and chlorine indicates that the formation of amphiboles in igneous and metamorphic rocks depends on mineralisers which enable them to crystallise at relatively low temperatures. The frequent replacement of pyroxenes by amphiboles also indicates their more recent formation. Soviet scientist D. P. Grigoryev has succeeded in obtaining amphiboles artificially but only when the silicate melt contained fluorine. Amphiboles corresponding to their natural counterparts, i.e., containing OH, have been obtained artificially by another Soviet scientist I. A. Ostrovsky.

The following mineral species of the amphibole group will be described:

Monoclinic amphiboles

Tremolite	$Ca_2Mg_5[Si_4O_{11}]_2[OH]_2$
Actinolite	$Ca(Mg, Fe)_5[Si_4O_{11}]_2[OH]_2$
Hornblende	$Ca_2Na(Mg, Fe)_4(Al, Fe)[(Si, Al)_4O_{11}]_2[OH]_2$
Glaucophane	$Na_2(Mg, Fe)_3Al_2[Si_4O_{11}]_2[OH, F]_2$
Arfvedsonite	$Na_3(Fe, Mg)_4(Fe, Al)[Si_4O_{11}]_2[OH, F]_2$

Orthorhombic amphiboles

Anthophyllite	$(Mg, Fe)_7[Si_4O_{11}]_2[OH]_2$

TREMOLITE, $Ca_2Mg_5[Si_4O_{11}]_2[OH]_2$. Named after the place of discovery, Tremola Valley on the southern slope of Saint Gotthard. One of the most common amphiboles in nature.

Chemical composition. CaO 13.8%, MgO 24.6%, SiO_2 58.8%, H_2O 2.8%. MgO may have insignificant isomorphous admixtures (up to 3 per cent) of FeO (in varieties transitional to actinolite) and MnO, and also Al_2O_3, alkalis, etc.

System, monoclinic; symmetry, prismatic L^2PC. Space group $C2/m(C_{2h}^3)$. $a_0 = 9.78$; $b_0 = 17.8$; $c_0 = 5.26$; $\beta = 106°02'$. **Habit.** Crystals rather simple in form, long prismatic, acicular, sometimes capillary, elongated parallel to the *c* axis. Occurs mostly in thin radial, rod-like or fibrous, sometimes felted aggregates. Less often in compact cryptocrystalline, extremely tough masses, splintery on fracture and white in colour which are known as *nephrite* (cf. actinolite), and also as asbestos which is of great economic importance.

Colour, white or light-coloured with predominantly greyish tints. **Lustre**, vitreous. $n_x = 1.624$, $n_y = 1.613$, and $n_z = 1.599$.

Hardness, 5.5 to 6. Brittle. Acicular and capillary crystals are friable. **Cleavage**, parallel to the {110} prism perfect, with an angle of 124°, (010) imperfect. **Specific gravity**, 2.9 to 3.0.

Diagnostic features. Tremolite differs from actinolite, which is very similar to it in physical properties, chiefly by its light colouring (white or greyish white).

Before the blowpipe fuses with difficulty to transparent colourless glass (in distinction from actinolite). Almost insoluble in acids.

Genesis and occurrence. As all the other amphiboles, tremolite in igneous rocks is a typical epimagmatic, low-temperature mineral, frequently formed after calcium-magnesial pyroxenes. It is often found in metamorphosed crystalline limestones and dolomites, and also in crystalline schists and hornfelses.

Well-developed crystals occur in Alpine clefts in many places in Switzerland, in the East Alps, Bohemia, and elsewhere. In the U.S.S.R., tremolite has been recorded from dolomites along *Sanarka* and *Kamenka rivers*, Kochkar district (Southern Urals), at *Slyudyanka*, South-Western Baikal province, and elsewhere.

ACTINOLITE, $Ca_2(Mg, Fe'')_5[Si_4O_{11}]_2[OH]_2$. From the Greek "actis" meaning ray, and "litos" stone, since the mineral commonly occurs in acicular-radial aggregates.

In many physical properties, actinolite is perfectly similar to tremolite, from which it differs by green colour (due to iron content) and optical constants. We shall mention some of its peculiar features.

Chemical composition. From the chemical viewpoint, actinolite is a ferruginous variety of tremolite. The FeO content normally varies from 6 to 13 per cent. Often contains also Al_2O_3, and hence some alkalis (Na_2O).

Colour, bottle-green of varying shades: from light greenish grey to dark green. **Specific gravity**, 3.1 to 3.3 (increasing with FeO content).

Before the blowpipe fuses with difficulty to greyish-green or greenish-black glass.

Varieties. According to morphological features and the structure of aggregates, the following varieties are distinguished:

1. *Nephrite* (jade). Cryptocrystalline compact, extremely tough, tinted green, possessing a splintery fracture and sometimes glimmering lustre. "Nephros" is the Greek for kidney.

2. *Amianthus*, amphibole asbestos (tremolite asbestos, actinolite asbestos, etc.). This amphibole variety characteristically occurs in veinlets (up to several centimetres thick) which possess a strictly parallel fibrous texture, the fibres being perpendicular to the walls of the veinlets. A very important feature of typical amphibole-asbestos minerals is their ability to split into very thin *elastic* and strong fibres the cross section of which approaches the dimensions of the dispersed phase in colloids. Owing to their refractory and acid-resistant properties they find use in many industries.

Genesis and occurrence. Like all the other amphiboles, actinolite is stable at relatively low temperatures. It occurs mostly in crystalline schists formed at shallow depths (sometimes in very large quantities). Together with tremolite, it is detected under the microscope in many igneous, chiefly basic, rocks which have undergone hydrothermal metamorphism. Is associated with epidote, chlorite, quartz, zoisite, and talc.

In the U.S.S.R., actinolite asbestos occurs in veinlets in the pyrite-chalcopyrite deposits of *Belorechenskoye* and *Kalatinskoye* deposits, north of Sverdlovsk (the Urals). The asbestos veinlets characteristically occur together with long acicular actinolite crystals. The latter are older formations in the pyrite-chalcopyrite mass of typically metacolloidal structure.

Well-rounded smooth boulders of grass-green nephrite are found along the *Onon* and *Chikoy rivers*, and also as primary deposits in actinolite schists along the *Khara-Zhelga* spring (south of Lake Baikal), as well as in Central Asia at the *Raskom-Darya River* (eastern Pamirs), and elsewhere. Outside the Soviet Union, nephrite occurrences are known in *New Zealand*, *Tasmania*, *New Caledonia*, and in the other islands of Polynesia where the indigenous population until recently used it for making axes, spear-heads, and other objects. Nephrite occurs also in the *Kuenlun* mountains (western China) and farther east up to the *Kwansu* province, where large amounts of it have been quarried from placers and primary deposits since antiquity. Since nephrite rather easily lends itself to the lapidary's art, and is very durable, it has been fashioned into images of deities, charms, vases, plates, and other objects now on display in many museums.

HORNBLENDE, $Ca_2Na(Mg, Fe^{\cdot\cdot})_4(Al, Fe^{\cdot\cdot\cdot})[(Si, Al)_4O_{11}]_2[OH]_2$. The term hornblende is often erroneously identified with the term amphibole. "Amphibole" is a name applied to the whole group under consideration, while hornblende is only a species of the group.

Chemical composition is variable. Thus the magnesium-divalent iron and the aluminium-trivalent iron ratios vary in wide limits. Sometimes potassium prevails over sodium. Certain varieties contain

up to 0.3 per cent of fluorine. TiO_2 is almost always present (usually from 0.1 to 1.25%).

System, monoclinic; symmetry, prismatic L^2PC. Space group $C2/m(C_{2h}^3)$. $a_0 = 9.8$; $b_0 = 17.9$; $c_0 = 5.28$; $\beta = 106°$. **Habit**, prismatic, columnar, less often isometric. The most common forms are shown in Fig. 322. A twin with twin plane (100) is shown in Fig. 322, right.

Colour. Usually various shades of green or brown, mostly dark to black. **Streak**, white with a greenish tint. **Lustre**, vitreous. $n_x = 1.65$ to 1.69, and $n_z = 1.63$ to 1.66.

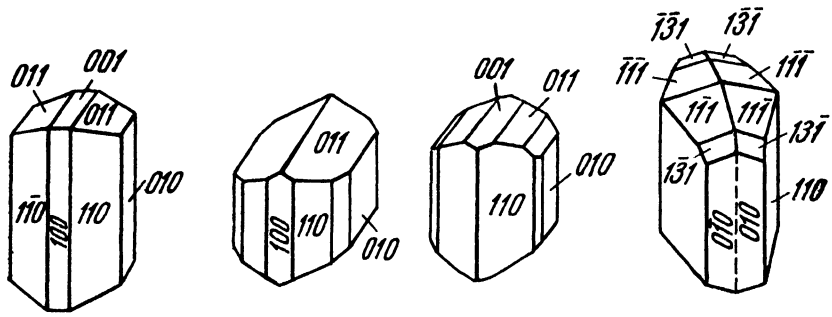


Fig. 322. Hornblende crystals. Right—twin on (100).

Hardness, 5.5 to 6. **Cleavage**, parallel to the {110} prism perfect, with an angle of about 124° (cf. Fig. 316, right), {001} imperfect. **Specific gravity**, 3.1 to 3.3.

Varieties. The following of the numerous varieties which differ mainly in chemical composition and hence in optical properties, will be mentioned.

1. *Basaltic* hornblende, usually brown (in thin polished sections). Occurs in effusive igneous rocks. Characteristically contains much sesquioxides, such as Fe_2O_3 and TiO_2 (2 to 3 per cent).

2. *Uralite*, a hornblende pseudomorph after pyroxene. This variety has the external form of pyroxene crystals (augite or diopside).

The prismatic cleavage revealed in cross sections and polished sections under the microscope is irregular. The uralitisation of pyroxenes is a common occurrence.

Diagnostic features. Crystals of common hornblende are readily recognised by external habit and angle of cleavages (124°), dark-green or dark-brown colour, and by optical properties under the microscope.

Fuses with difficulty before the blowpipe to a dark-green glass. Insoluble in acids, being decomposed by them only upon fusion.

Genesis and occurrence. Common hornblende is a typical mineral of many medium-basic intrusive igneous rocks such as syenites, diorites, granodiorites, etc. In effusive rocks reaching the surface, hornblende rarely occurs as a primary mineral, and then predominantly in alkaline varieties.

Large crystalline grains or crystals are found in comparatively rare *gabbro pegmatites* on Mt. Sokolinaya (Issovsk district in the Northern Urals); well-formed crystals of hornblende in pegmatite dikes may be as long as 0.5 m. Hornblende-bearing rocks may also develop as reaction-metasomatic formations through the action of acidic pegmatites upon ultrabasic igneous rocks.

Hornblende is widely distributed in metamorphic rocks, being the chief constituent of the so-called amphibolites or amphibolitic schists and gneisses. The amphibolites composed of hornblende and plagioclase in many instances had formed in the course of metamorphism of basic rocks, such as gabbro.

In the course of late, hydrothermal processes, hornblende often alters to serpentine, chlorite, and epidote with calcite and quartz. Upon weathering, hornblende, like other ferro-magnesian silicates (e.g., pyroxenes), decomposes to nontronite or carbonates, and, at the surface, to limonite with opal, halloysite, etc.

GLAUCOPHANE, $Na_2(Mg, Fe)_3Al_2[Si_4O_{11}]_2[OH, F]_2$. Composition variable. Contains also Fe_2O_3, CaO, etc. Transitional varieties to actinolite and hornblende are known.

System, monoclinic. Occurs in elongated grains, columnar, radial, fibrous aggregates of greyish-blue, bright-blue or bluish-black colour. **Streak**, bluish-grey. **Lustre**, vitreous. For the purest non-ferruginous variety $n_x = 1.639$, $n_y = 1.638$, and $n_z = 1.621$.

Hardness, 6.0 to 6.5. **Cleavage**, parallel to the {110} prism. **Specific gravity**, 3.1 to 3.2. Before the blowpipe readily fuses to a green glass. Colours the flame yellow (as do all the alkaline sodium-rich amphiboles). Insoluble in acids.

Glaucophane is a typical mineral of certain crystalline (glaucophane, mica, etc.) schists, in association with albite, chlorites, epidote, quartz, etc. In the U.S.S.R. it is found at Krivoy Rog, in magnetite-amphibole schists of the Kalbin ridge (Eastern Kazakhstan), on the Apsheron Peninsula (Azerbaijan), and elsewhere.

ARFVEDSONITE, $Na_3(Mg, Fe)_4(Fe, Al)[Si_4O_{11}]_2[OH, F]_2$. System, monoclinic. Occurs in columnar crystalls and in rod-like or granular block aggregates. Slightly translucent in thin polished sections. Streak, dark bluish-grey. $n_x = 1.686$ to 1.708, and $n_z = 1.676$ to 1.695.

Hardness, 5.5 to 6. Cleavage, prismatic parallel to {110}. **Specific gravity**, 3.44 to 3.46. Before the blowpipe readily fuses to a magnetic globule. Insoluble in acids.

Occurs in alkali-rich igneous rocks, often in nepheline-syenites in association with sodalite, eudyalite, etc. Some crystals in pegmatites may be as large as 20 cm. In the U.S.S.R. occurs in the Zhdanov district (the Ukraine), and elsewhere.

ANTHOPHYLLITE, $(Mg, Fe)_7[Si_4O_{11}]_2[OH]_2$. **Chemical composition.** Chemical analyses show the existence of an isomorphous series of mixtures of magnesial ferruginous varieties. Pure ferruginous or pure magnesial varieties have not been found in nature as yet.

System, orthorhombic. **Habit.** Rare crystals are prismatic. Usually massive in radial, rod-like, often fibrous aggregates.

Colour, brownish- or yellowish-grey, brownish-green, sometimes reddish-brown. **Lustre**, vitreous. $n_x = 1.625$ to 1.698, and $n_z = 1.605$ to 1.668.

Hardness, 5.5 to 6. **Cleavage**, parallel to the {110} prism, perfect, with an angle of 125°37′. **Specific gravity**, 2.8 to 3.2.

Fusible with difficulty before the blowpipe. Insoluble in acids. When heated above 400°, alters to a monoclinic modification. Therefore, anthophyllite remains stable only at relatively low temperatures. It is also significant that at 1000° the mineral, according to X-ray tests, alters to enstatite. This means that at higher temperatures with the removal of OH the double chains of SiO_4 tetrahedra turn into single chains.

Occurrence. As a rock-forming mineral, anthophyllite is present in certain crystalline schists. In the U.S.S.R., it has been found in the vicinity of the Mramor mines, Sverdlovsk Region (the Urals), and elsewhere.

c. *Silicates with* $[Si_3O_9]_\infty$ *Anionic Chains*

WOLLASTONITE GROUP

Included in this group are minerals formerly known as "pyroxenoids" or "triclinic pyroxenes". Their empiric formulas are absolutely identical with those of pyroxenes, and therefore the minerals were regarded as metasilicates. In certain structural and other properties, however, these minerals differ materially from the pyroxenes.

WOLLASTONITE, $Ca_3[Si_3O_9]$ or $CaSiO_3$. Named after the chemist W. Wollaston (1766-1828). Synonym: table spar.

Chemical composition. CaO 48.3%, SiO_2 51.7%. Sometimes contains FeO (up to 9%), and negligible impurities of Na_2O, MgO, and Al_2O_3.

System, triclinic; symmetry, pinacoidal. Space group $P\bar{1}(C_i^1)$. $a_0 = 7.88$; $b_0 = 7.27$; $c_0 = 7.03$; $\alpha = 90°$; $\beta = 95°16'$; $\gamma = 103°25'$.

Crystal structure. Contrary to Barnik's conception, the findings of N. Belov and Kh. Mamedov show that in the wollastonite structure the anionic radical is a single $[Si_3O_9]_\infty$ chain in which the active oxygen ions of two $[SiO_4]$ tetrahedra are on one side of the axis, while the third, alternately single $[SiO_4]$ tetrahedron is on the other side. This conception fully accords with such properties of the minerals as cleavage, determining the tabular form of fragments and the frequent fibrous texture of aggregates.

Habit. Wollastonite occurs in tabular (Fig. 324) crystals often elongated parallel to the *b* axis, which accounts for its former name (table spar). The {001} pinacoid is the most developed, next comes {100}, then the {110}, {101} prism faces, etc. Twins are with a composition plane (100) or (001). **Aggregates**, foliated, radially fibrous or rod-like, conchoidal, less often fibrous with parallel and meshed fibres.

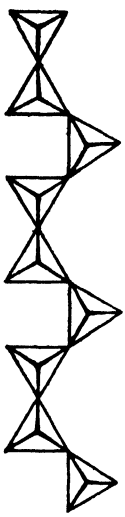


Fig. 323. $[Si_3O_9]_\infty$ anionic chain of the wollastonite type.

Colour, white with a greyish or reddish tinge, less often beef-red. Transparent colourless varieties are also known. **Lustre**, vitreous, on cleavage surfaces sometimes pearly. $n_x = 1.631$, $n_y = 1.623$, and $n_z = 1.616$.

Hardness, 4.5 to 5. **Cleavage**, {100} perfect; {001} distinct, with an angle of 74°; in other directions imperfect. **Specific gravity**, 2.78 to 2.91.

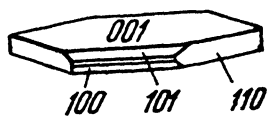


Fig. 324. Wollastonite crystal.

Diagnostic features. In contact-altered limestones wollastonite masses are usually recognised by white or greyish-white colour, radial rod-like aggregates, cleavage, and by paragenetic association with other minerals of contact-metasomatic formation, such as garnets and diopside.

Fusible with difficulty before the blowpipe. Decomposes completely in hydrochloric acid with the separation of silica.

Genesis and occurrence. Occurs mainly in marbled limestones acted upon by acidic magma or in xenoliths of recrystallised limestones in igneous rocks. Common associates: red garnets, diopside, vesuvianite, and other skarn-zone minerals. Such, for instance, are the wollastonite occurrences in the *Turya mines* (Northern Urals), *Minusinsk* contact-metasomatic ore deposits, etc. Mention must be made of exceptionally large wollastonite masses (several thousand cubic metres) at *Sante Fe* in Mexico. Crystals are found in the ejectamenta of Mount Vesuvius.

Wollastonite is also found in calcareous crystalline schists formed through metamorphism at great depths.

Purely wollastonite rocks are used to make the so-called rock wool of white colour, high strength, and long fibres. The rocks are melted in electric furnaces.

RHODONITE, (Mn, Ca) SiO_3. "Rhodon" is the Greek for pink. Synonym: fowlerite.

Chemical composition (per cent): MnO 46.0 to 30.0, FeO 2 to 12, CaO 4 to 6.5, (the maximum content in natural specimens, in which it differs from bustamite, $CaMn[SiO_3]_2$), SiO_2 45 to 48. Impurities: FeO, negligible quantities of alkalis and Al_2O_3.

System, triclinic; symmetry, pinacoidal. **Habit.** Rare crystals occur in cavities and are usually poorly developed, with rough faces and rounded edges. However, Academician Koksharov described as many as 40 crystal forms. The most common crystals are tabular, isometric, less often prismatic. **Aggregates.** Generally massive or granular.

Colour, characteristically pink, sometimes pinkish grey. **Lustre**, vitreous, pearly on cleavage surfaces. $n_x = 1.730$, $n_y = 1.726$, and $n_z = 1.721$.

Hardness, 5 to 5.5. **Cleavage**, {110} and $\{1\bar{1}0\}$ perfect, {001} less perfect. **Specific gravity**, 3.40 to 3.75.

Diagnostic features. Continuous masses identifiable by pink colour. Slightly oxidised individuals characteristically show black streaks of manganese hydroxides (mostly vernadite).

In the oxidising flame turns brown, and then black (oxidation of manganese). In the reducing flame fuses to a red or brown glass. With borax and salt of phosphorous shows a Mn reaction. Slowly decomposes in hydrochloric acid with the separation of white silica powder.

Genesis and occurrence. As a comparatively low-temperature mineral is found in *hydrothermal* and also in *contact-metasomatic* deposits, associated with rhodochrosite, bustamite, and other manganese minerals, and sometimes with sulphides of Mn, Zn, Pb, etc.

Rhodonite is formed in large masses in the course of *regional metamorphism* in sedimentary manganese ores deriving from oxides or carbonates of manganese, and from opal or quartz. It is practically always paragenetically associated with bustamite segregations that are almost invisible to the naked eye, and also with manganous yellow garnets and manganese carbonates.

On weathering, most readily oxidises, forming coatings, crusts, and veinlets of black manganese hydroxides. Divalent manganese changes directly to tetravalent. In a single year blocks of freshly exposed pink rhodonite develop a coating of glossy black vernadite.

The best deposit of rhodonite in the U.S.S.R. is in the Urals. It was once a major source of huge rhodonite blocks used for facings and ornamental purposes. Numerous objects made out of these blocks are now on display in museums. Similar deposits of metamorphosed sedimentary manganese ores, though of smaller size, occur widely in laminated red jaspers, tuffites and other metamorphosed sedimentary rocks in the *Magnitogorsk district* (the Urals); the oxidised zones of this locality are composed of rich manganese ores which are used in steel making.

Uses. Massive rhodonite blocks are used for vases, writing sets, column facings, etc. In particular, rhodonite has been used for facings at the Mayakovskaya Station of the Moscow subway.

SILICATES WITH CONTINUOUS SHEETS OF SiO_4 TETRAHEDRA IN CRYSTAL STUCTURES

Under this heading we shall review mica-like silicates with layered crystal lattices of hexagonal or pseudohexagonal structure (Fig. 325).

A characteristic chemical feature of the mica-like minerals, just as in the amphibole group, is the constant presence of the OH hydroxyl,

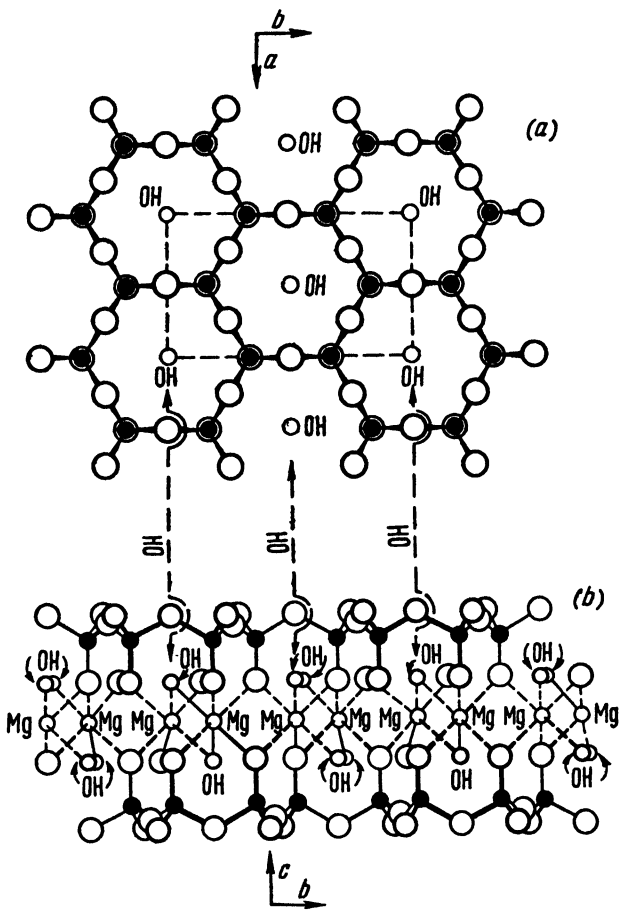


Fig. 325. Hexagonal network of linked SiO_4 groups forming a continuous sheet (*a*).

Below (*b*) —side view of a structure composed of two layers of SiO_4 groups and with one $Mg(OH)_2$ layer in between. Note that the apexes of the SiO_4 tetrahedra in both layers face each other.

often together with F. The most common cations that together with the hydroxyl groups are linked directly to the sheets of silicon-oxygen tetrahedra are Mg^{2+} and Al^{3+}, sometimes replaced respectively by Fe^{2+}, Ni^{2+}, (Mn^{2+}), Li^{1+}, and Fe^{3+}, more seldom by Cr^{3+} and V^{3+}. Moreover, many minerals in which the SiO_4 tetrahedra are partially replaced by AlO_4 contain additional large cations: K^{1+}, Na^{1+}, Ca^{2+}, and

also H_2O molecules (it will be subsequently shown that all of them provide links between the sandwiched silicon-oxygen layers and the ions directly attached to them).

The physical properties of the mica-like minerals naturally most closely depend on their crystal structure. Thus, the structure of planar nets are primarily reflected in the habit of the crystals, the symmetry of which is very close to hexagonal, and optical properties close to uniaxiality; and also in the so-called percussion and pressure figures on cleavage surfaces. The layered crystal structure of the

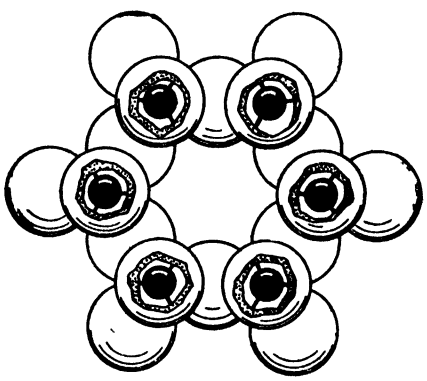


Fig. 326. Hexagonal ring of SiO_4 tetrahedra on plan. Tetrahedral apexes with active oxygen ions face the viewer. Black spheres – Si^{4+} ions, surrounded by four ions of oxygen.

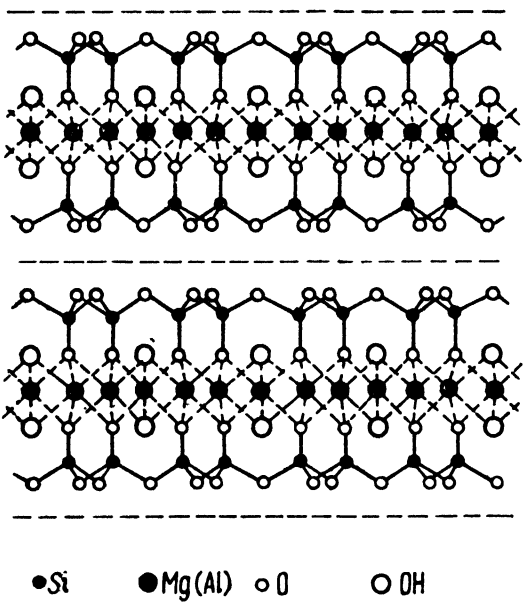


Fig. 327. Crystal structure of talc (or pyrophyllite).

minerals is reflected in their remarkably easy foliation. The foliae of minerals of different groups vary in elasticity depending on the chemical composition, which also has bearing on crystal structure. This needs some explanation. Let us take, for instance, the crystal structure of talc, $Mg_3[Si_4O_{10}][OH]_2$.

The formula for a sheet of silicon-oxygen tetrahedra for all the mica-like minerals is expressed by the $[Si_2O_5]_\infty$ radical, the active oxygen apexes of all tetrahedra being oriented all in one direction (Fig. 326). Each two hexagonally latticed layers, the active sides of which face each other, are linked into one planar sandwich through a "brucite" layer of $Mg[OH]_2$ between them (Fig. 327) which neutralises the total negative charge of the two $[Si_2O_5]^{2-}$ layers. The positive charge of the "brucite" layer is due to the fact that when it enters into the structure, it loses, as it were, a part of its hydroxyls (which are replaced by the active oxygen ions of the $[Si_2O_5]$ radicals. The formation of such planar sandwiches may be expressed by the following equation:

$$[Si_4O_{10}] - 3Mg[OH]_2 - 4[OH] = Mg_3[Si_4O_{10}][OH]_2 \text{ (for talc)}$$

The "brucite" layer may be replaced by a "hydrargillite" layer ($Al[OH]_3$). Then we shall have by analogy:

$$[Si_4O_{10}]+2Al[OH]_3-4[OH]=Al_2[Si_4O_{10}][OH]_2 \text{ (for pyrophyllite)}$$

In the structures of both talc and pyrophyllite the sandwiches possess very strong, almost completely balanced internal bonds. Therefore, such sandwiches are interlinked by very weak residual van der Waals forces (on the flat outer surfaces of the sandwiches the oxygen ions in each SiO_4 tetrahedron are bonded with two Si ions, leaving, therefore, no active valences to maintain a strong link between the sandwiches). This explains the very low hardness of talc and pyrophyllite and their extremely easy cleavage into elastic plates.

In those mica-like minerals in which the Si^{4+} ions are partially replaced by Al^{3+} ions (with the same fourfold coordination) possess materially different properties. As in the case of amphiboles, the replacement of one Si^{4+} ion by an Al^{3+} ion increases the anionic negative charge by a unit. This means that the flat external surfaces of the sandwich become active. The acquired charge is balanced by large *univalent* K^{1+} cations, which can fit *between the sandwiches* only in the large "voids" opposite the centres of the hexagonal or, according to Belov, ditrigonal, rings in the silicon-oxygen layers. These cations formerly believed to be in twelvefold coordination actually are in sixfold coordination. The resulting sandwiches are held together by rather strong bonds. Therefore, the hardness of such minerals (typical micas) is much higher than that of talc: the separated thin foliae are elastic, i.e., when bent they tend to resume their original shape.

When two Si^{4+} ions in a Si_4O_{10} anionic radical are replaced by two Al^{3+} ions, its negative charge increases to 2. In this case it may be balanced by *divalent* cations such as Ca^{2+} whose ions (being of smaller size) are located in other positions than the potassium ions. The *stronger inter-sandwich bonds* resulting from the replacement cause more essential changes in the properties of the mica-like minerals, viz., greater hardness, less pronounced cleavability, brittleness of the separated plates; in view of the latter property minerals of this group are called brittle micas.

Of special interest with regard to the minerals of this subclass is the question of isomorphous replacements. Besides the common isovalent replacement of Mg^{2+} ions by Fe^{2+}, Ni^{2+}, etc., as well as of Al^{3+} ions by Fe^{3+}, Cr^{3+}, etc., a very common phenomenon is heterovalent substitution, provided the number of replacing ions is such that the total charge remains unchanged. Thus, three Mg^{2+} may be replaced by two Al^{3+}. The replacement in this case should proceed in abrupt steps ($Mg_{12}-Mg_9Al_2-Mg_6Al_4-Mg_3Al_6-Al_8$), though these steps so far have not been detected by any chemical analyses. The replacement of ions in this mode takes place in the "brucite-hydrar-

gillite" layers of the sandwiches, three Mg^{2+} ions being replaced by two Al^{3+}, the third place remaining vacant. With the exception of optical properties and specific gravity, the physical properties remain unaltered. Such changes in the chemical compositions of the minerals under consideration constitute *one of the basic features* for their classification.

In some of the micaceous minerals, the laminated sandwiches bonded by weak residual forces alternate with "brucite-hydrargillite" sandwiches (in chlorites) or with layers of H_2O molecules (in hydromicas and similar formations). On crystallochemical grounds, the H_2O molecules in these layers should be strictly oriented, as in all other hydrous minerals.

1. TALC-PYROPHYLLITE GROUP

The group comprises two minerals that have very characteristic physical properties and are probably the end members of an isomorphous series.

As stated in the introduction to micaceous minerals, the two species are very similar in crystal structure. The only difference is that in the talc structure the Mg^{2+} cations occupy all the hexahedral spaces between the two $[Si_4O_{10}]$ hexagonally latticed layers, whereas in the pyrophyllite structure the Al^{2+} cations occupy only two-thirds of the spaces. The less common varieties of intermediate composition (e.g., pyrophyllite with some 30 per cent of talc molecules) evidently periodically include magnesial or aluminous sandwiches, depending on their general composition.

In contrast to many other mineral groups of this subclass, the isomorphous replacement of Mg^{2+} by Fe^{2+} and Ni^{2+} and also of Al^{3+} by Fe^{3+} in the talc-pyrophyllite series has so far been observed on a limited scale. The minerals are so similar in physical properties that externally pyrophyllite is often mistaken for talc and vice versa.

TALC, $Mg_3[Si_4O_{10}][OH]_2$, or $3\,MgO \cdot 4SiO_2 \cdot H_2O$.

Chemical composition, MgO 31.7%, SiO_2 63.5%, H_2O 4.8%. Usually MgO is partially replaced by FeO (2 to 5%). Fairly often contains Al_2O_3 (up to 2%), and occasionally NiO (up to tenths of one per cent).

System, monoclinic. Space group $C2/c(C_{2h}^6)$ or $Cc(C_s^4)$. $a_0 = 5.26$; $b_0 = 9.10$; $c_0 = 18.81$; $\beta = 100°00'$. Very rarely found in tabular crystals of hexagonal or rhombic habit which however cannot be measured. **Aggregates.** Characteristically occurs in foliated, scaly, often compact masses, known as steatite, soapstone or potstone.

Colour, pale green (for thick-foliated masses) or white with yellowish, brownish, greenish tints, sometimes intense. Thin foliae are transparent or translucent. **Lustre**, vitreous with a pearly chatoyancy. $n_x = 1.575$ to 1.590 and $n_z = 1.538$ to 1.545.

Hardness, about 1. Greasy feel. Foliae flexible but not elastic. **Cleavage**, {001}, excellent. Cleavage surfaces develop six-rayed percussion figures, the percussion lines being often parallel to the directions of cleavage. Therefore, talc often breaks into rhombic or hexagonal fragments. **Specific gravity**, 2.7 to 2.8. **Other properties.** Poor conductor of heat and electricity. Refractory. Soapstone has a melting point of 1300 to 1400°C.

Diagnostic features. Talc can be distinguished from other minerals by its extreme softness, greasy feel, light colour, and perfect cleavage of foliated varieties, but from pyrophyllite, especially in finely crystalline masses, it can be distinguished only by chemical tests.

Before the blowpipe turns white, splits, and fuses on edges with difficulty to a white enamel. When strongly ignited, becomes very hard (about 6). Insoluble in acids, even on heating. With a nitric-cobalt solution after ignition turns pale pink (in distinction from pyrophyllite).

Genesis and occurrence. Talc occurs mostly as a product of *hydrothermal alteration* of magnesia-rich ultrabasic rocks. In this case it usually associates with residual grains of chrome-spinellids and with recent formations of magnesium carbonates (breunnerite, magnesite) and sometimes also with calcium carbonates. Also very characteristic as recent formations are metacrystals of hematite or magnesite, and occasionally of apatite. Judging by the mineral paragenesis, talc is derived from magnesium silicates under the action of hydrothermal solutions containing carbon dioxide after the following reaction:

$$4(Mg,Fe)_2SiO_4 + H_2O + 3CO_2 \rightarrow Mg_3[Si_4O_{10}][OH]_2 + 3MgCO_3 + Fe_2O_3$$

olivine — talc — magnesite — hematite

The presence of hematite indicates that the reaction proceeds under oxidising conditions. In a reducing environment magnetite and breunnerite are formed, and the talc itself contains some FeO.

An example of such a formation is the *Shabrovskoye* soapstone deposit (25 km south of Sverdlovsk) discovered in the 1820's. It has formed through the alteration of serpentinites under the action of hydrothermal solutions rich in carbon dioxide and genetically associated with more recent granite intrusions. As a result, there developed rocks of most diverse composition: talc-chlorites frequently enclosing crystals of tourmaline, sometimes magnetite and grains of epidote, apatite, and other minerals; pyroxene-garnet-epidote rocks which were formed as a result of introduction of silica with the volatiles; talc-carbonate rocks with hematite and magnetite; talc-chlorite-actinolite rocks, etc. Coarse-foliated talc occurs in veinlets and veins running across the strike of talc-bearing rocks.

Talc deposits are also associated with contact-metasomatic processes. They are formed during the hydrothermal stage at the contact of dolomites with intrusive rocks. In such cases, talc occurs in the form of lenticular bodies, is very pure and of high grade. Its formation evidently occurs as follows:

$$3CaMg[CO_3]_2 + 4SiO_2 + H_2O \rightarrow Mg_3[Si_4O_{10}][OH]_2 + 3CaCO_3 + 3CO_2$$

dolomite talc calcite

Large deposits associated with carbonate rocks occur in *Canada* in the Madoc district where lenticular talc bodies are composed of foliated snow-white, light-grey, and brown talcs with admixture of carbonates (calcite and dolomite), tremolite, and other minerals.

Uses. Talc has many economic uses, mostly in the powdered form and also in slabs and plates.

Finely-ground talc is used in the manufacture of paper and rubber as a filler to increase the volume of the given material without detriment to its useful properties. High-grade non-ferruginous talc is used in talcum and face powders, ointments, and pastes, also in making fireproof and unfading paints, soft pencils for marking glass, fabrics, and metals. In the textile industry, the adsorption capacity of powdered talc is used for bleaching cotton, removing grease spots, etc. Powdered talc is used to make high-voltage insulators, glazes, acid- and alkali-proof vessels, rain water piping, etc.

Talc stone usually containing admixtures of carbonates and chlorites is used as bricks, slabs, etc. Especially refractory are varieties of talc stone rich in magnesite. They are used for lining furnaces, locomotive fire-boxes, etc. Finally, pure talc may be obtained by flotation of powdered talc stone.

PYROPHYLLITE, $Al_2[Si_4O_{10}][OH]_2$, or $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$. "Pyros" is the Greek for fire, "phyllon", a leaf. The name derives from its ability to split into thin leaves in the blowpipe flame. First established as a mineral species by R. Hermann (1829) in the Beryozovskoye gold mine (the Urals).

Chemical composition. Al_2O_3 28.3%, SiO_2 66.7%, H_2O 5.0%. The contents of individual constituents vary within a fairly wide range. Common impurities: MgO (up to 9%, and probably more), FeO (up to 5%), Fe_2O_3, negligible quantities of CaO, alkalis, and titanium oxide.

System, monoclinic. Space group $C2/c(C_{2h}^6)$ or $Cc(C_S^4)$. $a_0 = 5.14$; $b_0 = 8.90$; $c_0 = 18.55$; $\beta = 99°59'$. Never occurs in measurable crystals, usually in lamellar-radial aggregates (cf. Fig. 38) or as cryptoscaly compact rock called *agalmatolite* or *pagodite*. "Agalma" is the Greek for statue, "pagoda" is the Buddhist term for idol and temple. The stone was used by the Chinese for making figures of deities.

Colour, white with a yellowish tint, or pale green, often translucent.

Lustre, vitreous with a pearly chatoyancy in the case of platy aggregates. $n_x = 1.600$, $n_y = 1.588$, and $n_z = 1.552$.

Hardness, about 1. Greasy feel. Thin laminae flexible but not elastic. **Cleavage**, {001} perfect. **Specific gravity**, 2.66 to 2.90.

Diagnostic features. Pyrophyllite is characterised by very low hardness, light colour, pearly or glimmering lustre. Can be distinguished from talc only by chemical analyses or its reaction with nitric cobalt. Pyrophyllite is often mistaken for talc. Cases are known when pyrophyllite deposits were initially explored as talc deposits for which they were mistaken. Infusible before the blowpipe. Separates into very thin leaves and turns into a snow-white mass. When ignited at high temperature in the closed tube, yields water and acquires silvery chatoyancy. Insoluble in acids. On ignition, turns blue in Co $[NO_3]_2$ solution (presence of Al).

Genesis and occurrence. Pyrophyllite occurs in certain *hydrothermal* vein deposits as a low-temperature mineral associated with quartz, carbonates, hematite, and other minerals deriving from hydrothermal decomposition of igneous, usually acid rocks.

It is also common in some alumina-rich metamorphic schists in which it sometimes occurs in large masses. May be pseudomorphous after andalusite, disthene, muscovite, and other aluminium silicates and alumosilicates, probably as a result of hydrothermal processes.

Stellate (cf. Fig. 39) and lamellar-radial pyrophyllite aggregates of remainable pale-green colour and pearly chatoyancy occur in quartz veins among pyrophyllite-carbonate rocks in the area between the *Beryozovskoye* and the *Pushma* mines near Sverdlovsk (the Urals). There pyrophyllite forms fringes on the walls of quartz-filled veins. Finely-lamellar and compact pyrophyllite masses have also been found at Miass (the Southern Urals).

Large agalmatolite deposits are known in *China*. Considerable masses of pyrophyllite schists occur in Arkansas, Georgia, and North Carolina (U.S.A.). Another important locality is *Ouro Preto* (Minas Geraes, Brazil), where it occurs in lamellar aggregates associated with topaz. In general, pyrophyllite is a widespread mineral.

Uses. When found in quantity, pyrophyllite is of definite economic importance. Because of its properties pyrophyllite has many uses in the manufacture of paper, ceramics, refractories (furnace linings), electrical equipment (insulators), rubber (as a filler), etc., (cf. talc). In ancient times the Chinese used its compact varieties for various carvings, statuettes, slate pencils, etc.

2. MICA GROUP

Micas are widely distributed in nature, and often are rock-forming minerals. The total amount of micas in the earth's crust is approximately 3.8 per cent, principally in acidic intrusive rocks and in crystalline mica schists.

The chemical composition of micas is highly variable, and cation replacement is very frequent. From the chemical standpoint, these minerals constitute a special group of alumosilicates, the most typical compositions of which may be expressed as follows: $R^{\cdot}R_3^{\cdot\cdot}[AlSi_3O_{10}][OH]_2$, or $R^{\cdot}R_2^{\cdot\cdot\cdot}[AlSi_3O_{10}][OH]_2$, where $R^{\cdot} = K$; $R^{\cdot\cdot\cdot} = Al$, often Fe^{3+}, Mn^{3+}, occasionally Cr^{3+}, V^{3+}, sometimes Ti^{4+}; $R^{\cdot\cdot} = Mg$, often Fe^{2+}, Mn^{2+}, and also Li^{1+}*, etc. The Na^{1+} ion is rarely present in micas in considerable amounts, and Ca^{2+} and Ba^{2+} are usually absent. The hydroxyl may be replaced by F (mostly in magnesium and lithium micas).

Thus, the micas exhibit wide isomorphous mixtures, in which on the one hand, Mg^{2+} is replaced as usual by Fe^{2+}, Al^{3+} by Fe^{3+}, and on the other hand, there certainly occurs heterovalent isomorphous replacement of $Mg^{2+}(Fe^{2+})$ by $Al^{3+}(Fe^{3+})$, etc.

All the minerals of the mica group crystallise in the monoclinic system; their crystals are usually hexagonal in outline. The crystal structures are characteristically lamellar. The behaviour of Al in these structures is of special interest. According to the current interpretation of the structure of micas, this element in the form of alumo-oxygen tetrahedra only partially enters into the composition of the complex anion, replacing a quarter of silicon-oxygen tetrahedra.

The surplus of Al enters into the composition of the mineral but in sixfold coordination, replacing the Mg cations. The behaviour of Fe^{3+} in iron-rich micas is probably very much the same.

Though widely differing in chemical composition, micas are very much alike in physical properties since these minerals have the same type of crystal structure.

The natural mode of formation of micas is rather specific. These minerals never occur in high-temperature effusive rocks as early segregations directly from the magma. In acid or intermediate intrusive igneous rocks they appear as late magmatic and postmagmatic minerals, probably through the action of highly volatile agents (muscovite granites, greisens). Large mica crystals occur in pegmatites, often in high- and medium-temperature hydrothermal deposits of tungsten, molybdenum, etc. They are also widespread in many metamorphic rocks, such as crystalline schists (gneisses, mica schists, etc.).

According to chemical composition, micas may be divided into the following subgroups:

(1) biotite subgroup (magnesium-iron micas);
(2) muscovite subgroup (aluminium micas);
(3) lepidolite subgroup (lithium micas).

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* The magnesium is replaced by lithium together with aluminium as follows: $3Mg^{2+} \rightarrow Li^{1+}_{1.5} + Al^{3+}_{1.5}$.

Biotite Subgroup

This subgroup includes magnesium-iron micas: phlogopite and biotite.

PHLOGOPITE,

$KMg_3[Si_3AlO_{10}][F, OH]_2$, or $K_2O \cdot 6MgO \cdot Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$. The name derives from the Greek "phlogopos" for firelike (reference to the colour of the mineral). Synonym: magnesium mica.

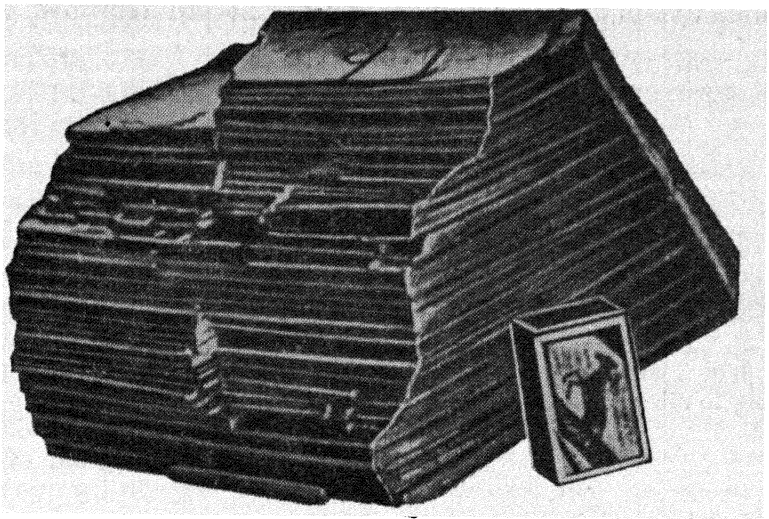


Fig. 328. Large phlogopite crystal.

Chemical composition (per cent): K_2O 7.0 to 10.3, MgO 21.4 to 29.4, Al_2O_3 10.8 to 17 (should be 12.2 according to formula), SiO_2 38.7 to 45.0 (should be 43.2 according to formula), H_2O 0.3 to 5.4, F up to 6. Most frequent impurities are FeO (up to 9%), BaO up to 2.5% (barium phlogopite), Na_2O (up to 2%), and also Fe_2O_3, sometimes MnO, CaO, Cr_2O_3, NiO, etc.

System, monoclinic; symmetry, monoclinic prismatic L^2PC. Space group $C/2c(C_{2h}^6)$. $a_0 = 5.32$; $b_0 = 9.21$; $c_0 = 20.48$; $\beta = 100°12'$. The **crystal structure** of micas, as we have already said, is characterised by the presence of aluminium-oxygen tetrahedra in the layers of silicon-oxygen tetrahedra with an Al : Si ratio of 1 : 3. As a result, between the three-layer sandwiches with a formula of $Mg_3[Si_3AlO_{10}][F, OH]_2$ there appears a residual negative charge which is balanced by the univalent K^{1+} cation (see below, Fig. 334*a*). In distinction from other micas, the Mg ions occupy all the sites of sixfold coordination between two aluminium-silicon-oxygen layers inside the lamellar phlogopite sandwiches. **Habit**, tabular (pseudohexagonal), short-prismatic, and sometimes truncated pyramidal. Crystals are often coarsely developed (Fig. 328) with distinct parallel striations on the side faces. Crystals of phlogopite are indistinguishable by form from those of biotite. Twins are frequent and may obey different laws

The most common are those in which the twinning axis coincides with the (001) composition plane and is perpendicular to the *c* axis and to the (001) : (110) edge (Fig. 329); hence, the twinning plane will be perpendicular to the (001) plane and parallel to the M {110} face. This is the so-called *mica law* of twinning. Trillings may develop according to the same law with the {001} pinacoid shared. In such trillings individuals interpenetrate (Fig. 330) and often show a pinnate texture in relation to the composition faces, due to thin rectilinear folds or coarse striations running perpendicular to the (110) : (001) edge. There also exists another law known as the chlorite law, which is not

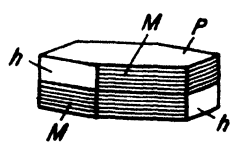


Fig. 329. Twin according to mica law.

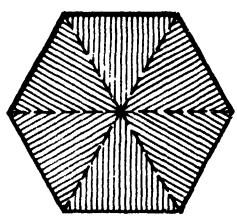


Fig. 330. Penetration trilling according to mica law.

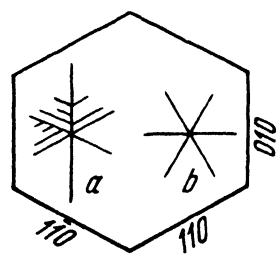


Fig. 331. Percussion figure (*a*) and pressure figure (*b*) on cleavage plane of mica.

characteristic of the micas. Under this law the (001) plane is both the twinning and the composition plane. **Aggregates** are lamellar-platy and scaly.

Colour, light yellowish or reddish brown; more seldom the mineral is colourless, silvery, sometimes with a greenish tinge; thick plates are dark brown. **Lustre**, vitreous, pearly on cleavage surfaces. $n_x = n_y = 1.565$ to 1.606 and $n_z = 1.535$ to 1.562.

Hardness, 2 to 3. Thin plates are elastic. **Cleavage**, {001} hihgly perfect; {110} and {010} imperfect, the latter being glide planes. These planes are clearly brought out in the so-called *percussion figure* which is obtained in all micas on the (001) cleavage surface by placing a blunt needle against it and striking it with a hammer. As a result, a network of three intersecting lines is produced resembling a six-rayed star (Fig. 331). While two of the rays are almost parallel to the edges of the {110} prism, the third and the longest is parallel to the plane of symmetry. If a thick plate of the mineral is placed on something soft and pressure exerted upon it with a small ball or a ball-pointed cylinder, *a pressure figure* will develop, i.e., a six-rayed star with the rays perpendicular to the edges (Fig. 331). The rays are rotated over 30° as compared with those of the percussion figure. Both figures are characteristic of all the mica minerals. **Specific gravity**, 2.70 to 2.85. **Other properties.** Very high specific ohmic resistance and other dielectric properties.

Diagnostic features. Light-coloured phlogopites cannot be distinguished from muscovite externally, but have different optical constants; phlogopite like other dark magnesium-ferruginous micas is optically almost uniaxial while muscovite is definitely biaxial and has a large angle of optic axes. Phlogopite is distinguished from biotite by lighter colour.

Fuses with difficulty before the blowpipe (at 1330°). Soluble in acids, especially in H_2SO_4.

Genesis and occurrence. Phlogopite is quite common in *contact-metasomatic* formations and in *pegmatite* dikes which intersect dolomitised limestones and other magnesium rock poor in silica and iron (e.g., serpentinites). The most common associates are diopside, forsterite, spinel, dolomite, calcite, feldspars, scapolites, etc.

Also found in metamorphic rocks (crystalline schists) usually associated with minerals relatively poor in iron. In polished sections, may be easily mistaken for muscovite, unless the optical constants are measured.

A notable phlogopite occurrence is in the vicinity of the *Slyudyanka* station (Trans-Baikal Region). Numerous pegmatite dikes and metasomatic formations genetically associated with granite intrusions, have formed there among a large complex of crystalline schists, gneisses, and marbles. Phlogopite-bearing mineral bodies are usually associated with pyroxene-amphibole gneisses and commonly occur in groups. Such veins are of a rather complex structure. The diopside-phlogopite formations develop in their wall rocks (irrespective of their composition). Coarse-crystalline phlogopite is usually associated with diopside, scapolites, calcite, apatite, and other minerals. Crystals are often barrel-shaped, acutely terminated, and may be up to 1.5 m long. Phlogopite crystals may be colourless or with a yellowish tinge; silver white, occurring chiefly in limestones; amber-coloured, occuring among aplitoid gneisses; cherry-coloured or amber-red; dark brown, sometimes with a golden chatoyancy; dark green; and almost black, occurring among pyroxene-hornblende and biotite gneisses. On weathering ferruginous phlogopites fade and turn blue. Often phlogopite crystals contain inclusions of calcite, scapolite, and diopside, and also of rutile, which under the microscope appears as extremely thin needles (sagenite), etc. Apart from Slyudyanka, such phlogopite deposits are found in the Aldan district of Eastern Siberia.

Approximately the same mode of occurrence is characteristic of the *Ontario* phlogopites (Canada) where the mineral occurs in veins and irregular pockets. It is associated with calcite, diopside, and apatite in most diverse proportions. Crystals sometimes measure 2 m across. Amber colour is predominant. Similar deposits occur in *Madagascar, Ceylon, India, Korea,* and elsewhere.

Uses. Coarse-crystalline masses of phlogopite are important economically. For uses see "Muscovite".

BIOTITE,

$K(Mg, Fe)_3[Si_3AlO_{10}][OH, F]_2$, or $K_2O \cdot 6(Mg, Fe)O \cdot Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$. A very widespread mineral.

Chemical composition. Analyses of minerals classed as biotites have shown the following variations in composition (per cent): K_2O 6.18 to 11.43, MgO 0.28 to 28.34, FeO 2.74 to 27.60, Fe_2O_3 0.13 to 20.65, Al_2O_3 9.43 to 31.69, SiO_2 32.83 to 44.94, H_2O 0.89 to 4.64, F 0 to 4.23. Impurities: TiO_2, Na_2O, and also V_2O_3, Li_2O, MnO, BaO, SrO, Cs_2O, etc.

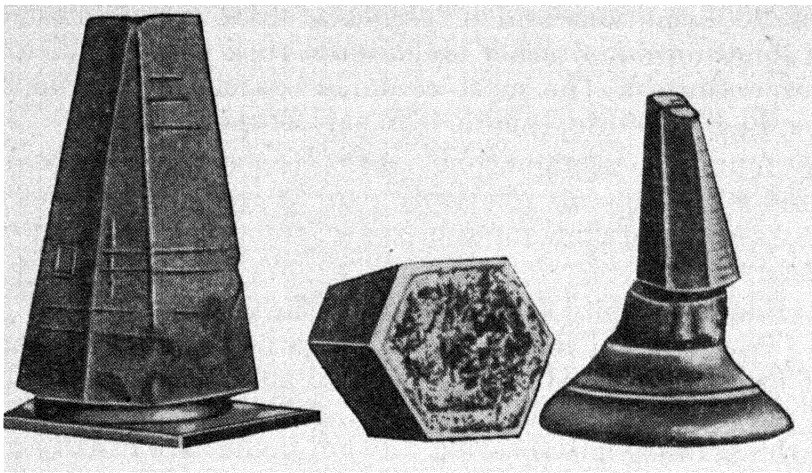


Fig. 332. Biotite crystals.

System, monoclinic; symmetry, monoclinic prismatic L^2PC. Space group $C2/c(C_{2h}^6)$. $a_0 = 5.30$; $b_0 = 9.21$; $c_0 = 20.32$; $\beta = 99°18'$. **Habit**, tabular, pseudohexagonal, *often* columnar, pyramidal (Fig. 332). Large crystals sometimes show a zonal structure. Twins usually according to the mica law. **Aggregates.** Occurs in massive platy- and scaly-granular aggregates. Crystal druses are comparatively rare.

Colour, black, brown, sometimes with orange, reddish, greenish, and other shades. Opaque or translucent. **Lustre**, vitreous, with pearly chatoyancy on cleavage surfaces. $n_x = n_y = 1.60$ to 1.66, and $n_z = 1.56$ to 1.60.

Hardness, 2 to 3. Thin foliae are elastic. **Cleavage**, {001} highly perfect; {110} and {010} imperfect. **Specific gravity**, 3.02 to 3.12.

Diagnostic features. Identifiable by black colour and external features. Under the microscope is recognised by deep colouring and pronounced pleochroism.

Before the blowpipe fuses with difficulty to a grey or black glass. Slightly soluble in hydrochloric acid but decomposes completely in concentrated sulphuric acid with precipitation of a white silica skeleton.

Genesis and occurrence. As a rock-forming mineral, biotite occurs as impregnations in many magmatic rocks.

Large crystals are found in *pegmatite* dikes. May be associated with muscovite, with which it forms parallel or zonal intergrowths,

the cleavage planes extending unbroken through the individuals of the two micas. Often occurs as impregnations in the so-called *contact hornfelses* formed through the action of granitic magmas on rocks of generally noncarbonate composition.

In mineralised hydrothermal veins, biotite occurs extremely seldom, usually in a semi-decomposed condition.

It is very widespread in such *metamorphic* rocks as crystalline schists, particularly in gneisses.

In the course of intensive chemical weathering, it decomposes. The alkalis are leached out and divalent iron becomes trivalent. The process also evidently involves hydrtation (transformation into hydrobiotite). The mineral becomes lustreless, inelastic, and friable. At the final stage of chemical decomposition it turns into iron hydroxides and clayey matter.

Upon rapid erosion biotite, as a chemically inert mineral, passes into placers, is readily split, attrited and deposited, together with finely dispersed slimes in stagnant waters. In the course of time biotite undergoes certain alterations and assumes an intense golden tinge. These golden spangles are easily detected on panning. Being lighter they appear on the surface of the panning residue. In the miners' vernacular they are known as "cat's gold".

In recent marine sediments biotite grains are subjected to halmyrolysis, i.e., underwater weathering in the course of which they are gradually converted to glauconite (green-coloured hydrosilicate of potassium and trivalent iron).

After mica, biotite is the second most widespread mica mineral. Of the countless biotite occurrences we shall mention only some familiar pegmatite deposits. Thus, in the *Ilmen Mountains* biotite, as a mineral of secondary importance, occurs widely in all the types of pegmatite dikes in the form of large plates (up to 0.5 m in diameter), crystals, and finely-laminated aggregates, associated with potassium-sodium feldspars, nepheline, sometimes with topaz, magnetite, ilmenite, and other minerals. It also occurs in pegmatites near Savvatyeva village, in the vicinity of the *Slyudyanka River* (Borshchovochny Ridge), and elsewhere. Finally, enormous tabular biotite crystals have been recorded from pegmatites in *Greenland* and *Scandinavia* (a 7 m^2 slab was found at Evjo).

Biotite is of little or no use commercially, though craftsmen in the Urals use it as spangles on toys made of coloured stones and various ornamental objects.

Muscovite Subgroup

The subgroup comprises the aluminium micas, chiefly the widespread muscovite and the rare paragonite. Unlike the minerals of the biotite group, and similarly to the talc-pyrophyllite minerals, the $3(Mg, Fe)^{2+}$ in this subgroup are replaced by $2Al^{3+}$.

MUSCOVITE, $KAl_2[AlSi_3O_{10}][OH]_2$, or $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$. From "Musca", the old Italian word for Moscow. In its time, large slabs of muscovite went through Moscow to the western countries, where it was known as "Moscow glass".

Chemical composition. K_2O 11.8%, Al_2O_3 38.5%, SiO_2 45.2%, H_2O 4.5%. The bright-green chromium-bearing (up to several per cent Cr_2O_3) mica is called *fuchsite.*

System, monoclinic; symmetry, monoclinic prismatic L^2PC. Space group $C2/c(C_{2h}^6)$. $a_0 = 5.18$; $b_0 = 9.02$; $c_0 = 20.04$; $\beta = 95°30'$. Crystal structure is shown in Fig. 334*a*. **Habit**, commonly tabular or platy of pseudohexagonal or rhomboidal cross section. Some individuals are columnar-pyramidal. Side faces often have numerous and sharp horizontal striations. Twins are frequent according to mica law (cf. Fig. 329) and rare according to chlorite law. **Aggregates.** Muscovite may occur in continuous foliate-granular or scaly masses. Occasionally in reniform masses with a concentrical conchoidal parting. Cryptoscaly masses with silky lustre, whose scales are hardly visible even under the microscope, are referred to as *sericite.*

Colour. In thin cleavage plates colourless, but often with yellowish, greyish, greenish, and seldom with reddish tinge. Fuchsite is bright green. **Lustre**, vitreous; pearly and silvery on cleavage surfaces. $n_x = 1.588$ to 1.615, $n_y = 1.582$ to 1.611, and $n_z = 1.552$ to 1.572.

Hardness, 2 to 3. Foliae are flexible as in all micas and elastic; some varieties are transitional to brittle micas, whereas others, on the contrary, resemble talc. **Cleavage**, {001} highly perfect; {110} and {010} (glide planes) imperfect. **Specific gravity**, 2.76 to 3.10. **Other properties.** A very good electrical insulator, possessing high resistance to puncture.

Diagnostic features. Muscovite is readily identifiable by external features: light colour, pearly of silvery lustre, excellent cleavage, and easy cleavability into thin transparent elastic foliae. Distinguished from phlogopite by optical constants, chiefly by the angle of optic axes (which is extremely small for phlogopite).

Before the blowpipe the thin foliae fuse with difficulty to a white opaque enamel. Insoluble in acids. Begins to give off water only when red-hot (above 850°).

Genesis and occurrence. A most widespread mineral of the mica group. As a rock-forming mineral enters into the composition of certain *intrusive* rocks, such as granites, especially *greisens*, i.e., their pneumatolytically altered varieties, in which it associates with topaz, lithium mica, quartz, sometimes with wolframite, cassiterite, molybdenite, etc. In this case muscovite chiefly derives from earlier potassium feldspars (orthoclase and microcline).

Commercially valuable large crystals of muscovite occur fairly often in granite *pegmatite* dikes. In such dikes, particularly, in their central portions, muscovite forms pockets 1 to 2 m in diameter, but

usually is sporadically disseminated as large crystals either throughout the pegmatite or along definite zones.

Muscovite crystals sometimes contain minute inclusions of zircon, rutile in the form of a sagenite lattice, apatite, spinel, garnets, tourmaline, quartz, magnetite, etc. Detailed investigation in a number of instances establishes certain regularities in the orientation of these inclusions corresponding to the structural features of the minerals.

Muscovite is seldom found in contact-metasomatic deposits. Sometimes fine grains of muscovite are formed in sandstones at their contact with granites and other acidic igneous rocks.

In *hydrothermal* ore deposits enclosed in hydrothermally altered rocks, very intense sericitisation takes place, i.e., the formation of sericite, a cryptocrystalline water-enriched mica variety.

Muscovite and sericite are very widespread in *metamorphic* rocks. There are known whole blocks of micaceous crystalline schists, sericite-bearing clay shales (phyllites), and quartzites with muscovite. Feldspars are usually absent from such rocks.

Being rather inert chemically muscovite, often on weathering passes into placers. Owing to its high cleavability and low specific gravity, it is usually accumulated as tiny silvery specks in silts or laminated clays, that have formed in bodies of slowly flowing water.

On intensive chemical weathering, muscovite may alter to water-richer hydromicas, hydromuscovites and when alkalis enter into the solution, kaolinite may result.

We shall mention only the most important of the numerous muscovite deposits in pegmatites.

The north-west of the European part of the U.S.S.R. has been a source of mica ever since the 15th century. The mica-bearing pegmatites occur in granites, gneisses, mica schists, and other metamorphic rocks. Muscovite associates with feldspars, quartz, less often with tourmaline, apatite, etc.

Mica deposits are widely distributed in the *Mamsk* district of Eastern Siberia, where a thick mica-bearing band of metamorphic schists is bounded on the north-western and south-eastern sides by granite masses. Muscovite crystals (up to 50 cm) of reddish or yellow-greenish tints are observed in paragenetic association with acidic plagioclases, microcline, quartz, biotite, occasionally with black tourmaline, apatite, garnet, etc. The mica is perfectly transparent and readily splits into thin leaves with a flat smooth surface.

Outside the U.S.S.R., the largest muscovite deposits in pegmatites are in *Bengal* and *Madras* (India) where crystals 3 to 5 m^2 and even larger are found, in North Carolina and Maryland (U.S.A.), in *Brazil*, *Canada*, etc.

Uses. The most important commercial property of muscovite and phlogopite is its high dielectric strength. Mica is usual in sheet form, ground into powder as well as in the form of various mica products.

Sheet mica, the most valuable of all, is used chiefly in making insulators, capacitors, rheostats, telephones, magnetos, incandescent lamps, kerosene stoves, goggles, etc. Sheet mica is graded according to size, transparency, and colour.

Ground mica is made out of trimmings of sheet or scrap mica, and used in some fire-resistant materials—roofing, wallpaper, writing paper, mica board, heat-resistant paints, ceramics, tyres, high explosives (as an adsorbent), lubricants, etc.

Moulded mica, such as micanite, is a substitute for sheet mica wherever requirements are not very stringent (insulation gaskets in some electrical appliances), electrical kettles, pots and irons. Micanite is made out of scrap sheet mica by cementing it with shellac and subjecting the mix to high pressure.

Lepidolite Subgroup

Lepidolite and zinnwaldite are the two principal minerals of the subgroup.

LEPIDOLITE, $KLi_{1.5}Al_{1.5}[Si_3AlO_{10}][F, OH]_2$. As different from the biotite formula, the magnesium ions here are replaced by lithium and aluminium: $3Mg^{2+} \rightarrow Li^{1+}{}_{1.5} + Al^{3+}{}_{1.5}$. "Lepidos" is the genitive of the Greek "lepis" meaning scale. Synonym: lithionite. A rare mica.

Chemical composition is variable (per cent): K_2O 4.82 to 13.85, Li_2O 1.23 to 5.90, Al_2O_3 11.33 to 28.80, SiO_2 46.90 to 60.06, H_2O 0.65 to 3.15, F 1.36 to 8.71. Common impurities: MgO (up to several per cent), FeO, MnO, CaO, Na_2O, Cs_2O, Rb_2O (sometimes up to 3.73 per cent), etc.

System, monoclinic; symmetry, monoclinic prismatic L^2PC. Space group $C2/c(C_{2h}^6)$. $a_0 = 5.20$; $b_0 = 8.95$; $c_0 = 20.12$; $\beta = 100°48'$. **Habit**, tabular, pseudohexagonal. No well-developed crystals. Twins according to the mica law. **Aggregates**, foliated tabular or thin scaly. Occasionally in druses of crystals.

Colour, white but more commonly pink, pale violet, sometimes peach-red (presence of manganese). **Lustre**, vitreous, pearly, silvery on cleavage surfaces. $n_x = n_y = 1.55$, and $n_z = 1.53$. **Hardness**, 2 to 3. The foliae are flexible and elastic. **Cleavage**, {001} excellent; {110} imperfect. **Specific gravity**, 2.8 to 2.9.

Diagnostic features. Is usually recognised by its pink or violet tints. Differs from muscovite in somewhat lower refractive indices, blowpipe behaviour, and the presence of lithium detected by spectral analysis.

Before the blowpipe readily fuses to a white enamel. Colours the flame red. Soluble in acids only on fusion.

Genesis and occurrence. Occurs in altered granites (greisens) and certain pegmatites, sometimes in high-temperature hydrothermal veins. Associated commonly with feldspars, quartz, muscovite (sometimes in parallel intergrowth with the latter), spodumene, lithium tour-

maline, topaz, cassiterite, fluorite, etc. On weathering lepidolite is altered in the same way as muscovite.

In the U.S.S.R., lepidolite is found in certain mines of the Middle Urals and elsewhere in pegmatites, in association with strongly altered soda-potash feldspars, tourmalines of varying colours, topaz, rock crystal, etc. Occurs in thin scaly masses of lilac colour, in coarsely foliated aggregates of a striking violet colour, and in muscovite-like silvery tabular crystals.

Outside the Soviet Union, large long-worked deposits of pink lepidolite are found at *Rozena* (Moravia), on the *Island of Uta* (near Stockholm), and in Maine (U.S.A.).

Uses. Together with zinnwaldite lepidolite is one of the principal sources of lithium salts which are used in alkali storage batteries (in submarines), special optical glass (flint glass, opal and white glasses), in fireworks (bright red light), medicine, organic synthesis, artificial mineral water, air-conditioning (as LiCl), purification of helium, photography, etc. Of late, it is also used in the manufacture of special lithium-calcium alloys (in the steel industry to improve mechanical properties and increase yield points) and lithium-copper-aluminium alloys (to increase stability), etc. Recently metallic lithium has become especially important for thermonuclear reactions.

ZINNWALDITE, $KLiFe^{\cdot}\cdot Al[Si_3AlO_{10}][F, OH]_2$. Named after the place of occurrence, Zinnwald, in the Erzgebirge (Saxony). Composition is widely variable. The FeO content may be as high as 12.5 per cent. **System**, monoclinic. Thin to thick tabular crystals of grey, brown, seldom of dark-green colour, similar in shape to biotite. Also occurs in scaly aggregates. Commonly opaque or translucent. **Lustre**, vitreous, pearly on cleavage surface. $n_x = 1.58$, $n_y = 1.57$, and $n_z = 1.55$.

Hardness, 2 to 3. **Cleavage**, the same as for muscovite. **Specific gravity**, 2.9 to 3.2. Before the blowpipe readily fuses to dark, slightly magnetic glass. Colours the flame red. Soluble in acids.

The mode of occurrence is the same as that of lepidolite (chiefly in greisens), often in association with wolframite, scheelite, cassiterite, fluorite, topaz, quartz, etc. Upon weathering changes to a kaolinite-like product coloured intense yellow-brown or brown by iron hydroxides. Outside the Soviet Union, occurs at Zinnwald in the Erzgebirge in stockworks in granite, in Cornwall (England) in tin deposits as druses and crystal growths very rich in iron.

3. GROUP OF BRITTLE MICAS

MARGARITE, $CaAl_2[Al_2Si_2O_{10}][OH]_2$, or $CaO \cdot 2Al_2O_3 \cdot 2SiO_2 \cdot H_2O$. From the Greek "margarites", pearl. Synonym: pearly mica.

Chemical composition (theoretical). CaO 14.0%; Al_2O_3 51.3%, SiO_2 30.1%, H_2O 4.6%. Impurities: Na_2O, MgO, FeO, Fe_2O_3, sometimes Cr_2O_3, Li_2O, MnO, and F.

System, monoclinic; symmetry, monoclinic prismatic L^2PC. Space group $C2/c(C_{2h}^6)$. $a_0 = 5.12$; $b_0 = 8.90$; $c_0 = 19.46$; $\beta = 100°48'$. **Crystal structure** similar to that of muscovite with the only difference that the total negative charge of the laminated sandwiches is twice as great and is balanced by divalent Ca^{2+} cations located between the sandwiches. **Habit**, thin tabular. Well-developed crystals do not occur. Twins according to the mica laws. **Aggregates**, foliated, scaly.

Colour, pearl-white with greyish, pink, and yellowish tinges. **Lustre** on cleavage surfaces, pearly. $n_x = 1.645$, $n_y = 1.643$, and $n_z = 1.632$.

Hardness, 3.5 to 5.5. Brittle; the foliae break on bending. **Cleavage**, {001} perfect. Percussion and pressure figures, as in the case of all brittle micas, are reversed in relation to the true micas, i.e., the percussion figures correspond to the pressure figures of micas (cf. phlogopite). **Specific gravity**, 2.99 to 3.08.

Diagnostic features. Characteristic pearl-white colour, brittleness, high hardness, in which it also differs from micas of similar colour.

Before the blowpipe flame exfoliates, turns white, and fuses with difficulty along the edges. Partly soluble in hot hydrochloric acid.

Genesis and occurrence. Is formed in the course of regional metamorphism in crystalline schists, e.g., chlorite, in *Zillerthal* (Tirol) where it was first discovered, and in many other places. Occurs in the Urals in mica schists (was named diphenite), in emery deposits, and in other metamorphic rocks.

CHLORITOID, $Fe^{\cdot\cdot}Al_2[Al_2Si_2O_{10}][OH]_4$. Named for the external similarity to minerals of the chlorite group.

Chemical composition. The following variations have been established by chemical analyses: FeO 26 to 28%, MgO 2 to 4%, Al_2O_3 39 to 41%, SiO_2 24 to 26%, H_2O 7 to 8%. Impurities: CaO (up to 1.38%), MnO (up to 9%). The MnO-enriched variety is called *ottrelite*.

System, monoclinic or triclinic. **Habit**, tabular hexagonal. Well-developed crystals are rare. Twins fairly frequent (Fig. 333). Usually in laminated and conchoidal aggregates.

Colour, yellow with a greenish tinge, sometimes blackishgreen. Translucent only in thin plates. **Streak**, greenish white. **Lustre**, vitreous, sometimes weakly pearly on cleavage surfaces. $n_y = 1.72$ to 1.77.

Hardness, 5 to 6. Brittle. **Cleavage**, {001} perfect. Percussion and pressure figures are the same as for margarite. **Specific gravity**, 3.4 to 3.6.

Diagnostic features. Differs from the similar chlorites in higher hardness, brittleness, and optical constants which are also different from those of the other brittle micas.

Before the blowpipe fuses with difficulty to a blackish-grey slightly magnetic glass. Insoluble in hydrochloric acid, but decomposes completely in concentrated sulphuric acid.

Genesis and occurrence. Associated with corundum, diaspore, chlorites, quartz, and other minerals, chloritoid occurs in certain contact-metasomatic deposits among marbles, but more often in mica schists and clay shales, sometimes in such large quantities that the schists are called chloritoid. First reported under the name of

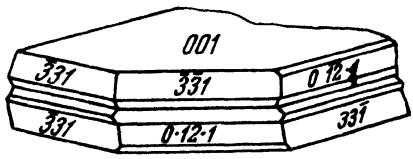


Fig. 333. Chloritoid twin.

baritophyllite in the *Kosoy Brod* locality near the Mramorsky mine, Sverdlovsk Region (the Urals). Chloritoid schists are a common variety of crystalline schists. Chloritoid is formed during early stages of regional metamorphism, and does not occur in more strongly metamorphosed rocks.

4. CHLORITE GROUP

The members of this group in many respects closely resemble micas. They crystallise in the monoclinic system, possess a mica-like cleavage, low hardness, and low specific gravity. Most of them are coloured bottle-green and hence their name ("chloros" is the Greek for green).

From the chemical standpoint, the chlorites are alumosilicates, chiefly of Mg, $Fe^{\cdot\cdot}$, and Al, sometimes of Ni, $Fe^{\cdot\cdot\cdot}$, and $Cr^{\cdot\cdot\cdot}$. The magnesia-rich species with quite distinctive crystallographic features have received the general name of *orthochlorites*. Their chemical formula is written as follows: $(Mg, Fe)_{6-p}(Al, Fe)_{2p}Si_{4-p}O_{10}[OH]_6$. Half the trivalent ions (p) form the anionic $[AlO_4]^{5-}$ radical, the other half are simple cations. The iron-rich, chiefly colloform species, often extremely variable in composition, are usually regarded as a subgroup of alumo-ferrisilicates under the general name of *leptochlorites*. Most of them are the poorest in silica content not only among the mica-like minerals, but among the silicates in general. In many of these species $F^{\cdot\cdot}$ prevails over $Fe^{\cdot\cdot\cdot}$, the p factor is higher than in the other orthosilicates, and they often contain molecular water. Their general formula is: $(Fe, Mg)_{n-p}(Fe, Al)_{2p}Si_{4-p}O_{10}[OH]_{2(n-2)}\cdot xH_2O$, where n is usually about 5.

Chlorites are widely distributed in nature and are mostly formed through low-temperature hydrothermal processes, especially in the course of alteration of rocks containing alumomagnesial and ferruginous silicates. The leptochlorites occur principally in sedimentary iron-ore deposits as a special facies of iron-ore silicates developing, according to geological data, in marine iron-rich sediments under conditions of oxygen deficiency.

Many researchers (Tschermak, Winchell, Aurselle, etc.) attempted to classify chlorites. According to Tschermak, the orthochlorites constitute isomorphous mixtures: antigorite (Ant), $Mg_6[Si_4O_{10}][OH]_8$, and relatively poor in silica but richer in alumina amesite (Am), $Mg_4Al_2[Al_2Si_2O_{10}][OH]_8$. Mg^{2+} may be replaced by Fe^{2+} and Ni^{2+}, and Al^{3+} by Fe^{3+} and Cr^{3+}. The numerous chlorite varieties differing in chemical composition have been given different names.

According to Tschermak, among the orthochlorites there are the following distinct mineral species crystallising in the monoclinic system (in the order from low alumina content to higher R_2O_3 content):

		Content of $0.5R^{\cdots}(p)$in the formula	Per cent of amesite molecule (Am)
Penninite, $(Mg, Fe)_5Al[AlSi_3O_{10}][OH]_8$*		0.75-1.00	37.5-50
Clinochlore	(100—n) Ant · nAm...	1.00-1.25	50-62.5
Prochlorite		1.25-1.50	62.5-75
Corundophillite		1.50-1.75	75-87.5
Amesite, $(Mg, Fe)_4Al_2[Al_2Si_2O_{10}][OH]_8$**		1.75-2.00	87.5-100

The iron-rich chlorites, according to composition and X-ray data, correspond in part to the above magnesium chlorites, and in part to the leptochlorites. We shall review here only chamosite and thuringite.

The most important physical property of the crystalline chlorites is that the easily-separated thin leaves, although flexible, are inelastic. This property is related to their crystal structure. If we compare the crystal structure of the chlorites (Fig. 335) with that of the micas (Fig. 334) we shall see that the laminated sandwiches $(Mg, Al)_3[Si_3AlO_{10}][OH]_2$ present in both groups alternate in the micas with strongly-bonded cationic sheets of univalent alkaline or divalent alkali-earth metals; in the chlorites, they alternate with "brucite" layers with the composition $Mg_2Al[OH]_6$ instead of $Mg_3[OH]_6$, with a residual positive charge of 1 (the same as the K^{1+} in the micas). Although these layers are but weakly bonded with the upper and lower laminated sandwiches, the bonds are stronger than those of talc and kaolinite groups, hence their lower cleavability as compared with the latter and their relatively higher hardness.

PENNINITE,

$(Mg, Fe)_5Al[AlSi_3O_{10}][OH]_8$, or $5(Mg, Fe)O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 4H_2O$. Named after the place of discovery, the Pennine Alps.

Chemical composition, according to the numerous analyses, varies as follows (per cent): MgO 17.4 to 35.9, FeO 0.7 to 17.4, Fe_2O_3 0 to 5.7, Al_2O_3 13.8 to 21.3, SiO_2 29.8 to 33.7, H_2O 11.5 to 14.6. The chro-

* The formula for a variety containing 50% of amesite molecule.
** The formula for pure amesite.

mium-rich carmine-red or violet variety is called *kaemmererite* (after the Russian engineer Kammerer) or *rhodochrome*, when it occurs as thin-scaly rose-coloured coatings on chromite ("rhodon" is the Greek for rose).

System, monoclinic; symmetry, monoclinic prismatic L^2PC. Space group $C2/c(C_{2h}^6)$. $a_0 = 5.2$ to 5.3; $b_0 = 9.2$ to 9.3; $c_0 = 28.6$; $\beta = 96°50'$. **Habit**, pseudohexagonal-platy, tabular, sometimes barrel-shaped (in

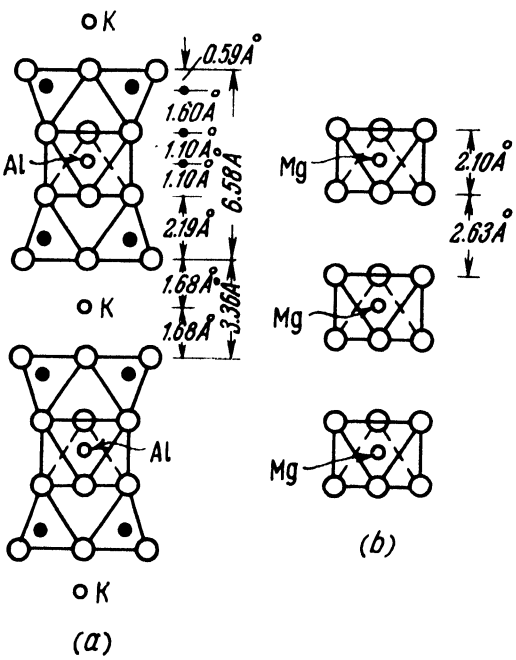


Fig. 334. Diagrammatic crystal structures of muscovite (*a*) and brucite (*b*).

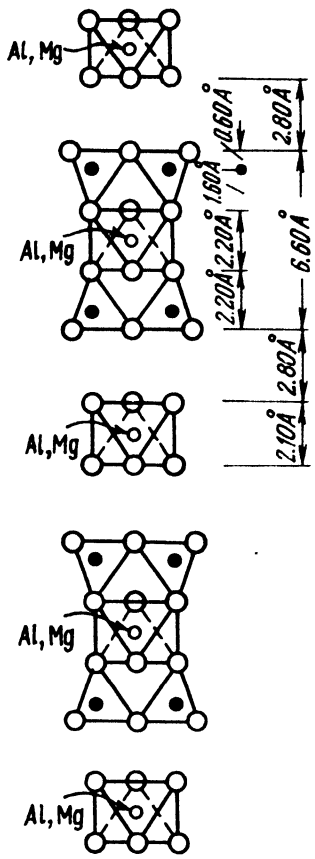


Fig. 335. Diagrammatic crystal structure of chlorite-group minerals. (cf. Fig. 334).

miarolitic cavities). Principal forms: {001}, {$\bar{1}$01}, {132}, {$\bar{1}$10}, etc. Side faces are often horizontally striated. Twins are frequent, usually according to the *chlorite law*, i.e., with (100) as the twinning and composition plane (Fig. 336). Twinning according to this law may often be repeated. Sometimes twinning is according to the mica law. **Aggregates** are scaly, platy. Crystal druses often barrel-shaped, occur in cavities.

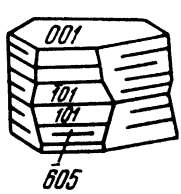


Fig. 336. Pennite twin according to chlorite law.

Colour, bottle-green of different shades to greenish black, sometimes pink and violet (for chromium-bearing varieties), less often silver-grey. In thin foliae, transparent and light-coloured. Some of the varieties have a banded coloration of different shades, especially in large crystals. **Lustre** on cleavage surface, pearly. $n_y = 1.56$ to 1.60.

Hardness, 2 to 2.5. Foliae are flexible but inelastic. **Cleavage**, {001}, excellent. **Specific gravity**, 2.60 to 2.85.

Diagnostic features. Identifiable by green, often black-green colour, excellent cleavage, low hardness, and the inelasticity of thin foliae. From other species of the chlorite group can be positively distinguished only by chemical tests.

Before the blowpipe exfoliates without fusing. When strongly ignited, loses hydroxyls and turns white. Generally soluble in sulphuric acid.

Genesis and occurrence. Penninite occurs chiefly in *metamorphic* rocks and often forms large masses of chlorite schists also known as greenstone rocks. In hollow fissures in such rocks it is often found in well-formed crystals. Excellent crystals have been recorded from the *Nikolae-Maximilianovskaya* mine in the Nazyam mountains (Southern Urals), in the asbestos mines of *Bazhenovo* deposit (east of Sverdlovsk) and elsewhere.

Kaemmererite was first discovered in fissures in chromite deposits among ultrabasic rocks at the Saranovsk deposit (the Urals).

Only chlorite schists are of certain practical value; they are sometimes mined as a source of powdered chlorite for wallpaper and for other uses.

CLINOCHLORE $(Mg, Fe)_{4.75}Al_{1.25}[Si_{2.75}Al_{1.25}O_{10}]\ [OH]_8$ (for the variety where $p = 1.25$). "Klino" is the Greek for to incline. Named by Academician Koksharov because of the pronounced monoclinic system of its crystals.

Chemical composition varies as follows (per cent): MgO 17.0 to 34.5, FeO 1.8 to 12.2 Fe_2O_3 0 to 3, Al_2O_3 13.1 to 17.6, SiO_2 28.3 to 33.9, H_2O 11.7 to 14.2. Impurities: CaO (up to 9%), MnO (up to 2.3%), Cr_2O_3 (up to 8%). The iron-poor variety is called *leuchtenbergite*, while the chromium-bearing clinochlore, also discovered by Koksharov, is known as *kotschubeite*.

System, monoclinic; simmetry, monoclinic prismatic. **Habit**, platy-hexagonal or tabular, less often prismatic or barrel-shaped (Fig. 337); well-developed crystals are common. Most common forms: {001}, {010}, {043}, {112}, {11$\bar{1}$}, and others, sometimes with very complex symbols. Twins are according to the chlorite and the mica laws (Fig. 338). **Aggregates**, coarse scaly-granular to cryptoscaly. May be present in cavities as druses of tabular crystals.

Colour, grass-green to pale olive-green, yellow, sometimes white (leuchtenbergite) with grey, pink, violet (chromium-bearing varieties), and other tinges. Thin foliae transparent or translucent. **Lustre** on cleavage surfaces, pearly. $n_y = 1.57$ to 1.59.

Hardness, 2 to 2.5. Foliae soft, flexible but not elastic. **Cleavage**, {001} highly perfect. **Specific gravity**, 2.61 to 2.78.

Diagnostic features. Having much in common with penninite clinochlore is positively identifiable only by chemical analysis.

Blowpipe behaviour is identical with that of penninite. Completely, soluble only in concentrated sulphuric acid.

Genesis and occurrence. Along with penninite, clinochlore is widely distributed in chlorite schists in which it is often the principal rock-forming mineral. The formation of these schists is usually related to the metamorphism of igneous rocks rich in magnesial-iron silicates (mostly porphyrites, serpentinites, etc.).

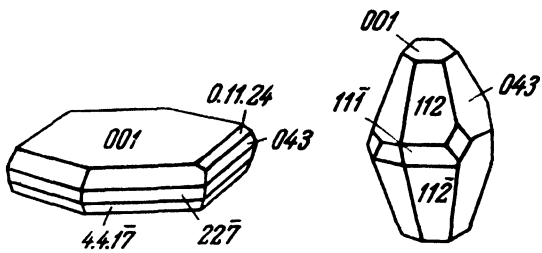


Fig. 337. Clinochlore crystals.

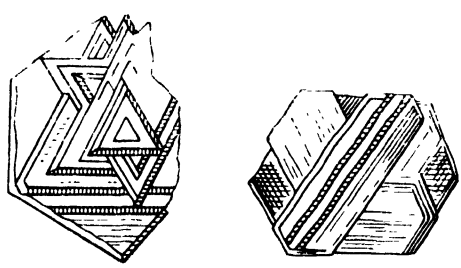


Fig. 338. Repeated clinochlore twins parallel to (001).

Excellent museum specimens of crystal druses of clinochlore have come from the mines in the *Shishim* and *Nazyam* mountains near Zlatoust (the western slope of the Southern Urals). Especially famous is the Akhmatovskaya mine (Nazyam mountains) where the druses of clinochlore and leuchtenbergite of striking appearance and rich variety of forms are found associated with epidote, diopside, garnet, vezuvianite, calcite, and sphene. They occur usually in fissures in chlorite schists and epidosite.

Chromium-bearing *kotschubeite* was first discovered at Ufaley (the Urals) in chromite deposits.

PROCHLORITE, $(Mg, Fe)_{4.5}Al_{1.5}[Al_{1.5}Si_{2.5}O_{10}][OH]_8$ (for the variety where $p = 1.50$). According to analyses the content of oxides is extremely variable.

System, monoclinic; symmetry, monoclinic prismatic L^2PC. Space group $C2/c(C_{2h}^6)$. $a_0 = 5.2$ to 5.3; $b_0 = 9.2$ to 9.3; $c_0 = 28.3$ to 28.6; $\beta = 96°50'$. Occurs in platy pseudohexagonal crystal and scaly aggregates of green or black-green colour. $n_y = 1.59$ to 1.61. **Hardness**, 1.5 to 2. **Cleavage** to {001} excellent. **Specific gravity**, 2.78 to 2.96.

Prochlorite occurs in chlorite schists (more rarely than clinochlore) and in Alpine clefts in association with rock crystal and adular, sometimes implanted on the surface of other crystals that have grown on the walls of hollow fissures. Found in numerous veins in the Alps, in the Northern Urals, and elsewhere.

CHAMOSITE, $Fe_4^{\cdot\cdot}Al[Si_3AlO_{10}]\ [OH]_6 \cdot nH_2O$. The formula is approximate. Named after the place of discovery: Chamoison, Valais Canton (Switzerland).

Chemical composition variable (per cent): FeO 34.3 to 42.3, Fe_2O_3 0 to 6, Al_2O_3 13 to 20.1, SiO_2 22.8 to 29, H_2O 10 to 13. Impurities: MgO up to 4.4 or even to 7%, CaO up to 1.6%, TiO_2 up to 1.1%.

System, monoclinic. Occurs usually in the form of oölitic concretions with a concentric zonal structure. Found also as cement between sand particles or as cryptocrystalline or earthy masses.

Colour, greenish-dark-grey to black. Opaque. **Streak,** light greenish grey. **Lustre,** commonly dull or slightly vitreous. n_g = 1.62 to 1.66. **Hardness,** 3. **Specific gravity,** 3.03 to 3.40.

Diagnostic features. Externally may be recognised by oölitic texture, dark-green or black colour, greenish-grey streak.

Turns red in the oxidising flame. In the reducing flame fuses to a black magnetic glass. Readily gelatinises in hydrochloric acid.

Genesis and occurrence. Chamosite occurs in certain sedimentary iron-ore deposits of different ages, mostly Jurassic. Judging by its paragenetic association with iron sulphides, siderite, and its ferrous iron constituent, chamosite forms in the near-shore marine zones under oxygen deficiency conditions. It has not been found in recent marine sediments.

On weathering chamosite readily oxidises to iron hydroxides in the form of brown iron ore composing typical iron hats in chamosite deposits.

In the U.S.S.R., chamosite masses have been discovered in Paleozoic and Mesozoic sediments on the eastern slope of the *Urals* (Serov, Alapaevsk, Ayat, and other districts), in some localities in the *Northern Caucasus* in Jurassic deposits, and elsewhere.

Uses. Chamosite occurs sometimes as large sheet-like bodies which are of economic importance as iron ore.

THURINGITE, $Fe_{3.5}(Al, Fe)_{1.5}[Si_{2.5}Al_{1.5}O_{10}]\ [OH]_6 \cdot nH_2O$. The formula is approximate. Named after the place of discovery.

Chemical composition, variable (per cent): FeO 19.8 to 39.3, Fe_2O_3 7.2 to 31.7, Al_2O_3 15.6 to 25.1, SiO_2 19.4 to 28.8, H_2O 4.6 to 13.2. Impurities: MgO (up to 6%), CaO (up to 1.9%), MnO (up to 2.7%), P_2O_5 (up to 1.2%), etc.

System, monoclinic. Occurs occasionally in small scales, but generally in cryptocrystalline compact or earthy masses.

Colour, olive-green to greenish black. **Streak**, greenish grey. **Lustre** of distinctly scaly varieties, pearly. $n_y = 1.64$ to 1.68.

Hardness, 2 to 2.5. **Cleavage**, evidently parallel to {001} perfect. **Specific gravity**, 3.15 to 3.19.

Diagnostic features. Characteristic dark-green colour, pale-green streak, sometimes pearly lustre (for scaly aggregates). Recognised positively only by chemical analysis.

Before the blowpipe fuses to a black magnetic glass. Gelatinises in hydrochloric acid.

Genesis and occurrence. In large masses thuringite occurs in slightly metamorphosed sedimentary iron deposits. It is often associated with small magnetite octahedra, and sometimes with more recent siderite. The mineral may be also formed endogenously through hydrothermal alteration of iron-rich rocks.

The largest thuringite deposits are found in *Thuringia* (Germany) at Schmiedefeld, etc. As beds among Lower Silurian schists. In the U.S.S.R., a mineral very similar to thuringite has been found in an iron-ore sedimentary deposit at Karajal (Central Kazakhstan).

Uses. When found in large masses, may be of commercial importance as an iron ore.

5. HYDROMICAS AND SIMILAR MINERALS

There exist some mica- or chlorite-like minerals distinguished by the fact that they have fewer bonding cations, but a great number of chemically combined H_2O molecules which are rather readily removed on heating.

Although their formation is sometimes ascribed to low-temperature hydrothermal processes, hydromicas predominantly derive from the weathering of igneous rocks and pegmatites, i.e., from the micas or mica-like minerals they contain. Some of the hydromicas derive from the decomposition of marine sediments. In all cases the essential prerequisite of their existence is a water-rich environment.

The chemical composition of these minerals is variable due to diversity of the content of the cations bonding the sandwiches anp water.

Hydromuscovite, vermiculite, and glauconite will be reviewed in this group.

HYDROMUSCOVITE, $K_{<1}Al_2[(Si, Al)_4O_{10}][OH]_2 \cdot nH_2O$. The formula is approximate. The names "illite", "monothermite", etc., are synonymous. Hydromuscovite, as a rule, is the product of partial hydrolysis of muscovite.

Chemical composition is variable. As compared with muscovite, the K_2O diminishes to 6 or even to 2-3%; H_2O is increased up to 8-9%. The SiO_2 content in hydromuscovite may be as high as 50-55%,

Al_2O_3 content is lower than in muscovite (25-33%). Impurities: Fe_2O_3, MgO (up to a few per cent), CaO, etc.

Crystal structure differs little from that of muscovite, being as it were, transitional to the structure of montmorillonite. Probably, the laminated sandwiches of the muscovite type alternate with those of the montmorillonite type.

Hydromuscovite occurs in scaly and thin tabular white masses with a greasy feel, usually mixed with kaolinite and other minerals. Individual scales are less elastic than in muscovite. The refractive indices are lower than for muscovite, and may vary depending on composition from 1.55 to 1.58 (diminishing with increasing H_2O).

Hydromuscovite occurs mostly in clays derived from the weathering of mica (muscovite) schists, gneisses, quartz-sericite rocks, and sometimes apparently is an alteration product in the course of transformation of feldspars into kaolinite. It is also often found in the soils resulting from acidic and medium igneous rocks upon weathering, in association with montmorillonite and other minerals.

VERMICULITE, $(Mg, Fe^{\cdot\cdot}, Fe^{\cdot\cdot\cdot})_3[(Si, Al)_4O_{10}][OH]_2 \cdot 4H_2O$. The name comes from the Latin "vermiculus" meaning little worm, and is due to the fact that on heating the mineral expands into worm-like forms.

Chemical composition varies with the content of molecular water as follows (per cent): MgO 14 to 23, Fe_2O_3 5 to 17, FeO 1 to 3, SiO_2 37 to 42, Al_2O_3 10 to 13, H_2O 8 to 18. May contain also up to 5% of K_2O, and in certain varieties up to 11% of NiO.

System, probably monoclinic. Vermiculite usually occurs pseudomorphous after biotite or ferruginous phlogopite.

Colour, brown, yellow-brown, golden-yellow, bronze-yellow; sometimes with greenish tints. **Lustre** is not so strong as of biotite, commonly greasy. $n_x = n_y = 1.54$ to 1.58, and $n_z = 1.52$ to 1.56.

Hardness, 1 to 1.5. Thin foliae are slightly elastic or completely inelastic. **Cleavage**, {001} perfect. **Specific gravity**, 2.4 to 2.7. **Other properties.** The outstanding characteristic of the mineral is its ability to expand on heating (at temperatures from 900 to 1000°) as much as 15 to 25 times against its original volume. This is due to the fact that under the pressure of evaporating molecular water the individuals exfoliate and rapidly expand parallel to the *c* axis. The expansion is so great that worm-like forms result (depending on the grain size and the cleavage planes) of golden or silvery colour developing most thin cross-wise scales. The formation of a tremendous number of minute interlayers of air within the individuals causes a sharp reduction in unit weight (down to 0.6-0.9). Ignited masses of vermiculite float on water. This texture of expanded vermiculite accounts for its extremely low heat-conductivity factor: $\lambda = 0.04$ to 0.05 kcal/m/hour °C (for asbestos it is 0.15 to 0.40).

Diagnostic features. Vermiculite resembles externally weathered biotite or chlorite. The most characteristic feature is its behaviour in the blowpipe flame in which it strongly expands into long worm-like forms.

Genesis and occurrence. In minor amounts vermiculite usually forms as the product of biotite weathering. In more considerable quantities it is found in hydrothermally altered (evidently at low temperatures) biotite and phlogopite veins, lenses, and bodies that have developed metasomatically from ultrabasic rocks.

Outside the Soviet Union, large deposits occur near *Libby*, Montana (U.S.A.) and in Western Australia.

Uses. Expanded vermiculite is used as a heat-insulator for steam pipes, boilers, furnaces, etc. As a sound insulator, it is used in aircraft cabins and saloons, in some special laboratories, etc. Owing to the attractive golden or silvery colour it assumes upon ignition, vermiculite is used in the manufacture of wallpaper. It can also be used as a lubricant. Finally, vermiculite possesses very good cationic exchange properties, in which it favourably compares with the montmorillonite group.

GLAUCONITE, $K_{<1}(Fe^{\cdots}, Fe^{\cdot\cdot}, Al, Mg)_{2-3}[Si_3(Si,Al)O_{10}][OH]_2 \cdot nH_2O$. "Glaucos" is the Greek for bluish green.

Chemical composition. Basically it is a hydrous alumosilicate of iron and magnesium. The percentage of principal constituents for typical glauconites varies as follows: K_2O 4.0 to 9.5, Na_2O 0 to 3.0, Al_2O_3 5.5 to 22.6, Fe_2O_3 6.1 to 2.79, FeO 0.8 to 8.6, MgO 2.4 to 4.5, SiO_2 47.6 to 52.9, H_2O 4.9 to 13.5.

System, monoclinic. $a_0 = 5.24$; $b_0 = 9.07$; $c_0 = 20.03$; $\beta = 95°00'$. Small roughly hexagonal crystals are very rare. Usually occurs as rounded grains or globules up to several millimetres in diameter impregnated in loose siliceous or argillaceous carbonate rocks.

Colour, dark green to greenish black, green in thin polished sections.

Lustre, usually dull, vitreous and greasy for compact varieties. $n_x = 1.610$ to 1.644, and $n_z = 1.590$ to 1.612.

Hardness, 2 to 3. Brittle. **Cleavage**, extremely rare and only in large individuals, parallel to {001}. **Specific gravity**, 2.2 to 2.8.

Diagnostic features. Recognised by dark-green colour, low hardness, and paragenetic association with minerals entering into the composition of sedimentary rocks. Distinguished from the leptochlorites by lower refractive indices and chemical composition (glauconite contains considerable potassium).

Before the blowpipe fuses with difficulty to a blebby slag-like mass and later to a black glass. Decomposes in concentrated hydrochloric acid leaving a very thin silica skeleton which retains the general shape of the grains.

Genesis and occurrence. Glauconite occurs in marine sediments (sandstones, gaizes, clays, carbonate rocks, and phosphorite layers)

at shallow depths, chiefly in the near-shore zones of seas and oceans, and also in recent marine sediments (green silts and sands). Sometimes is found in the soils and in the upper part of eluvium (gruss) on intrusive rocks (in marshy localities).

Glauconite is decomposed by weathering into iron hydroxides and silica. This process often gave rise to certain brown iron ore deposits, especially in bogs.

Glauconite deposits are quite numerous and are confined to shallow-water sediments of most diverse ages. We shall mention only the principal ones occurring in the U.S.S.R.

A huge deposit of Upper Cretaceous glauconite sands underlying phosphorite beds, occurs in the so-called *South-Russian depression* in the Ukraine. The sands often contain phosphorite nodules. Glauconite sandstones are widespread in Tertiary strata in siliceous clays and gaizes along the eastern slope of the Urals, in Western Kazakhstan, the Volga country, the Ukraine, and in many other places.

Uses. As a potassium-bearing mineral, glauconite both crude and, better still, after heat-treatment, is used as a fertiliser.

Glauconite concentrates are used as a cheap green pigment which compares advantageously with other green pigments in being acid- and alkali-resistant, non-toxic, etc.

Under the name of neopermutite glauconite is also used as a water-softener in sugar-refining, brewing, distilling of alcoholic beverages, textile industry, etc. These applications are based on its cationic exchange properties. For this purpose glauconite concentrates are treated with NaCl solution, the Na ions being absorbed by the concentrates. When hard water is filtered through such a concentrate, cationic exchange takes place: the alkali-earth cations of the water are absorbed and the sodium cations pass into the solution, and as a result the water becomes soft.

6. SERPENTINE-KAOLINITE GROUP

This group of minerals, as many other previously reviewed groups, comprises hydrosilicates of magnesium (nickel) and of aluminium (iron) and falls accordingly into two subgroups: (a) *serpentine* subgroup, and (b) *kaolinite* subgroup. Although serpentine (magnesium hydrosilicate) contains sometimes minor quantities of Al_2O_3 (up to 5.68 per cent) and practically always a few per cent of Fe_2O_3, and in turn, kaolinite also always contains some MgO along with Al_2O_3, minerals of intermediate composition are not common in nature and, therefore, the division of the minerals of this group into two subgroups is fully warranted.

The common feature of this and the two subsequent groups of minerals is that their compounds are very much prone to form colloidal substances and cryptoscaly aggregates. Phanerocrystalline formations are extremely rare.

In addition to serpentine with its varieties, and revdinskite, we shall also review in this subgroup the magnesium-alumina hydrosilicates known collectively as palygorskite.

SERPENTINE, $Mg_6[Si_4O_{10}][OH]_8$, or $3MgO \cdot 2SiO_2 \cdot 2H_2O$.

Serpentine rocks, especially in polished specimens, reveal a mottled snakeskin-like pattern. The old name *ophite* (the Greek for snake), or more recent serpophite is still used for an opaline or gelatinous water-rich variety of serpentine with a waxy lustre and uniform colouring (pale green, yellowish white, less often brownish green). This variety was called noble serpentine; in optical and other properties it is a typical gel.

A foliated variety, resembling chlorite, but with less perfect basal cleavage, and more brittle than chlorite, is called *antigorite* (Antigorio Valley, near Piedmont, Italy). It was mentioned in the description of the chlorites.

Chemical composition. MgO 43.0%, SiO_2 44.1%, H_2O 12.9%. The ratio of the different constituents is somewhat variable, especially in varieties corresponding to typical colloids and containing more water (usually 13 to 17%). Almost constantly present are FeO, Fe_2O_3, and NiO.

System, monoclinic. Never occurs in well-developed crystals. The only phanerocrystalline variety is antigorite, which probably crystallises in the monoclinic system. **Crystal structure.** The basic difference in crystal structure between antigorite and kaolinite is that in antigorite the "brucite" layers of the laminated sandwiches face each other (Fig. 340), i.e., they are divided by double hydroxyl layers. **Aggregates.** Usually occurs in compact masses, often crumpled, with traces of gliding, sometimes with extremely thin veinlets of asbestos or ophite. In rare instances antigorite serpentinites show a platy structure.

Colour, dark green in thin fragments, bottle-green of different shades to greenish black, and sometimes brownish green. Ophite is often pale olive-green with a yellow tinge. Antigorite is grey, often slightly bluish. **Lustre**, vitreous, greasy, and waxy for ophite.

Hardness, for common serpentine 2.5 to 3, antigorite 3.5, and ophite 2. **Cleavage**, only for coarse tabular antigorites: {001} perfect, {010} less perfect. Foliae are brittle. **Specific gravity**, 2.5 to 2.7.

Diagnostic features. Externally serpentine masses are rather readily recognised by dark-green tints, low hardness, gliding planes, greasy lustre on fracture, etc. Antigorite serpentinites show characteristic grey tints, very high toughness when trimmed with a hammer, and greater hardness than common serpentinites.

Before the blowpipe fuses with difficulty along the edges. Serpentine and its varieties are soluble in hydrochloric and sulphuric acids. In the closed tube gives off much water.

Genesis and occurrence. Serpentinites are formed through extensive processes of *hydrothermal* alteration of ultrabasic, predominantly olivine-bearing rocks (dunites, peridotites, etc.). Olivine and enstatite are replaced by serpentine most readily, next come diopside, hornblendes, etc.

Without enumerating the deposits we shall merely say that serpentinites are widely distributed throughout the Urals, in the North Caucasus, Transcaucasia (Armenia), and in some localities in Siberia and Kazakhstan.

On weathering, serpentinised rocks are gradually carbonated and decomposed, especially in the tropical and subtropical climates, earthy iron hydroxides being accumulated on the surface as residual products. The magnesia combines with the atmospheric carbon dioxide and percolates in the form of bicarbonates into the lower part of the zone of oxidation. The silica passes into colloidal solution and segregates as opal that often replaces the country rocks. In the same way, the nickel of hydrosilicates is transported and redeposited in the lower horizons.

Uses. Compact beautifully coloured varieties of serpentinite are sometimes used as facing stones and for fashioning ornamental objects (trinket boxes, ash-trays, writing sets, etc.). Varieties poorer in silica (serpentinised dunites) are used with addition of some magnesite as a material for high-grade forsterite refractories by the steel industry. Serpentine also finds employment in chemical industry as a stock material for magnesium compounds.

CHRYSOTILE-ASBESTOS. This mineral in effect is a fine-fibrous variety of serpentine. Initially it was simply called chrysotile. "Chrysos" is the Greek for gold, "tilos" fibre. Indeed, it sometimes shows a golden chatoyancy. It is usually called asbestos, or chrysotile-asbestos in distinction from the amphibole asbestos.

Chemical composition is the same as that of serpentine: MgO 43.0%, SiO_2 44.1%, H_2O 12.9%.

System, as shown by X-ray study, is monoclinic; symmetry, prismatic. Space group $C2/m(C_{2h}^3)$. $a_0 = 14.46$; $b_0 = 18.5$; $c_0 = 5.33$; $\beta = 93°16'$. **Aggregates.** Against the background of massive serpentine, asbestos stands out prominently as "veinlets" (Fig. 339), in which the fibres are usually perpendicular to the walls of the veins. The fibres vary in length from tenths of a millimetre to 25 mm, sometimes they are 50 mm, and occasionally up to 160 mm long.

Colour, greenish yellow with a golden chatoyancy, sometimes white, rarely brown; snow-white when the fibres are separated. **Lustre,** silky.

Hardness, 2 to 3. Separates into very thin, elastic, and strong fibres which may be less than 0.0001 mm thick (i.e., comparable in diameter to the colloidal dispersed phase). **Other properties.** Fire- and alkali-resistant. Poor conductor of heat, electricity, and sound.

Diagnostic features. Readily identifiable by parallel-fibrous structure and elasticity of the fibres. May be distinguished from amphi-

bole asbestos by optical properties (birefringence) and by reaction with acids.

Infusible in the blowpipe flame, but turns white. As different from the amphibole-asbestos, is dissolved in hydrochloric acid with the separation of a fibrous silica skeleton. Is also attacked by sea water.

Genesis and occurrence. The formation conditions are generally the same as for serpentine, i.e., involve the hydrothermal alteration of magnesia-rich ultrabasic rocks. Chrysotile-asbestos occurs, however, much

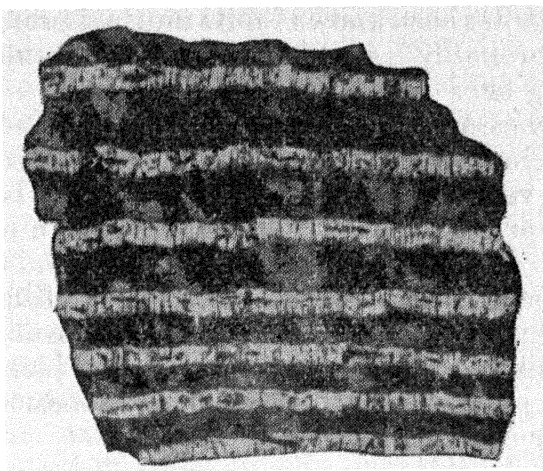


Fig. 339. Parallel banding of chrysotile-asbestos.

more seldom than common serpentine, which indicates a somewhat different mode of formation.

Chrysotile-asbestos occurs within vein-like bands or irregular patches of massive serpentine which is externally different from the enclosing serpentinised rocks. The mechanism of formation of chrysotile-asbestos still remains obscure. In all probability, at the outset of formation the continuous serpentine masses constituted a gel which upon drying developed contraction cracks. As the walls of the cracks draw apart, fine-fibrous masses might have developed in between, with the fibres strictly parallel to the direction of expansion, regardless of the size or number of the cracks. Such strict parallelism of the fibres may be compared with what happens to rubber adhesive when one tries to detach a freshly applied patch from the parched material (the rubber molecules acquire a strictly oriented fibrous nature and characteristic silky lustre). The chrysotile-asbestos fibres, in that case, depend for their growth on the enclosing serpentine colloidal mass.

Chrysotile-asbestos occurs at *Bazhenovskoye* deposit (U.S.S.R.) in serpentinites. The asbestos-serpentinites are enclosed in peridotites extending for several kilometres in the north-south direction as a network of interwoven bands. Parallel to these bands run veins of diorite-aplites and quartz-porphyrys, at the contact with which the serpentinites are crumpled, talcised, and chloritised. Constant associates

of the chrysotile-asbestos veins and veinlets are massive serpentine, ophite, sometimes carbonates, talc, brucite, etc. Deposits of that type are also found in the Alapaevsk, Rezhevsk, Krasnouralsk, and other districts of the Urals as well as in the serpentinite belt of the Eastern and Western Sayany ridges.

Outside the U.S.S.R., large deposits of chrysotile-asbestos are found in the *Quebec* province (Canada) and in the *Island of Cyprus*, where the asbestos was known already in the days of Plutarch; and at *Shabani* (Southern Rhodesia).

Uses. Asbestos has been known for its unusual properties since antiquity. Man has probably learned to spin asbestos into yarn and make cloth a very long time ago.

At present asbestos is used extensively in many industries. Asbestos fibre over 8 mm long goes for the manufacture of fire-proof suits and theatre curtains, various filters, extra-durable brake bands, and various asbestos-rubber articles. Short fibres (2 to 8 mm) are admixed to cement (up to 15%) to make refractory, durable, and light-weight roofing, pipes, cardboard, heat- and electricity-insulating paper and other materials. Fine-fibre asbestos is used in heat-insulating gaskets (asbestite), heat-resistant paints, boiler insulation, plaster, etc.

Beneficiation plant wastes are used in the production of chemicals and fertilisers for certain crops (e.g., beat).

REVDINSKITE, $(Ni, Mg)_6[Si_4O_{10}][OH]_8$, or $3(Ni,Mg)\,O \cdot 2SiO_2 \cdot 2H_2O$. Named after the place of discovery: Revdinsk district in the Middle Urals (1867). Revdinskite also occurs in a colloidal variety similar to serpentine.

In 1908, a phanerocrystalline variety of the same composition was discovered and called *nepouite* (also after the place of discovery at Nepoui, New Caledonia).

Chemical composition is similar to that of serpentine, with the only difference that revdinskite (nepouite) contains much more NiO, which is sometimes predominant over MgO.

System, monoclinic. X-ray studies of nepouite show that it is closely related in crystal structure to the kaolinite minerals. **Habit.** Nepouite occurs (like kaolinite) in small vermicular crystals, but more often in scaly aggregates. Revdinskite is found in cryptocrystalline compact pulverulent and earthy masses.

Colour, pale green with a bluish tinge (turquoise-coloured) to green or greyish green with a yellowish tinge. **Lustre** for crystalline varieties, pearly (on cleavage surfaces); for colloidal varieties, greasy, waxy, and dull. For the variety with Ni : Mg = 3 : 7 refractive indices are $n_x = n_y = 1.56$, $n_z = 1.53$.

Hardness, 2 to 2.5. **Cleavage,** {001} perfect. **Specific gravity,** 2.5 to 3.2 (depending on nickel content).

Diagnostic features. Identifiable externally by scaly and fine-platy chlorite-like aggregates usually bluish green in colour.

Infusible before the blowpipe or fusible with difficulty. Ignited on charcoal, becomes brown in the oxidising flame, or velvet-brown in the reducing flame. In the closed tube, gives off water. Decomposes in hot hydrochloric acid with the separation of slimy silica. Gives a characteristic borax bead and nickel reactions with dimethylglyoxime.

Genesis and occurrence. Revdinskite occurs exclusively in the weathering crust of ultrabasic igneous rock masses containing nickel-poor magnesium silicates (olivine, enstatite, serpentine, etc). Has been found pseudomorphous after clastic serpentinite, with its original texture retained. This indicates that revdinskite forms metasomatically, through the displacement of magnesium from the crystal lattice by nickel. Nickel is evidently brought by percolating waters which carry this element in the form of some compounds deriving from the decomposition of the primary minerals in the upper crust of weathering of ultrabasic rocks.

Considerable revdinskite is found in nickel silicate ore deposits in the *Revdinsk* and *Ufaley* districts (the Middle Urals). Crystalline varieties of revdinskite were recorded chiefly from serpentinite deluvium filling karst sinks in limestones at the contact with ultrabasic rock masses (Tyulenevskoye deposit). Has also been found at *Khalilovo* and *Akkerman* deposits (the Middle Urals).

Uses. Together with other nickel hydrosilicates, revdinskite enters into the composition of commercially important nickel ores.

PALYGORSKITE, $m2MgO \cdot 3SiO_2 \cdot 4H_2O - nAl_2O_3 \cdot 4SiO_2 \cdot 5H_2O$. Composition variable. According to A.Y. Fersman, the Mg to Al ratio varies widely: from varieties in which the MgO content is vastly predominant over that of Al_2O_3, to those in which the ratio of these constituents is reversed. The Al_2O_3-rich varieties with Al : Mg = 1 : 1 are called *palygorskites*, while those poor in Al_2O_3 and closer in composition to sepiolite ($2MgO \cdot 3SiO_2 \cdot 2H_2O$) are known as *pilolites*. Moreover, some Al may be replaced by $Fe^{\cdots}$.

All these minerals have characteristic felted fibrous structure, sometimes visible only under the microscope, and also rather specific physical properties which are reflected in such old names as rock leather, rock cork, wood rock (resembling dry disintegrated wood), etc. Owing to high porosity, the minerals have very low unit weight and float in water.

Colour, white, sometimes with a yellowish tinge or grey with a yellowish or brownish tinge. n_y about 1.55. **Hardness**, 2 to 2.5. Thin flat plates are readily bent. **Specific gravity**, 2.1 to 2.3. When dry, absorbs much water. Before the blowpipe fuses to a blebby milky glass. In hot sulphuric acid decomposes with the separation of a SiO_2 skeleton. On heating to 220° gradually loses H_2O (up to 15%), after which evolution of water ceases to resume at 370 to 410° (the remaining 5 to 6%).

The mineral is comparatively rare. It is formed mostly through the weathering of rocks relatively rich in magnesia, being often deposited

in fissures, and resembling compact cardboard sheets. Also forms in sedimentary rocks, as irregular sheet-like bodies and pockets.

When found in quantity, may be used as a heat- and sound-insulator for room partitions and for other purposes.

In the U.S.S.R., fairly large deposits are found on river banks in the Middle-Volga country, Gorky Region, Tatar Autonomous Republic (Tetyushi district), the Ukraine (Korosten, Berdichev, and other districts), the Crimea (Kurtsy village near Simferopol), the North Caucasus – along the tributaries of the Malka River, in Western Siberia (in the Kuznetsk Alatau mountains), and elsewhere.

Kaolinite Subgroup

This subgroup comprises three monoclinic polymorphous modifications of the same substance which, from the chemical standpoint, is a basic silicate of aluminium.

KAOLINITE, $Al_4[Si_4O_{10}][OH]_8$, or $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. This old name deriving from the Chinese "Kao-ling" which means high ridge (where a kaolin deposit of this name was found). It is the most common mineral of the subgroup and the principal constituent of most clays.

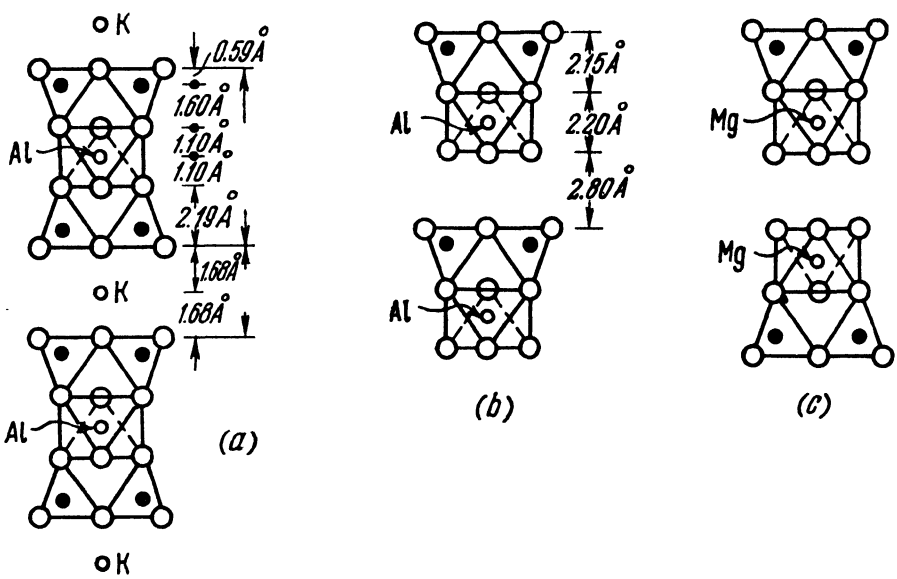


Fig. 340. Diagrammatic crystal structure of kaolinite (*b*) compared with structures of muscovite (*a*) and antigorite (*c*).

Chemical composition. Al_2O_3 39.5%, SiO_2 46.5%, H_2O 14%. The content of individual constituents may vary. May have negligible admixtures of Fe_2O_3, MgO, CaO, Na_2O, K_2O, BaO, SiO_2, etc.

System, monoclinic; domatic *P*. Space group $Cc(C_s^4)$. $a_0 = 5.14$; $b_0 = 8.90$; $c_0 = 14.45$; $\beta = 100°12'$. **Crystal structure.** As in the other micaceous

minerals, the tetrahedral oxygen-silicon groups (without aluminium) are linked by three corners into a layer of common hexagonal network. Each fourth apex occupied by oxygen forms part of the lower "hydrargillite" layer (Fig. 340). In such double-layer packages, the total negative charge of the complex anion and hydroxyl anions is almost fully balanced by the positive charge of the Al cations. Figure 341 shows that at the contact of each package with the adjacent one we have, on one side, the hydroxyls and, on the other, the oxygen ions

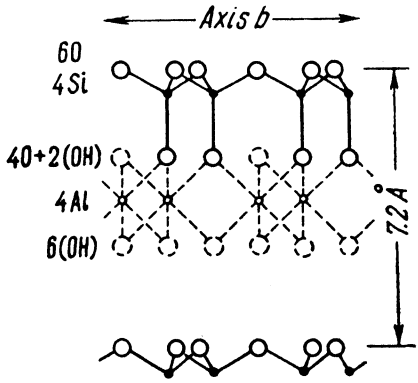


Fig. 341. Arrangement and number of ions in individual sheets of kaolinite structure.

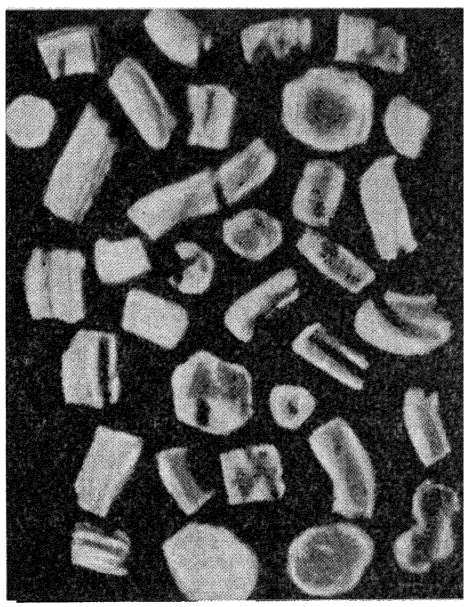


Fig. 342. Fragments of vermicular crystals of kaolinite. × 20.

of the adjacent tetrahedral layer. This structure explains the perfect basal cleavage and easy cleavability of the kaolinite minerals.

Habit. Well-developed crystals are extremely rare and small (under 1 mm). They are very probably those of dickite rather than of kaolinite. More frequent are fragments of bent columnar crystalline formations externally resembling rainworms (Fig. 342). Individual scales and plates have a hexagonal, more seldom rhombic or trigonal habit. **Aggregates** are friable, scaly or compact fine-granular; sinter forms are also known.

Colour. Individual scales and plates are colourless. Massive kaolinite is white, often with yellow, brownish, reddish, sometimes greenish or bluish tinges. **Lustre** in separate scales and plates pearly; in massive varieties dull. $n_x = 1.566$ and $n_y = 1.565$ and $n_z = 1.560$.

Hardness, about 1. Some of the scales are flexible but not elastic. In dry earthy masses kaolinite has a meagre feel. **Cleavage,** {001} excellent; may also have cleavage coinciding with six-rayed percussion figures. **Specific gravity,** 2.58 to 2.60.

Diagnostic features. Massive earthy kaolinite is easily rubbed to powder between the fingers, vigorously absorbs water when dry, and be-

comes very plastic when moistened. Fine crystalline varieties are recognised under the microscope by characteristic scales and optical constants. Cryptocrystalline masses are identified approximately by refractive indices, and more positively by X-ray analysis, heating curves, and other methods.

Infusible before the blowpipe. Almost insoluble in hydrochloric and nitric acids. Decomposes rather easily in sulphuric acid, especially on heating. After ignition to 500° kaolinite is completely decomposed in hydrochloric acid. White varieties free from iron hydroxides after ignition with cobalt nitrate assume a beautiful blue colour (due to the presence of Al).

Genesis and occurrence. The bulk of kaolinite is formed through the *weathering* of igneous and metamorphic rocks rich in alumosilicates (feldspars, micas, zeolites), such as granites, gneisses, quartz-porphyrys, etc. The formation of kaolinite involves the action of H_2O and CO_2. Alkalis, part of the SiO_2 content, and alkaline-earths are leached out as carbonates, while quartz and other chemically inert minerals remain as inclusions in the clayey residue known as *kaolin* or China clay. Often these masses of kaolin are eroded by water and redeposited far from their place of formation in stagnant basins as finely dispersed silt sediments free from coarse inclusions of foreign minerals.

Kaolinisation may also take place in the conditions of low-temperature *hydrothermal* processes, possibly through the action of acidic waters, containing mainly CO_2, on the same alumosilicates and aluminous silicates devoid of alkalis. This process in point of fact results in the formation of kaolinite pseudomorphs after other minerals, whose external forms or outlines are retained. Such are, for instance, kaolinite pseudomorphs after feldspars, muscovite, topaz, scapolites, leucite, andalusite, pyrophyllite, etc.

In the course of high-temperature regional metamorphism, clays are converted to compact clay shales (argillites and phyllites). At a temperature over 300° kaolinite is completely decomposed and in the presence of alkalis alters to sericite, micas, feldspars, etc., and in the absence of alkalis to aluminium silicates, such as andalusite, sillimanite, disthene, garnets, and other minerals composing crystalline schists.

We shall mention but a few of the numerous deposits in the U.S.S.R. Thus, kaolin occurs in many deposits in the *Ukraine* in the weathering zones of outcrops of massive crystalline rocks of the South-Russian shield (granites, gneisses, syenites, etc.). The largest are the Glukhovetskoye, Turbovskoye and Raykovskoye deposits (Vinnitsa Region), those at Belaya Balka and Chasov-Yar (Donetsk Region). Numerous primary and secondary occurrences, chiefly of refractory kaolins, are found on the eastern slope of the Urals (Sverdlovsk and Chelyabinsk regions), viz., Kuryinskoye, Troitsk-Baynovskoye, and Yelenovskoye deposits. Refractory clays, deriving from lacustrine and palustrine carbonaceous sediments, are found in the Moscow coal basin.

Outside the Soviet Union, large deposits of kaolin occur in *Cornwall* and *Devonshire* (England); at *Karlovy Vary* (Czechoslovakia); in *Bavaria* and *Saxony* (Saxonian and Bavarian porcelain), near *Limoges* in France (Sevres and Limoges porcelain); especially high-grade kaolin is mined in *China* on Mt. Kau-Ling, etc.

Uses. Kaolin has many industrial uses. Depending on the degree of purity, it is used either raw, i.e., without preliminary purification, or after elutriation in special basins.

1. The principal and the original consumer is the manufacture of *ceramics*. Kaolin free from iron oxides is used mostly in fine ceramics for manufacture of china-ware porcelain and tiles. This is due to its plastic properties, the ability to form stable suspensions in water and, most important, the fact that on baking or firing it turns into a stone-hard material which does not soak in water and is stable both at low and high temperatures. Refractory clays with a high melting point (above 1580°) often containing hydrates of free alumina are used mainly in metallurgy as fire bricks, plugs, pipes, funnels, etc. Low-grade fusible kaolins which are designated as terracota, shingle, brick clays, etc., are used in the manufacture of pottery, tiles and piping.

2. In the *building* trade clays are used in waterproof underfloor pillows in basements, in the construction of dams, for manufacture of adobe bricks, brick cement, etc.

3. In the *paper* production kaolin is used as a filler and finishing agent to impart smoothness, density, etc., to paper. Certain kinds of paper may contain as much as 40 per cent of kaolin.

4. Kaolinite is used also in the manufacture of oilcloth, linoleum, mixtures with drying oils, pencils, pigments, such as ultramarine (mixed with silica, soda, sulphur, and organic substances), for obtaining aluminium oxide, etc. It should also be mentioned that finely dispersed clays in the form of stable suspensions are used in drilling for oil, salt, and other unconsolidated minerals to plug small cavities in fissured wall rocks and thus to prevent the walls of the wells from caving; and also for easier extraction of drill cuttings with the drilling mud (specific gravity of the drilling fluid is increased by the clayey filler).

DICKITE, $Al_4[Si_4O_{10}][OH]_8$. **System**, monoclinic. Before the advent of X-ray methods was regarded as kaolinite. Named after its discoverer Dick who was the first to describe it as kaolinite in 1888.

In crystal structure it is similar to kaolinite. Although it has the same continuous layers of hexagonal-ring structure, in dickite, in contrast to kaolinite, each overlying hexagonal layer has a somewhat different orientation. Space group $Cc(C_s^4)$. $a_0 = 5.14$; $b_0 = 8.94$; $c_0 = 14.42$; $\beta = 96°50'$. Dickite is often found in rather well-developed transparent platy small crystals of hexagonal habit, up to fractions of a millimetre in diameter (Fig. 343). Its higher crystallisation ability is attributed to the more symmetrical positions of the OH ions in respect of the O ions, in comparison with kaolinite.

Colourless, white in pulverulent masses, sometimes with brownish, yellowish or greenish tinge. **Lustre**, pearly. $n_x = 1.566$, $n_y = 1.562$, and $n_z = 1.560$. **Hardness**, about 1. **Cleavage**, {001} perfect. **Specific gravity**, 2.589 (theoretical). Is dehydrated at 540°.

Dickite occurs mostly as a low-temperature hydrothermal mineral, often associated with sulphides, dolomite, fluorite, etc., in the form of crystal crusts in druse cavities. Has been observed also in chalcedony geodes.

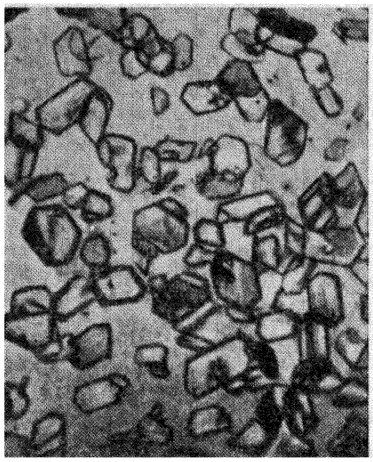


Fig. 343. Microcrystals of dickite. ×200.

In the U.S.S.R., large masses of dickite have been found in Central Kazakhstan, namely at Kara-Cheku (150 km south of Karkaralinsk) in hydrothermally altered lava and tuff breccias of porphyrys. A pure dickite (micaceous) tough rock has been found there. An interesting point is that dickite is formed directly following the sericitisation of feldspars. The size of dickite scales is 0.1 mm, increasing to 0.5 mm in massive rock.

NACRITE. $Al_4[Si_4O_{10}][OH]_8$. **System**, monoclinic. **Crystal structure** differs from that of kaolinite by smaller displacement of laminated sandwiches in relation to each other. Space group $Cc(C_s^4)$. $a_0 = 5.16$; $b_0 = 8.93$; $c_0 = 28.66$; $\beta = 91°43'$. Occurs in larger platy crystals (up to 5 mm in diameter) of hexagonal habit, also in radial-platy aggregates and compact or thin-scaly masses.

Colourless or white with a yellowish tinge. **Lustre**, pearly. $n_x = 1.563$, $n_y = 1.562$, and $n_z = 1.557$. **Hardness**, about 2. **Cleavage**, {001} highly perfect. **Specific gravity**, 2.627.

Nacrite is formed both in exogenous and endogenous conditions, evidently in acidic environment. In some localities in the Erzgebirge (Saxony), particularly at Brandt, it occurs as radial groups of platy crystals around galena, also at St. Peter's Dome, Colorado (U.S.A.) with mica and cryolite.

7. HALLOYSITE GROUP

The group embraces a rather large number of mineral species and varieties of comparatively complex composition, now being closely studied. We shall describe here a purely aluminium variety (halloysite), then a nickel variety (garnierite), and finally, formations of mixed composition—garnierite-halloysite. As a rule, these minerals occur either as colloidal or metacolloidal formations.

All the species included in this group have common physical properties and approach each other in the mode of formation, deriving as gels from the coagulation of sols only under exogenous conditions.

A characteristic feature of these minerals, distinguishing them from the previous group, is the presence of some molecular water loosely held in the crystal structure. A curious fact is that upon dehydration (even partial) *no re-absorption of water takes place*; this also places the minerals of this group distinctly apart from those of the next, the montmorillonite group. The dehydrated masses have relatively high hardness and plane-conchoidal fracture, the fracture surface taking a polish when rubbed with the fingernail. Another no less characteristic feature is that upon dehydration the minerals disintegrate into many small sharp angular fragments.

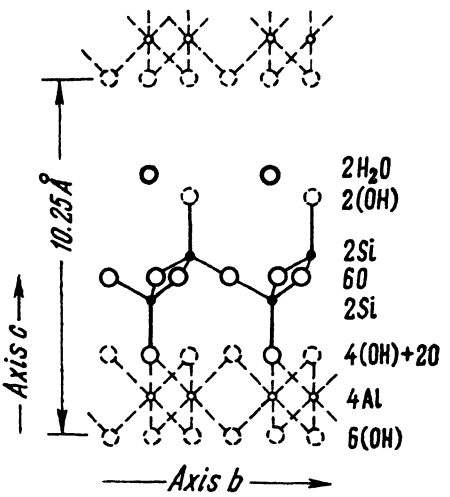


Fig. 344. Crystal structure of halloysite.

The crystal structure of halloysite, the best studied mineral of the group, is somewhat different from that of kaolinite, despite the identical composition (except for the $2H_2O$ in the halloysite) of the minerals. Figure 344 shows that the "hydrargillite" layer has the same type of linkage as in the structure of kaolinite (cf. Fig. 341). However, the layer of silicon-oxygen tetrahedra presumably has a different pattern. The tetrahedral apexes with the active oxygen ions are alternately oriented upwards and downwards. The upward apexes presumably have their oxygen ions replaced by weaker $[OH]^{1-}$ hydroxyl anions. This explains why the layers of H_2O molecules are retained in the structure. The molecules, naturally, have weaker linkage with the overlying "hydrargillite" layer.

The purely magnesian variety of the halloysite minerals is still awaiting further study; even its chemical formula is not clear. In general, it should be noted that magnesian hydrosilicates have often been described under identical names in spite of the differences in chemical properties.

HALLOYSITE, $Al_4[Si_4O_{10}][OH]_8 \cdot 4H_2O$*, or $Al_2O_5 \cdot 2SiO_2 \cdot 4H_2O$.

Chemical composition. Al_2O_3 34.7%, SiO_2 40.8%, H_2O 24.5%. Half the water is present in the mineral as a hydroxyl, the other half as H_2O molecules. The molecular water content is variable (less than $4H_2O$), which determines variations in the content of other constituents. Often contains as impurities negligible quantities of Fe_2O_3, Cr_2O_3, MgO, FeO, sometimes NiO, CuO, and ZnO.

* The formula is somewhat simplified.

System, monoclinic; domatic. Space group $Cm(C_s^3)$. $a_0 = 5.20$; $b_0 = 8.92$; $c = 10.25$; $\beta = 100°$. Occurs in gelatinous semi-dull masses with a plane-conchoidal fracture. The finely-dispersed particles of halloysite under the electron micrographs have a rod-like shape, in contrast to the platy particles of kaolinite.

Colour, white, often variously tinted: yellowish, brownish, reddish, bluish, and greenish. The outer shell is often ferruginous. **Lustre** for freshly extracted porcelainous varieties waxy, and dull for porous and friable varieties. The refractive index varies from 1.547 to 1.550 (increases with diminishing H_2O).

Hardness, 1 to 2. Brittle. Readily polished when rubbed with the finger-nail. The friable varieties often have a talc feel. The compact varieties crack on drying in the air, disintegrating into small *angular fragments* with a plane-conchoidal fracture (an important characteristic of all the halloysite minerals). **Specific gravity** varies from 2.0 to 2.2 depending on the H_2O content.

Diagnostic features. The friable varieties of halloysite do not differ externally from those of kaolinite. They have practically similar heating curves. However, they differ essentially in water content, optical constants, and also in dehydration curves, especially at the early stages (cf. Fig. 33). Also identifiable by low hardness, the ability to be polished by the finger-nail, and low specific gravity.

Infusible before the blowpipe. In the closed tube, yields much water. Partly decomposes in acids and alkalis, especially on heating. In water gradually disintegrates without swelling. When dry, sticks to the tongue.

Genesis and occurrence. Halloysite is a typical *exogenous* mineral and occurs mainly in the weathering crust of rocks (gabbro, diabases, porphyrites, etc.) and of certain nickel, copper, and zinc ore deposits. Usually forms small lenticular masses and concretions, often associated with other minerals of this group, as well as with alunite, diaspore, montmorillonite, etc.

Occurs also in karst sinks in limestones and in sour soils rich in organic acids.

Halloysite is rather widespread in the weathering crust of many deposits of nickel hydrosilicates in the Southern Urals, viz., *Aderlinsk*, *Khalilovo*, etc., where it is usually contaminated with various chemical and mechanical impurities. Found in the *Zhuravlinskoye* deposit at Chusovaya River (the Urals) in a karst sink together with alunite and hydrargillite at the contact of limestones and brown clays; in the *Krivoy Rog* area; in the Minusinsk district in *Khakassia*, and elsewhere.

Outside the U.S.S.R., it was first discovered in Belgium in the vicinity of old iron and zinc mines in the Angleur limestones near Liege.

Halloysite has no economic importance of its own.

GARNIERITE, $Ni_4[Si_4O_{10}][OH]_4 \cdot 4H_2O$, or $Ni_6[Si_4O_{10}][OH]_8 \cdot 4H_2O$? Synonym: noumeite.

Chemical composition is variable. NiO practically always has an isomorphous admixture of MgO (up to 15%, and more), which is an indication of high miscibility.

System, unknown. Forms as gels and cryptocrystalline aggregates, occasionally as stalactitic forms (in cavities) and earthy masses.

Colour, bright bluish green, less often bluish green or deep grass-green. **Lustre**, dull, sometimes waxy, greasy. The mean refractive index varies from 1.566 to 1.590.

Hardness, 2 to 2.5. Is not scratched, but polished by the fingernail. Brittle. Fracture, plane-conchoidal. **Specific gravity**, 2.3 to 2.8.

Diagnostic features. Physical properties closely resemble those of halloysite. Nickel-rich varieties are recognised by bright grass-green colour. Pale-coloured varieties are identifiable positively by chemical analyses and optical constants.

Infusible before the blowpipe. On igniton in the reducing flame becomes magnetic. Soluble in hot concentrated hydrochloric acid.

Genesis and occurrence. As a nickel hydrosilicate, garnierite derives from the intense weathering of ultrabasic rocks (dunites, peridotites, serpentinites) under the conditions of tropical and subtropical climates. Less often occurs in karst sinks at the contact of limestones and serpentinite masses, in association with the minerals of the halloysite-garnierite series. In the weathering crust of serpentinites, garnierite occurs at higher levels than nickel-poor magnesium hydrosilicates. It is probably formed in slightly alkaline or neutral environment. Its almost constant associate is exogenous quarts which is formed as veinlets in contraction cracks. When exposed to dry air, may lose part of water content, decrepitate and alter to earthy masses.

In the U.S.S.R., garnierite occurs in the *Ufaley* district (Middle Urals) in argillaceous formations of the halloysite-garnierite series, where it is concentrated in karst swallow-holes of limestones at the contact with serpentinite massifs. Occurs rather widely in the weathering crust of serpentinites in the *Akkerman* (near Orsk) and *Khalilovo* (Southern Urals) districts, and also in deposits in the *Kempirsay* district of the Aktyubinsk Region under the same conditions.

Discovered in *New Caledonia* near Noumea. As in the Urals, silicate nickel ores are overlain at this locality by ferruginous residual products of weathered serpentinite masses.

Uses. Together with other nickel hydrosilicates, garnierite is a constituent of important nickel ores.

GARNIERITE-HALLOYSITE $n\{(Ni,Mg)_4\ [Si_4O_{10}][OH]_4 \cdot 4H_2O\} - -(100-n)\{(Al,Fe)_4[Si_4O_{10}][OH]_8 \cdot 4H_2O\}$. This series comprises numerous minerals which differ form each other mostly in chemical composition and colour.

Chemical composition varies widely. Besides the constituents indicated by the formula, may contain minor amounts of Cr_2O_3, FeO, MnO, CaO, and alkalis. Characteristically, the $(RO+2R_2O_3) : RO_2$

ratio approaches 1, while RO : $(RO + R_2O_3)$ varies from 0 to 1. As in all the minerals of the series, the molecular water content is variable: usually because of partial dehydration in the air, it will be less than it should be by the formula.

Aggregates. Occur as gelatinous brittle concretions, often finely fragmented due to desiccation.

Colour varies widely depending on composition. It may change as follows from ferri-halloysite to garnierite: brown or chocolate-brown, light brown, yellow-brown, pale yellow; greenish yellow, pale green or bluish green, intense green. **Lustre**, waxy; dull for partly dehydrated varieties. n = 1.58 to 1.60.

Hardness, 1 to 2. Brittle. Upon dehydration in the air, all varieties disintegrate into small fragments with a plane-conchoidal fracture. In **specific gravity** they also are close to each other (2 to 2.5).

Diagnostic features, the same as for halloysite and garnierite: low hardness, fragmentation on dehydration, ability of taking readily a polish from the finger-nail, etc.

Genesis and occurrence. Form in the process of weathering of ultrabasic rocks. Their nickel, magnesium, and iron are furnished mostly by serpentine and the minerals from which it derived, whereas the source of aluminium, especially for alumina-rich members of the group, is usually the wall rock of serpentinite masses, such as porphyrites, clay shales, etc.

The minerals of this series have been studied in detail in the nickel-silicate ore deposits of the Middle Urals: *Petrovskoye*, *Tyulenevskoye*, *Novo-Cheremshanskoye*, *Golendukhinskoye*, etc., where minerals of this series are extensively developed in near-contact depressions as a mantle over marbles or as concretions in halloysite clays adjacent to serpentinite masses which were exposed to weathering in the remote past.

The concretions are usually finely fragmented and are strikingly varicoloured. Often even one and the same specimen exhibits a wide variety of colours.

8. ALLOPHANE GROUP

Next logically come the truly amorphous glassy or resinous, often transparent, minerals of variable chemical composition, consisting mainly of Al_2O_3, SiO_2, and H_2O. No systematic classification of the minerals is possible at present. Therefore, we shall describe them here in general under the collective name of "allophane".

ALLOPHANE, $mAl_2O_3 \cdot nSiO_2 \cdot pH_2O$. "Allophanes" is the Greek for to be different (the mineral was often mistaken for a copper ore because of its bluish or greenish hue).

Chemical composition. The minerals of this group are not chemical compounds but typical solid pseudosolutions. According to the complete chemical analyses available, the Al_2O_3 content varies from 23.5

to 41.6%, SiO_2 21.4 to 39.1%, H_2O 39.0 to 43.9%. In addition to this, the following constituents may be present (per cent): Fe_2O_3 (up to 0.8, or even more), MgO (up to 0.3), CaO (up to 2 and more), K_2O + + Na_2O (up to 0.3), CuO (up to 1.6 and more), ZnO (up to 4), CO (up to 1.2), P_2O_5 (up to 1.3), SO_3 (up to 0.2).

Appearance. Typical glassy masses with curved or conchoidal fracture surfaces. Also in crusts with a reniform surface, occasionally in pulverulent white masses. X-ray studies fail to reveal crystal structure.

Colour, mostly pale blue, greenish yellow, less often deep green, brown; often colourless. Transparent or translucent. **Lustre,** vitreous, greasy. n = 1.47 to 1.51.

Hardness, about 3. Very brittle. **Specific gravity,** 1.85 to 1.89.

Diagnostic features. Glassy texture, transparency or translucency, and low hardness (in distinction from transparent opals). Since they are amorphous, optically isotropic, and do not differ in refractive indices, the allophane minerals can be positively recognised only by chemical analysis. The heating curve is also rather characteristic, but in partly crystallised allophanes, the crystal phase may be determined only by X-ray study (most often features of the halloysite crystal phase are detected).

Before the blowpipe the allophanes decrepitate without fusing. In nitric-cobalt solution, powdered allophanes take a beautiful blue colour (Al). Gelatinise in hydrochloric acid.

Genesis and occurrence. The allophanes occur exclusively as exogenous formations, often in cracks and cavities in the oxidised zones of ore deposits and rocks, as well as in cavities in marls, in deposits of clays, coals, red-iron, lead and zinc, copper, and other ores, often associated with halloysite, sometimes with chrysocolla, quartz, carbonates, etc. Under the action of water containing CO_2 they are carbonated. Cases are known when they decompose, altering to halloysite.

Of the numerous allophane localities in the U.S.S.R. we shall mention the following: *Zhuravlinskoye* alunite deposit (the Urals); *Karamazar* mountains (Tajikistan); *Potekhino* village near Minusinsk (Khakassia), in association with alumohydrocalcite developing metasomatically after allophane; *Baranovka* village near Ivanovo-Voznesensk; *Khoper*, *Lipetsk*, and other iron-ore deposits of the Central-European U.S.S.R.; a deposit of sedimentary bleaching clays near Nalchik, and elsewhere.

9. MONTMORILLONITE GROUP

Similarly to the preceding serpentine-kaolinite and halloysite groups, the montmorillonite group comprises essentially magnesial, essentially aluminium and intermediate mineral species. Although similar externally, the montmorillonite minerals differ substantially from the previous groups in crystal structure and in some very peculiar physical properties.

The structure of these minerals, as in all micaceous substances is characterised by sheet-like arrangement of the anions and cations.

The minerals of this group differ from the kaolinites and halloysites in that the "hydrargillite" layer is located *between two layers* of silicon-oxygen tetrahedra (Fig. 345). In this respect, the montmorillonite group minerals closely resemble those of the talc group and other minerals of similar crystal structure. As for the orientation of silicon-oxygen tetrahedra in individual layers, there is practically no difference from the halloysite structure (cf. Fig. 344): the tetrahedra oxygen apexes form part of the "hydrargillite" layer, whereas the hydroxyl apexes are

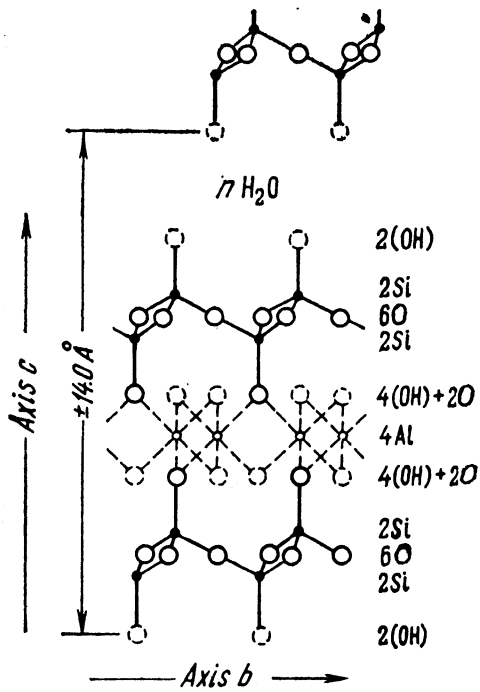


Fig. 345. Crystal structure of montmorillonite.

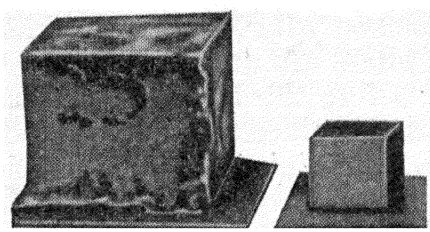


Fig. 346. Bentonite.
Right: bentonite cube when dry; left: the same cube after adsorption of water.

turned outwards. Thus, each laminated sandwich is fringed on both sides with the hydroxyl ions capable of retaining the H_2O molecules. The latter are probably arranged in sheets with a regular orientation within the sheets.

A remarkable property of montmorillonite minerals, and one that makes them exceedingly important commercially is their ability to swell in the presence of water (Fig. 346) and to gradually give up the absorbed water upon heating. As a resu t, the *c* value of the crystal lattice varies widely (from 9.6 to 28.4Å) depending on the quantity of H_2O molecules in the crystal structure of the mineral.* The high absorption capacity of clays, comprised mainly of the montmorillonite minerals, and their ability to extract suspended impurities (and in the dry state even petroleum gases) from liquids is made wide use of

* The H_2O molecules are located in the spaces between the sandwiches, i.e., penetrate along the planes dividing the planar sandwiches of the crystal structure since each sandwich has hydroxyl ions on both outer surfaces and therefore these surfaces adjoin each other along surfaces carrying charges of the some sign, no wonder that these sandwiches readily draw apart to permit penetration of water.

in various industries. Some clays are good absorbents of caustic and carbonic alkalis and, therefore, are used as saponifiers in soapboiling. They are called "bleaching" clays and are also known by various special names such as "bentonites", "Fuller's earth", "gumbrin", "nalchikite", etc.

Another very important feature of these minerals, which commonly occur as finely-dispersed masses, is their excellent cationic exchange property, which they share with zeolites and special substances called permutites. The clays consisting mainly of montmorillonite contain 60 to 100 mg-equ. of exchange cations per 100 g of substance (mostly Ca^{2+}, K^{1+}, and Na^{1+}), whereas the kaolins contain only 3 to 15 mg-equ. of exchange cations. Since on fine grinding the cationic exchange increases as much as threefold, it is assumed that the exchange cations may be distributed not only on the surface of particles but also within the crystal phases (evidently between the laminated sandwiches in the crystal structure).

According to Ross and Hendrix, these exchange cations ("outer bases"), although they enter into the composition of the montmorillonite minerals, do not take part in their crystal structure. Upon adsorption they only serve to balance the residual negative charge of the structure developing as a result of the replacement of high-valent cations by low-valent ones, e.g., Al^{3+} by Mg^{2+}, or Si^{4+} by Al^{3+}. Indeed, if in the crystal structure of beidellite, $Al_2[Si_4O_{10}]\,[OH]_2 \cdot nH_2O$, some of the Al^{3+} cations are replaced by Mg^{2+} cations, there will develop a residual negative charge which may be balanced by Na^{1+}, for instance (each exchange base receives an average charge of 0.33):

$$Al_{1.67}\,\overset{\uparrow}{Mg}_{0.33}\,[Si_4O_{10}]\,[OH]_2 \cdot nH_2O \qquad Na_{0.33}$$

The picture will be similar if Si^{4+} is replaced by Al^{3+}:

$$Al_2\,[(Si_{3.67},\ \overset{\uparrow}{Al}_{0.33})\ OH_{10}]\,[OH]_2 \cdot nH_2O \qquad Na_{0.33}$$

That is why the montmorillonite minerals have such complex formulas calculated by the method of Ross and Hendrix. We shall omit the calculations and merely say that the number of cations in sixfold coordination usually exceeds 2 (2.05 to 2.27). The presence of Al ions in fourfold coordination replacing Si^{4+} is characteristic of the aluminium-rich varieties.

In this group of minerals we shall review beidellite, montmorillonite, and nontronite.

BEIDELLITE, $Al_2\,[Si_4O_{10}]\,[OH]_2 \cdot nH_2O$. Named after Beidell, a locality in Colorado (U.S.A.).

Chemical composition is variable; the content of sesquioxides and silica varies depending on the content of water. The Al_2O_3 content

ranges from 20 to 27.6%, SiO_2 from 45 to 50%. Moreover, it practically always contains minor amounts of Fe_2O_3, CaO, alkalis: Na_2O and K_2O, sometimes MgO, NiO, MnO, etc.

System, monoclinic. Occasionally may be found in thin rhomboidal plates. Commonly occurs in earthy masses together with montmorillonite in bentonite clays. Crystal structure is similar to that of montmorillonite (Fig. 345).

Colour, white or yellowish, brownish, and reddish. **Lustre,** for compact varieties weak, waxy. Refractive indices vary depending on water content.

Hardness, for plates 1.5. **Cleavage,** {001}. **Specific gravity** for plates, 2.6. Beidellite, as all the other minerals of the group, has pronounced cationic exchange properties in strictly equivalent proportions, swells in water, etc. For uses see "Montmorillonite".

Genesis and occurrence. Occurs in the weathering crust of basic and ultrabasic rocks at Khalilovo, Akkerman, and other localities in the Southern Urals. This, among other things, determines the presence of nickel and chromium. Occurs also in the oxidized zones of certain ore deposits (antimony, manganese, etc.). In quantity has been found in loesses, e.g., in south-western Missouri (U.S.A.), in soils deriving from loesses and in grey soils over igneous rocks, sometimes as an alteration product of volcanic ash, in bentonite clays together with montmorillonite, etc.

MONTMORILLONITE, $m\{Mg_3[Si_4O_{10}][OH]_2\} \cdot \{p(Al,Fe)_2 \ldots [Si_4O_{10}][OH]_2\} \cdot nH_2O$. The $m : p$ ratio is usually 0.8 to 0.9. Named after the place of discovery, Montmorillon (France). Is widely distributed, chiefly in certain clays.

Chemical composition varies considerably with water content. According to the available data of analyses of pure varieties, its composition may vary as follows (per cent): SiO_2 48 to 56, Al_2O_3 11 to 22, Fe_2O_3 from 5 on, MgO 4 to 9, CaO 0.8 to 3.5 and more, H_2O 12 to 24. Sometimes contains K_2O, Na_2O, etc.

System, monoclinic. $a_0 = 5.10$; $b_0 = 8.83$; $c_0 = 15.2$ (on heating to 400°, c_0 diminishes to 9.6).

Colour, white with grey, sometimes bluish, tints, pink, pink-red, green. **Lustre,** dull (when dry). $n_y = 1.516$ to 1.526.

Hardness for individual scales, unknown. Very soft. Greasy feel. **Cleavage,** for scales, {001} perfect. **Specific gravity** variable.

Diagnostic features. The presence of montmorillonite in certain clay varieties may be detected by their strong swelling on wetting and the resultant greasy feel. However, positive identification is impossible without measurement of optical constants, and X-ray and chemical analyses.

The outcrops of bentonite clays rich in montmorillonite and beidellite have some specific external features. After rainfall, the outcrops turn into a thick mass of slippery gel. Upon drying the mass develops cracks and at the same time heaves due to the continued swelling of

the deeper portions. As a result, the outcrops become wrinkled, strongly fissured and coral-like. In stable dry weather the surface of the clays becomes very loose.

Genesis and occurrence. Montmorillonite is almost exclusively formed under *exogenous* conditions, chiefly upon weathering of basic igneous rocks in alkaline environment.

Many of the bentonite clays composed of montmorillonite derive from the decomposition of volcanic ashes deposited mainly in marine basins.

Montmorillonite is also widespread in the weathering crust of basic igneous rocks: diabases, basalts, gabbro, peridotites, etc. Also forms in soils derived from the weathering of granites and diorites. Montmorillonite accumulations are known in leached and medium-humic black and chestnut soils forming on igneous rocks.

Forming under surface conditions, montmorillonite is more or less stable. In deserts and semi-deserts its deposits turn into dust at the surface and are readily transported by winds. This gives rise to the formation of loesses which often contain considerable amounts of beidellite and montmorillonite.

In the U.S.S.R., high-grade bleaching clays occur in the vicinity of *Gumbry* village near Kutaisi (Western Georgia) as a bed of varying hues, from almost white to light yellow, yellowish green and grey. The clays have derived from volcanic ash which was washed down into the sea in the Upper Cretaceous period. High-grade montmorillonite-bearing clays are known in Lower Tertiary sediments near Nalchik.

Several deposits of bentonites possessing adsorbing and saponifying properties occur in the U.S.S.R. in the vicinity of *Askanya* village (south-east of the town of Makharadze in Western Georgia) as sheet-like bodies. Also noteworthy are deposits of kills in the *Crimea* (of the Upper Cretaceous age).

Outside the Soviet Union, deposits of bleaching clays (Fuller's earth) are widespread in the U.S.A.: Florida, Georgia, Alabama, California, and also at Montmorillon, Vienne in France, in Germany, Japan, and other countries.

Uses. As good adsorbents, the montmorillonite clays are extensively used in industry either simply dried or after chemical pre-activation.

The chief consumer of these clays is the oil-refining industry which uses them to purify fractionation products of suspended matter (resins, carbonaceous impurities, etc.). In the textile industry they are used for degreasing broadcloth for dyeing fabrics (silk, cotton, etc.), thanks to their ability to form stable and thick suspensions with water and oils. In rubber manufacture these clays and also kaolin are used as active fillers to impart such qualities as toughness, wear resistance, acid resistance, etc. In soap-boiling and cosmetics they also serve as fillers in cheap grades of soap, in powder, make-up, lipstick, tooth powder and paste, etc. The clays find uses as purifiers of water and food products (wine, vegetable oil, etc.), as additives in the making of paper and ceramics; and finally, as binders in medical preparations, as adsorb-

ents of bacilli and harmful substances in the treatment of gastric diseases, wounds, alkaloid-poisoning, etc.

NONTRONITE, $(Fe, Al)_2[Si_4O_{10}][OH]_2 \cdot nH_2O$. Since the name covers the Fe_2O_3-rich varieties of montmorillonite, it would be more appropriate to designate the mineral as ferrimontmorillonite. Named after the place of discovery, Nontron (France). Synonym: chloropal (in rare compact masses mixed with opal).

Chemical composition variable. Occasionally it corresponds to an almost purely ferruginous mineral giving the formula: $Fe_2[Si_4O_{10}][OH]_2 \cdot nH_2O$, i.e., the end member of the isomorphous series with $Al_2[Si_4O_{10}][OH]_2 \cdot nH_2O$ (beidellite). Usually contains considerable Al_2O_3 (up to 14%), and MgO (up to 8%). May contain CaO (up to 2%), minor quantities of K_2O, Na_2O, sometimes NiO, Cr_2O_3.

Occurs usually in earthy cryptocrystalline aggregates, occasionally in compact opaloid masses.

Colour, greenish yellow, pistachio-green, and brownish green (stained by iron hydroxides). **Lustre**, for friable varieties dull; waxy for compact ones. $n_y = 1.585$ to 1.600.

Hardness, approximately 2 to 2.5. Fracture of compact varieties is conchoidal. Brittle, friable, greasy feel. **Cleavage**, detected only for scaly varieties under the microscope. **Specific gravity**, 1.727 to 1.870.

Diagnostic features. In the products of weathering, especially of ultrabasic magnesial-ferruginous rocks (serpentinites, peridotites, dunites), may be tentatively identified by earthy aggregates of greenish-yellow or green colour.

Positive identification of nontronite requires determination of optical constants, chemical and spectral analyses, and X-ray data.

Infusible before the blowpipe. Decomposes with some difficulty in hydrochloric acid with the separation of gelatinous silica.

Genesis and occurrence. As stated earlier, forms exogenously, in weathered iron- and magnesium-rich, mostly igneous rocks, and also in a number of metalliferous, particularly iron ore deposits.

On weathering at the surface, gradually decomposes, forming iron hydroxides that retain the texture of nontronite and opal, altering to chalcedony and quartz.

Nontronite is widespread in the ancient crust of weathering in serpentinite masses of the *Khalilovo*, *Kempirsay* near Aktyubinsk, and other districts in the Southern Urals. It has also been found on Mt. *Magnitnaya*, in *Krivoy Rog*, near *Zhdanov*, and elsewhere.

Uses. Nickel-enriched masses of nontronite occurring in the crust of weathering of ultrabasic igneous rocks (dunites and serpentinites) may have commercial importance.

In many deposits of nickel-silicate ores, nontronite masses are the principal ore constituent, along with such magnesium- and nickel-hydrosilicates as revdinskite, sometimes garnierite, etc.

SILICATES WITH CONTINUOUS THREE-DIMENSIONAL FRAMEWORKS OF $(Si, Al)O_4$ TETRAHEDRA IN CRYSTAL STRUCTURES

Many of the silicates with three-dimensional frameworks of $(Si, Al)O_4$ anionic tetrahedra are widely distributed and important rock-forming minerals.

As we have already said, from the chemical standpoint the compounds in this subclass are almost exclusively alumosilicates, i.e., such whose crystal structures contain anionic complexes comprising AlO_4 tetrahedra in addition to the SiO_4 tetrahedra, no more than half the total number of the Si^{4+} ions being replaced by Al^{3+} ions. The stoichiometric Si : Al ratios are usually either 3 : 1 or 1 : 1, i.e., the complex anions often may be expressed by the following formulas: Si_3AlO_8 or $SiAlO_4$ ($Si_2Al_2O_8$).

The (Si + Al) : O ratio in the anionic radicals is always 1 : 2. Therefore, the minerals in this subclass are much nearer than other silicates to the SiO_2 minerals (quartz, tridymite, and cristobalite); accordingly their crystal structures are also very close to each other. The SiO_4 and AlO_4 tetrahedra are linked into three-dimensional frameworks exactly in the same way as the SiO_4 tetrahedra in the quartz minerals, i.e., each apex of every tetrahedron is shared by the adjacent tetrahedron. Nevertheless, the shape and structure of the spatial frameworks differ for different compounds.

It is characteristic that the cations occupying the "voids" in the frameworks are always ions with larger radii and hence with correspondingly larger coordination numbers: N^{1+}, Ca^{2+}, K^{1+}, Ba^{2+}, occasionally Cs^{1+}, and Rb^{1+}. Smaller cations with characteristic *sixfold* coordination are Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, etc., usually present in the previous subclasses are *entirely absent* from this subclass, which is explained very simply by the electrovalency principle.

Indeed, the feldspars and zeolites—the most common and important members of this subclass—have the following types of anionic radicals: $[Si_3AlO_8]^{1-}$, $[Si_2Al_2O_8]^{2-}$, $[Si_3Al_2O_{10}]^{2-}$, etc. Thus, each O^{2-} ion has in the first instance 1/8, in the second 1/4, and in the third 1/5 of negative valency to be balanced, whereas each Mg^{2+}-type cation, which can be surrounded by no more than six oxygen ions, requires 1/3 of negative valency from each surrounding oxygen ion, i.e., more than the alumo-silicon-oxygen tetrahedra have in their frameworks. These charges can be neutralised only by larger univalent Na^{1+}, K^{1+} or divalent Ca^{2+}, Ba^{2+} cations which of necessity require smaller portions of the charge for neutralisation, inasmuch as these cations may be surrounded by eight or more oxygen ions. Therefore, Mg^{2+}- and Fe^{2+}-type cations present in a melt or a solution enter into the composition of other minerals, forming paragenetically with feldspars (pyroxenes, hornblendes, micas, etc.).

Of special interest are the minerals with the so-called intrusion structures which, in addition to the three-dimensional anionic frameworks,

contain such anions as F^{1-}, Cl^{1-}, $[OH]^{1-}$, $[SO_4]^{2-}$, and $[CO_3]^{2-}$. The additional anions have no direct connection with Si^{4+} and Al^{3+} of the tetrahedra, but are independently linked with alkaline and alkaline-earth cations (Na^{1+}, Ca^{2+}, Ba^{2+}, etc.) whose total number in these minerals is naturally greater than in simpler compounds. Since the additional anions are rather large, they can be accommodated only in the larger "voids" of crystal structure.

A remarkable feature of the composition of the so-called zeolites is the presence of loosely held H_2O molecules. Upon dehydration, hydration, or upon replacement of the H_2O molecules by those of other substances (e.g., alcohol), the crystal structures of the zeolites are not destroyed. This characteristic feature of the zeolites is also explained by the presence of channels that are large enough to allow movement of water molecules and other substances. Another important chemical feature of the minerals of the zeolite group is their cation exchange property: Na^{1+} may be replaced by other ions – Ag^{1+}, Li^{1+}, $[NH_4]^{1+}$, etc. – present in solutions. This, as evident from X-ray data, does not cause any change in crystal structure.

The physical properties of the minerals with three-dimensional anionic radicals in the crystal structure are somewhat peculiar. Their most striking feature is their light colour (chromophore metals in sixfold co-ordination are absent from these minerals, as we have already said). Then, the minerals in this subclass as a whole have the lowest refractive indices as compared to the silicates of other subclasses, which is fully accounted for by the fact that the volumes of their crystal lattices per one O^{2-} ion are larger. This also explains their lower specific gravity. Characteristically, the replacement of univalent cations (Na^{1+}, K^{1+}) by divalent Ca^{2+} and Ba^{2+} causes not only a contraction of crystal structure and considerable deformation of the O^{2-} ions but also a certain increase in refractive and birefringence indices.

The hardness of the reviewed minerals usually ranges form 5 to 6, being inferior only to that of the silicate with isolated SiO_4 tetrahedra. As for cleavage, it is often distinct and even perfect in several directions, in contrast to the quartz minerals in which the principal Si – O – Si forces are equivalent in all three directions. The explanation is that in many crystal structures, despite the three-dimensional frameworks, the packing of anionic tetrahedra is closer in certain directions. Thus in the pseudotetragonal crystal structures of feldspars, scapolites, natrolite, etc., cleavage is parallel to the "pseudotetragonal" prism; in the hexagonal structures of nepheline and cancrinite it is parallel to the "pseudohexagonal" prism, while heulandite with a structure close to the layered type has unidirectional cleavage as the micaceous minerals. It should be noted in conclusion that the feldspars and some of the zeolites have rather pronounced symmetrical structure. This explains their definite tendency to twinning, the twins possessing a symmetry of higher order than that of single individuals.

1. GROUP OF FELDSPARS

The feldspars* are the most widely distributed silicates in the earth's crust, making up some 50 per cent of it by weight. Approximately 60 per cent of these minerals are contained in igneous rocks; about 30 per cent in metamorphic rocks, mostly crystalline schists; the remaining 10 to 11 per cent occur chiefly in sandstones and conglomerates, as rounded grains or pebbles.

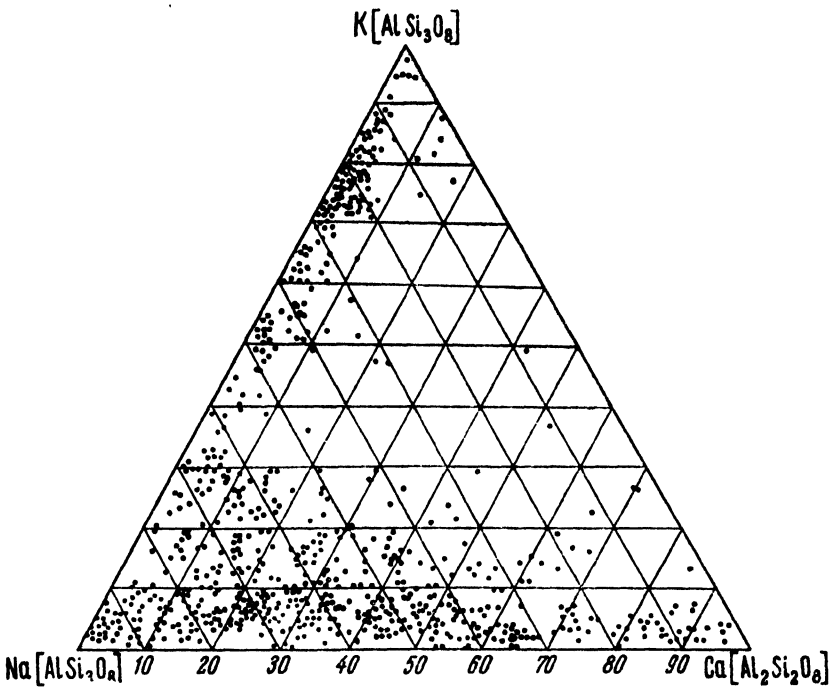


Fig. 347. Graph of variations in the chemical composition of feldspars.

Chemically, the feldspars are alumosilicates of Na, K, and Ca, such as $Na[AlSi_3O_8]$, $K[AlSi_3O_8]$, $Ca[Al_2Si_2O_8]$, and rarely of Ba, such as $Ba[Al_2Si_2O_8]$. Occasionally they may contain negligible amounts of Li, Rb, Cs as isomorphous admixtures to the alkalis, and also Sr as a substitute for Ca.

Another specific feature of these minerals is their ability to form isomorphous, chiefly binary, series, such as $Na[AlSi_3O_8]$-$Ca[Al_2Si_2O_8]$, $Na[AlSi_3O_8]$-$K[AlSi_3O_8]$, and $K[AlSi_3O_8]$-$Ba[Al_2Si_2O_8]$. The incidence and extent of isomorphism for the first two pairs is clearly illustrated by the composition graph of feldspars (Fig. 347).

The feldspars crystallise in the monoclinic or triclinic systems, both of which are almost indistinguishable morphologically. X-ray studies reveal great similarity in the crystal structure of all spars.

* The origin of the name "feldspar" is obscure. These spars, i.e., minerals possessing perfect cleavage in two directions, probably owe their name to their frequent occurrence in the field.

These minerals have also much in common in physical properties. Most of them are light-coloured, possess rather low refractive indices, high hardness (6 to 6.5), perfect cleavage in two directions at an angle close to 90°, and comparatively low specific gravity (2.5 to 2.7). These properties rather easily distinguish them from similar minerals.

As coarse-crystalline masses they occur in pegmatites associated with quartz, often with coarse-crystalline mica, and rare minerals

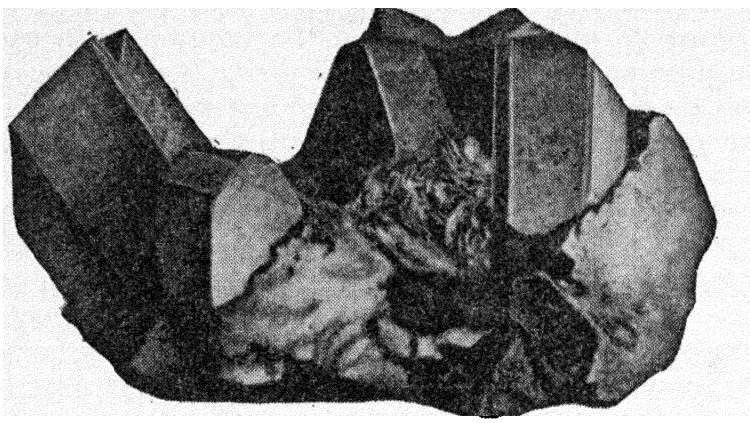


Fig. 348. Druse of large orthoclase crystals with aggregates of platy albite (cleavelandite) crystals from a pegmatite dike. $^1/_3$ of life size.

containing volatile constituents (topaz, beryl, and tourmaline). Druses of well-developed large crystals are found occasionally in miarolitic cavities (Fig. 348).

Depending on chemical composition, the feldspars fall into three subgroups:

(a) The *sodium-calcium* feldspars known as plagioclases giving continuous isomorphous series $Na[AlSi_3O_8]$-$Ca[Al_2Si_2O_8]$; they often contain minor quantities of $K[AlSi_3O_8]$ as an isomorphous admixture.

(b) The *potassium-sodium* feldspars, also giving at high temperatures continuous series of solid solutions $K[AlSi_3O_8]$-$Na[AlSi_3O_8]$ which decompose upon slow cooling into potassium-rich and sodium-rich components (cf. halite-sylvite). The content of $Ca[Al_2Si_2O_8]$ as an isomorphous admixture is usually negligible.

(c) The rare *potassium-barium* feldspars known as *hyalophanes* which also form isomorphous series $K[AlSi_3O_8]$-$Ba[Al_2Si_2O_8]$.

Plagioclase Subgroup

The minerals of this subgroup constitute, as has been stated earlier, a well-studied binary series of isomorphous mixtures with albite, $Na[AlSi_3O_8]$, and anorthite, $Ca[Al_2Si_2O_8]$, as the end members. According to the available data on the natural and artificial com-

pounds, there exist all the intermediate varieties of continually changing composition from pure albite (Ab) to anorthite (An).

The mineral species of this isomorphous series are tentatively classified as follows:

		Content of anorthite molecule, per cent	
Albite (Ab), $Na[AlSi_3O_8]$		0-10	Triclinic system
Oligoclase	Isomorphous mixtures Ab+An	10-30	Ditto
Andesine		30-50	Ditto
Labradorite		50-70	Ditto
Bytownite		70-90	Ditto
Anorthite (An), $Ca[Al_2Si_2O_8]$		90-100	Ditto

PLAGIOCLASES, $(100-n)Na[AlSi_3O_8]\cdot nCa[Al_2Si_2O_8]$ where n varies from 0 to 100. "Plagioclase" is the Greek for obliquely split. The intersection angle of the (001) and (010) cleavage planes for the plagioclases varies from 86°24′ to 86°50′, being less than this angle (close to 90°) for the other feldspars. "Albite" comes from the Latin "albus" meaning white. "Anorthos" is the Greek for oblique (cf. triclinic system of crystallisation).

Because of the exceptional importance of the composition of plagioclases for the classification of igneous rocks, Soviet scientist Y.S. Fyodorov suggested a very convenient and rational classification in which each plagioclase is designated by a definite number corresponding to the percentage of the anorthite molecule in it. Thus, plagioclase No. 72 is an isomorphous mixture containing 72 per cent of anorthite and 28 per cent of albite. Usually the minor isomorphous admixture of $K[AlSi_3O_8]$ is neglected.

Sometimes, for general considerations, in systematic classification of igneous rocks, it is convenient to roughly divide plagioclases according to composition:

Acid plagioclases	Nos. 0-30
Medium plagioclases	Nos. 30-60
Basic plagioclases	Nos. 60-100

The terms "acid", "medium", and "basic" are not used here in their customary sense; they are based on the gradual decrease of SiO_2 ("silicic acid") content from albite to anorthite; the decrease can be seen from a comparison of the formulas of the end members of the isomorphous series.

Chemical composition (theoretical) is given in the table below showing the contents of Na_2O, CaO, Al_2O_3, and SiO_2 for five numbers of the plagioclases.

Table 16

Chemical Composition and Specific Gravity of Plagioclases

Composition	Plagioclases				
	No. 0	No. 25	No. 50	No. 75	No. 100
Na_2O	10.76	8.84	5.89	2.92	—
CaO	—	5.03	10.05	15.08	20.10
Al_2O_3	19.40	23.70	28.01	32.33	36.62
SiO_2	68.81	62.43	56.05	49.67	43.28
Specific gravity	2.624	2.643	2.669	2.705	2.758

There is practically always an admixture of K_2O, sometimes as high as a few per cent, and often negligible quantities of BaO (up to 0.2%), SrO (up to 0.2%), FeO, Fe_2O_3, etc.

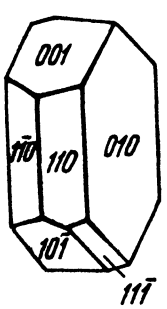


Fig. 349. Albite crystal. Angle between (010) and (001) equals 86°24′.

System, triclinic; symmetry, pinacoidal. Space group $P1(C_1^1)$. Albite: $a_0 = 8.23$; $b_0 = 13.00$; $c_0 = 7.25$; $\alpha = 94°03'$; $\beta = 116°29'$; $\gamma = 88°09'$. Anorthite: $a_0 = 8.18$; $b_0 = 12.89$; $c_0 = 2 \times 7.09$; $\alpha = 93°13'$; $\beta = 115°56'$; $\gamma = 91°12'$. **Habit.** Well-developed simple crystals are relatively rare. They have a tabular or tabular-prismatic habit. A typical crystal is shown in Fig. 349. Simple twins are rare, but complex polysynthetic ones are very frequent and are observed even in irregular grains. These complex twins are clearly seen in transparent polished sections with crossed nicols and are typical enough to distinguish promptly the plagioclases from other minerals.

Aggregates. Albite often occurs in miarolitic cavities in pegmatites, both as druses and aggregates of platy crystals, which are sometimes called cleavelandite (Fig. 348). Also known are some granular-crystalline rocks composed almost entirely of plagioclases, such as saccharoidal albite rocks often formed metasomatically in pegmatites, anorthosites and labradorites, used as facing stones, etc.

Colour, white, greyish white, sometimes with greenish, bluish, and less often with reddish hue. **Lustre**, vitreous. Refractive indices increase regularly from albite ($n_x = 1.536$, $n_y = 1.529$, $n_z = 1.525$) to anorthite ($n_x = 1.588$, $n_y = 1.583$, $n_z = 1.575$).

Varieties given special names due to peculiar optical phenomena: (1) *moonstone*, an acidic plagioclase (more often potassium-sodium feldspar) which shows a peculiar lightly-bluish opalescence resembling moonlight; (2) *aventurine* or *sunstone*, an acidic plagioclase, and a

potassium-sodium feldspar, with a beautiful sparkling golden chatoyancy due to inclusions of very fine specks of iron glance; (3) *labradorite*, the principal mineral of the so-called labrador stone, is a basic or medium plagioclase, often showing beautiful play of blue and green colours.

Hardness, 6 to 6.5. **Cleavage**, {001} and {010} perfect. **Specific gravity** increases continually from 2.61 (albite) to 2.76 (anorthite).

Diagnostic features. In larger crystals and grains the plagioclases may be distinguished from the similar potassium-sodium feldspars by their oblique angle of cleavage. It is impossible, however, to tell different mineral species of the plagioclase series from one another without microscopic examination.

Before the blowpipe fuses with difficulty to a glass, often colouring the flame yellow (Na). Insoluble in acids.

Genesis and alteration. Being the most common of the feldspars, the plagioclases are present in the majority of *igneous rocks*. It should be noted that the composition of plagioclases is closely related to the basicity of host rock. Thus, widespread in silica-poor basic rocks (gabbro, basalts, etc.) are calcium-rich basic plagioclases, usually associated with magnesial-ferroginous silicates, whereas more acidic igneous rocks (diorites, granites, and quartz-porphyries, etc.) contain medium and acid plagioclases as rock-forming minerals, often associated with potassium-sodium feldspars, quartz, etc.

Pegmatites genetically related to granites and to basic intrusive rocks in general have in their composition albite, generally developing later metasomatically as fine-grained masses deriving from potassium-sodium feldspars. Basic plagioclases occur only in the rare pegmatites of basic intrusive rocks (gabbro).

In the course of *regional metamorphism*, involving the formation of crystalline schists and Alpine clefts, albite will be mostly formed (the calcium-rich plagioclases are less stable).

In the course of weathering, the plagioclases gradually decompose completely under the action of ground waters containing CO_2, O_2, humic acids, etc.; the alkalis and alkaline earths are leached out in the process.

Uses and occurrence. Plagioclase masses rarely are of economic importance because of their low alkali content.

The dark-grey or almost black labradorites with a beautiful play of blue and green colour are polished and used as facing stone. Labradorites are quarried in the *Zhitomir* Region, the Ukraine, where they were discovered accidentally during the laying of a railway in 1835. At that time labradorites were valued very highly.

Plagioclases with a moonlight opalescence are recovered from pegmatite dikes at *Shaytanka* and *Lipovka* (the Middle Urals).

Sunstone, which also occurs in pegmatite dikes, is used for cheap ornaments.

Subgroup of Orthoclases (Sodium-potassium Feldspars)

The sodium-potassium feldspars crystallise, depending on temperature, either in the monoclinic or the triclinic system. Since K^{1+} and Na^{1+} differ considerably in ionic radii (1.33 and 0.98 Å, respectively), the solid solutions formed at high temperature disintegrate, upon gradual cooling, forming the so-called *perthites*, i.e., ordered intergrowths of the products of disintegration of solid solutions.

All this naturally greatly complicates the composition and structure of the mineral species. According to the data available, they may be generally classified as follows:

Monoclinic high-temperature series

Sanidine, $K[AlSi_3O_8]$	Monoclinic system
Natronsanidine, $(K, Na)[AlSi_3O_8]$	Ditto

Monoclinic low-temperature series

Orthoclase, $K[AlSi_3O_8]$	Monoclinic system
Natronorthoclase, $(Na, K)[AlSi_3O_8]$	Ditto

Triclinic series

Microcline, $K[AlSi_3O_8]$	Triclinic system
Anorthoclase, $(Na, K)[AlSi_3O_8]$	Ditto

Thus, for the $K[AlSi_3O_8]$ compound there are two monoclinic modifications (sanidine, stable at over 900°, and orthoclase, stable below that point) and a triclinic modification which is very close to the monoclinic ones and is called microcline.

SANIDINE, $K[AlSi_3O_8]$. Impurities: Na_2O, occasionally BaO (up to 5%).

System, monoclinic; symmetry, monoclinic prismatic L^2PC. Space group $C2/m(C_{2h}^3)$. $a_0 = 8.42$; $b_0 = 12.92$; $c_0 = 7.14$; $\beta = 116°06'$. Crystals, colourless, transparent. Being a *high-temperature* mineral, occurs as porphyric segregations in recent lavas and certain effusive igneous rocks (e.g., trachytes).

Lustre, typically vitreous. Refractive indices, cleavage, hardness, **specific gravity** are the same as for orthoclase (see below). Differs from orthoclase by certain optical constants, chiefly by smaller angle of optic axes: up to 30° for sanidine, 60 to 80° for orthoclase.

First discovered in trachytes on the Island of Pantelleria (Italy). Also found in trachytes and other effusives in the Caucasus, in the ejectamenta of Mount Vesuvius, and elsewhere.

ORTHOCLASE, $K[AlSi_3O_8]$, or $K_2O \cdot Al_2O_3 \cdot 6SiO_2$. "Orthoclase" is the Greek for straight-split. Indeed, the cleavage angle is 90°. The

colourless transparent variety of orthoclase is known as *adular*. At temperatures over 900° alters to sanidine, a modification with somewhat different optical constants.

Chemical composition. For the purely potassium variety: K_2O 16.9%, Al_2O_3 18.4%, SiO_2 64.7%. Often contains up to a few per cent of Na_2O, sometimes exceeding K_2O content (natronorthoclase). Impurities: BaO, FeO, Fe_2O_3, etc.

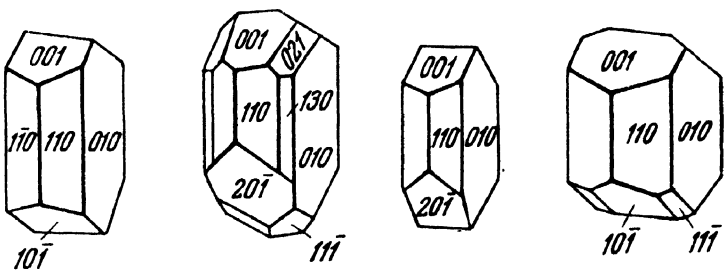


Fig. 350. Crystals of potash feldspar.

System, monoclinic; symmetry, monoclinic prismatic L^2PC. Space group $C2/m(C_{2h}^3)$. $a_0 = 8.60$; $b_0 = 13.06$; $c_0 = 7.19$. **Habit**, mostly prismatic (Fig. 350). Predominant prism faces {110} usually combined with pinacoidal faces {010}, {001}, and sometimes {101}, {201}, etc. Transparent or translucent crystals of adular have a characteristic form shown in Fig. 351. Simple twins are rather common. While the composition plane is usually ⊥ (010), the twinning axis is (010) which conforms to the Carlsbad law (Fig. 352). The (001) face

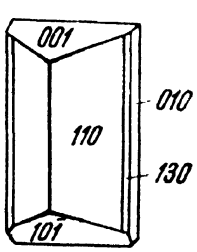


Fig. 351. Adular crystal.

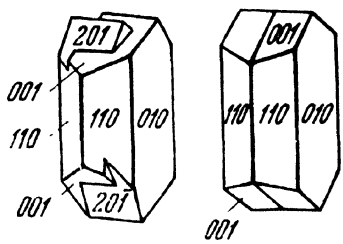


Fig. 352. Carlsbad twins.

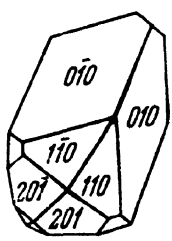


Fig. 353. Baveno twins.

of one individual may merge with that of another in a single plane (Fig. 352, right). The difference between them is established only by lustre and cleavage directions. Occasionally twinning may conform to the Baveno law with (021), the twinning plane (Fig. 353).

Colour. The common non-transparent orthoclases are light pink, brownish yellow, reddish white, and sometimes beef-red. **Lustre**, vitrous, especially for adular.

Hardness, 6 to 6.5. **Cleavage**, {001} and {010} perfect with the planes at an angle of 90°.

Diagnostic features. Externally, the orthoclases are quite easily identifiable by yellowish and reddish light colour, high hardness, and cleavage angle. They cannot be distinguished, however, from no less widespread, similarly coloured microclines without the aid of the microscope.

Genesis. Orthoclase, as the other sodium-potassium feldspars occurs mostly in *acidic* and partly in *medium igneous* rocks.

In granite *pegmatites* orthoclase is more rare than microcline. As microcline, it is albitised, i.e., replaced by albite, at later stages of the pegmatite process.

In the course of weathering, under the action of the surface agents (O_2, CO_2, H_2O, etc.), orthoclase, microcline, and other feldspars are kaolinised. The residual products of weathering in the form of kaolin clays are either accumulated in the crust of weathering or washed out by running water. Under the conditions of tropical and subtropical weathering, as we have already said, bauxites and other products of laterite weathering may be formed.

For uses of orthoclase rocks see "Microcline".

MICROCLINE, $K[AlSi_3O_8]$. "Microcline" is the Greek for slightly deviating: the angle between the cleavage planes—(010) : (001)—deviates from the right angle only by 20′.

Chemical composition is similar to that of orthoclase. Almost invariably contains considerable Na_2O. The green varieties of microcline contain Rb_2O (up to 1.4%) and Cs_2O (up to 0.2%) more frequently than common microclines and orthoclases.

System, triclinic; symmetry, pinacoidal *C*. Space group $P\bar{1}(C_i^1)$. The twins are similar to those of orthoclase. Very characteristic are thin polysynthetic and latticed twins, observable in individual grains under the microscope with crossed nicols. **Aggregates.** In pegmatite dikes microcline is often found as extremely coarse-crystalline aggregates which easily split along cleavage planes. The individuals, which are determined by cleavage, sometimes measure tens of centimetres or even metres. Microcline often occurs also in druses of well-developed crystals.

Colour, usually the same as of orthoclase, but there is also a green variety called *amazonite*. This colouring is uneven, either confined to perimeter of the crystals or extends inside the crystals as fine veinlets, lenses, and irregular spots, sometimes alongside of veinlets of white quartz. **Lustre**, vitreous; slightly pearly on cleavage surfaces.

Hardness, 6 to 6.5. **Cleavage**, the same as for orthoclase, parallel to (001) and (010). **Specific gravity**, 2.54 to 2.57.

Diagnostic features. Microcline cannot be distinguished from orthoclase externally. In thin polished sections under the microscope it is readily recognised by the peculiar latticed structure of some individuals, which is well visible with crossed nicols; non-latticed microcline is identified by optical constants.

Genesis and occurrence. Microcline occurs much more often than orthoclase in *intrusive acidic* and *basic* rocks (granites, granodiorites, syenites, etc.). It is also the principal mineral in *pegmatite* formations. Widespread in the latter are *microcline-perthites* in which albite as the product of decomposition of solid solution is disseminated through the microcline environment which sometimes has a latticed structure. The perthite ingrowths of albite are either visible to the naked eye or become conspicuous in polished specimens.

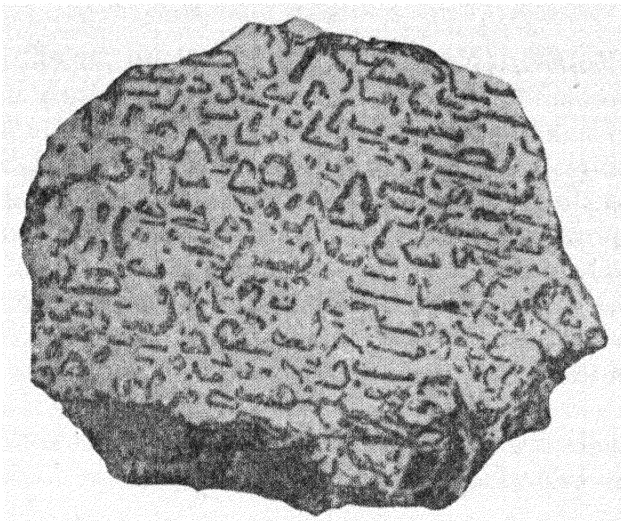


Fig. 354. Intergrowth of quartz (dark) with microcline ("jewstone").

The most frequent accessory minerals occurring with microcline are quartz, albite, sometimes nepheline (in alkaline-nepheline pegmatites) and micas. There also exist peculiar intergrowths of microcline with quartz known as *jewstone* or *graphic granite* (Fig. 354).

In the north-west of the European part of the Soviet Union, high-grade feldspars occur as intersecting pegmatite dikes or sheet veins in gneisses and contain, along with microcline and plagioclase, such minerals as quartz, muscovite, occasionally biotite. Also of very high grade are the pegmatites occurring in nepheline-syenites in the Middle Urals.

Well-known are the deposits of amazonite (of gemstone and ornamental quality) in the *Ilmen Mountains* where it was discovered as early as 1784, and where it forms large masses of intense-green, bluish-green, apple-green, occasionally of turquoise and other tints grading over into yellowish grey, and yellow.

Uses. Pegmatite deposits of sodium-potassium feldspars of which microcline is usually the principal one, are the most important commercially. They are used mainly in the manufacture of glass and ceramics.

Feldspars at rather low temperatures (1100-1300°) melt into a glass, which on addition of kaolin and quartz on solidification gives a compact white, slightly translucent mass called *porcelain*, which is used in making table ware, glazes, and enamels. A large quantity of soda-potash feldspars is consumed in the manufacture of the so-called electrical porcelain. The purest grades are used in making false teeth, special opalescent glass, etc.

Beautifully coloured green amazonite is fashioned into various ornamental objects.

ANORTHOCLASE, $(Na,K)[AlSi_3O_8]$. System, triclinic. "Anorthoclase" is the Greek for *not orthoclase* (similar to it only in appearance). Often contains CaO (up to several per cent). The name "anorthoclase" is applied to those triclinic feldspars in which the Na_2O content predominates over the K_2O content. In literature the name sometimes covers all the non-monoclinic feldspars including microcline (regardless of the Na_2O content).

Anorthoclase is similar to microcline in physical properties, except for its optical constants. Specific gravity, 2.56 to 2.60. Upon ignition changes to a monoclinic modification and resumes the triclinic state upon cooling.

Occurs in sodium-rich volcanic rocks. First discovered in andesite lavas on the Island of Pantelleria (Italy).

Hyalophane Subgroup

The group comprises potassium-barium feldspars crystallising in the monoclinic system. They form an isomorphous series of $K[AlSi_3O_8]$-$Ba[Al_2Si_2O_8]$ and containing minor amounts of $Na[AlSi_3O_8]$ and $Ca[Al_2Si_2O_8]$.

The mineral species recognised so far do not form a continuous series. There are hyalophanes with up to 35 per cent of the $Ba[Al_2Si_2O_8]$ molecule; others with up to 50 per cent, and still others approaching a purely barium monoclinic feldspar called celsian.

HYALOPHANES, $(100-n)\ K[AlSi_3O_8] \cdot nBa[Al_2Si_2O_8]$, where $n = 0\text{-}35\%$. Impurities: Na_2O, CaO, sometimes SrO, etc.

System, monoclinic. Hyalophane crystals are similar to those of orthoclase (adular). Twinning is the same. Crystal structures are also identical because of small difference between the K^{1+} and Ba^{2+} cationic radii (1.33 and 1.38 Å). The replacement of the K^{1+} ions by Ba^{2+} ions is reflected in the equivalent replacement of Si^{4+} by Al^{3+}.

Crystals are water-transparent, sometimes grey with yellowish, greenish, or bluish tints; more rarely red. Occur in druses in cavities or as veinlets. **Lustre**, vitreous, pearly on cleavage surfaces.

Hardness, 6 to 6.5. **Cleavage**, the same as for orthoclase. **Specific gravity**, 2.6 to 2.82 (the last figure for a hyalophane with 30% of

$Ba[Al_2Si_2O_8]$. Before the blowpipe fuses with much difficulty. Insoluble in acids. May be distinguished from orthoclase by barium content, definitely higher specific gravity, and also by optical constants.

Orthoclases containing little barium occur in magmatic extrusive rocks. Barium-rich varieties have been found in contact-metasomatic deposits in the vicinity of Slyudyanka River (Southern Baikal Region) in phlogopite-calcium veins, in the form of grey crystals associated with diopside scapolite, and calcite; may also develop metasomatically directly after pink orthoclase.

CELSIAN, $Ba[Al_2S_2O_8]$. The BaO content usually varies from 34 to 42 per cent. System, monoclinic. Occurs in well-developed crystals of short-prismatic orthoclase habit, sometimes multifaceted. Long-prismatic forms have been observed too. Twins are according to the Manebach, Baveno, and Carlsbad laws. Found also granular massive.

Transparent, colourless, or translucent. Sometimes allochromatically red or black, due to admixture of iron or manganese oxides. Lustre, vitreous. Hardness, 6. Cleavage, the same as for orthoclase. Specific gravity, 3.31 to 3.37.

Similarly to hyalophanes, celsian occurs in contact-metasomatic deposits at Jacobsberg (Sweden), on the Carnarvon Peninsula in Wales (England) where it is found in Ordovician sand-schist series intercalated with manganese-bearing tuffs, and elsewhere.

2. SCAPOLITE GROUP

Notable for its wide isomorphism, this group of minerals has much in common with the plagioclases as far as chemical composition is concerned. In contrast to the latter, this group possesses additional anions such as Cl^{1-}, $[SO_4]^{2-}$, $[CO_3]^{2-}$, sometimes F^{1-} and OH^{1-}. The total charge of the crystal lattices is accordingly balanced by the additional Na^{1+} and Ca^{2+} cations.

As in the plagioclase series, NaSi is evidently replaced by CaAl as the composition changes. The same principle holds for the relationship between the Cl anions, normally present in the sodium-rich varieties, and the $[SO_4]$ and $[CO_3]$ anionic radicals characteristic of the more calcium-rich varieties.

The end members of the series are marialite (Ma), a purely sodium mineral, and meionite (Me), a purely calcium one. The intermediate varieties are classified on the same principle as the plagioclases, i.e., by the percentage of the meionite molecule.

It is but natural that with changes in the chemical composition of the scapolites, their physical properties change accordingly.

SCAPOLITE, $(75-n)\,Na_4[AlSiO_3O_8]Cl \cdot nCa_4[Al_2Si_2O_8]_3\,[SO_4,\ CO_3]$, where n varies from 0 to 75 per cent. The name comes from the Greek "scapos" meaning pole and "lithos" stone, evidently reference to the

crystal habit. The *glaucolite* variety (not to be confused with glauconite, a hydrosilicate of Fe and K) is intermediate in composition. Many other names used formerly in literature in effect are synonyms.

Chemical composition. The SiO_2 content decreases with the increase of the meionite molecule from 56 to 74 per cent; accordingly the contents of Na_2O and Cl decrease and those of CaO and CO_2 increase.

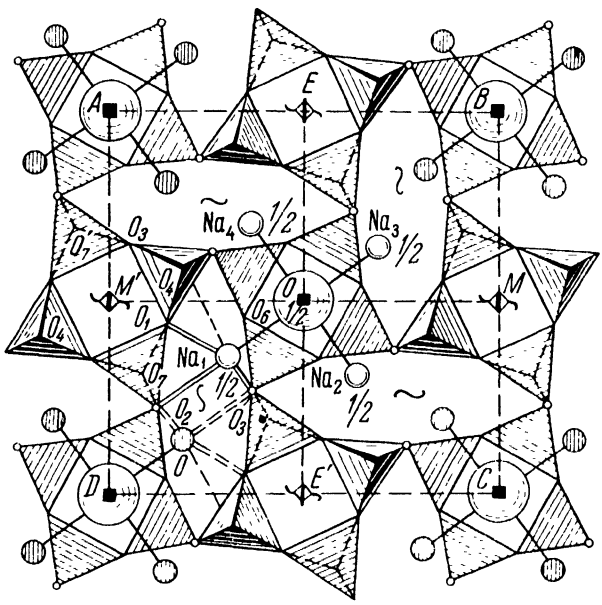


Fig. 355. Crystal structure of scapolite projected parallel to *c* axis.

Large spheres—Cl^{1-}, smaller spheres—Na^{1+} or Ca^{2+}. Small blank circles in the summits of fourfold rings around *A*, *B*, *C*, *D* and *O* stand for oxygen ions which link the rings together.

System, tetragonal; symmetry, tetragonal dipyramidal L^4PC. Space group $14/m(C_{4h}^5)$. $a_0 = 12.24$; $c_0 = 7.59$. **Crystal structure.** Scapolite is characterised by complex rings of four tetrahedra, the apexes of which are alternately pointed upwards and downwards. These rings form columns parallel to the *c* axis of the crystal. Figure 355 shows the tetrahedral framework projected on the (001) plane. Inside the framework there are spaces to accommodate the Na^{1+} and Ca^{2+} cations, and larger voids for the Cl^{1-}, $[SO_4]^{2-}$ or $[CO_3]^{2-}$ anions. **Habit.** Crystals are prismatic and usually elongated parallel to the vertical axis (Fig. 356). The most common are the prism faces {100}, {110}, and {210} which are truncated by dipyramidal faces {111}, {131}, {331}, {101}, etc. Crystals occur exclusively in druse cavities, whereas in massive rock scapolite develops as irregular grains or granular aggregates, sometimes forming massive scapolite rock.

Colour. Scapolites occurring in volcanic rocks are usually colo urless, while those in crystalline schists and limestones are opaque, grey, sometimes intense blue (glaucolite), less often red. **Lustre**, vitreous,

with pearly opalescence on cleavage surfaces. n_y = 1.550 to 1.595, and n_z = 1.540 to 1.556 (increasing with the increase of the meionite molecule).

Hardness, 5 to 6. Brittle. **Cleavage**, {100} distinct; {110} imperfect; often stepped. Fracture, uneven. **Specific gravity** increases towards meionite from 2.61 to 2.75.

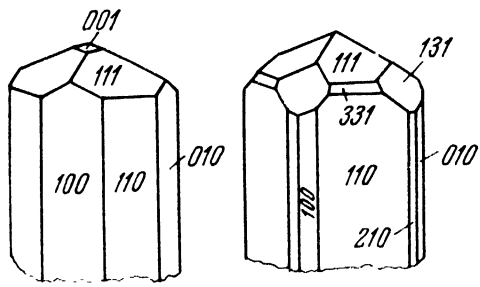


Fig. 356. Scapolite crystals.

Diagnostic features. Scapolites differ from the similar feldspars in distinctly tetragonal crystal form, poor cleavage (tetragonal prismatic) and by somewhat lower hardness.

In the blowpipe flame they evolve volatile components and fuse with intumescence to a white blebby glass. Scapolites partly decompose in hydrochloric acid, the process being the faster the greater is the meionite molecule content. The silica is separated in the form of a silt-like rather than gelatinous sediment.

Genesis and occurrence. As the products of *pneumatolitic* processes, scapolites occur in cavities of volcanic rocks as druses of well-developed colourless crystals. Often found in *contact-metasomatic* deposits near the contact of acidic or basic instrusives with limestones and dolomites. Associates are garnets, pyroxenes, sometimes apatite, etc. Quite frequently replace other minerals, especially plagioclases. It has been observed that the composition of scapolites is generally more basic than that of plagioclases (Na_2O being partly removed). They are sometimes accompanied by zeolites.

Scapolites are widespread in magnetite deposits in the *Kustanai* Region, where they enter into the composition of not only the metasomatically altered host rocks, but also of the magnetite ores themselves.

Long since known are scapolites in many phlogopite deposits along the *Slyudyanka River* (Southern Baikal Region) where they usually associate with diopside and calcite. Individual scapolite crystals (stroganovite) are 0.5 m long. Their colour is generally pale straw-yellow or dirty green. They have been formed metasomatically through reactions between pegmatites and limestones. At the same locality massive glaucolite of light-blue, greyish-blue, and bluish-violet colour has been found.

The scapolites are rather susceptible to secondary alteration, especially on weathering. Chlorites, epidote, albite, micas, and other minerals have been observed pseudomorphous after scapolite. In the process of weathering scapolites decompose to kaolin clays.

3. LEUCITE GROUP

In addition to leucite and pollucite, we shall review in this group analcime, a mineral very close to leucite in a number of properties and containing zeolite water.

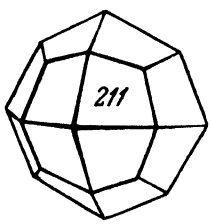


Fig. 357. Leucite crystal.

LEUCITE, $K[AlSi_2O_6]$ or $K_2O \cdot Al_2O_3 \cdot 4SiO_2$. From the Greek "leucos" for light-coloured. A rock-forming mineral of certain alkali-rich and relatively silica-poor effusive rocks (leucite-basalts, phonolites, trachytes, etc.).

Chemical composition. K_2O 21.5%, Al_2O_3 23.5%, SiO_2 55.0%. Contains negligible quantities of Na_2O, CaO, H_2O as impurities.

System. Dimorphous. At temperatures above 620° the cubic modification is stable; below that point leucite undergoes polymorphous modification becoming tetragonal. **Habit**, very characteristic: the mineral occurs in well-developed polyhedral crystals, viz., tetragon-trioctahedra (Fig. 357). Common forms: {211}, rarely {110} and {100}. The surface of the faces is dull; sometimes with twinning striations. Twins are with composition plane (100). Occasionally occurs in granular aggregates.

Colour. Colourless; white with greyish or yellowish tints; often ash-grey. **Lustre** on fracture surfaces, vitreous, greasy. $n_x = 1.509$ and $n_z = 1.508$.

Hardness, 5 to 6. Brittle. **Cleavage**, none. Fracture, conchoidal. **Specific gravity**, 2.45 to 2.50.

Diagnostic features. Very characteristic crystal form, light colour. Under the microscope is identified by optical anomalies and low refractive index.

Infusible before the blowpipe. Dissolves in hydrochloric acid with the separation of pulverulent silica.

Genesis and occurrence. Leucite is a typical high-temperature *magmatic* mineral forming in congealing alkali-rich (chiefly K_2O) lavas, poor in SiO_2. Therefore, it never occurs together with quartz. Commonly associated with alkaline pyroxenes (aegirine, or aegirine-augite), nepheline, etc. Individual crystals occur also in volcanic products such as ash and tuffs.

Often is chemically altered by later processes. Orthoclase and sericite (potash mica) may be pseudomorphous after leucite crystals. Sometimes they are replaced also by nepheline and albite in various ratios. These pseudomorphs are known as pseudoleucite or epileu-

cite. Leucite is often altered to analcime through reactions with sodium-bearing solutions. This process is very common in soils, in which potassium passes into solution. This explains the fertility of soils forming on leucite-bearing rocks.

In the U.S.S.R., leucite-bearing effusive rocks occur in Armenia. Considerable leucite in the form of large and small crystals is found in lavas on Mount Vesuvius. Epileucitic effusive rocks have been found in Turkestan, along the Ishim River, in Eastern Siberia, and elsewhere.

Uses. In certain countries, e.g., in Italy, leucite rocks are worked as a material for making potassium products and metallic aluminium. It should be borne in mind that leucite contains less SiO_2 and more Al_2O_3 than orthoclase.

ANALCIME, $Na[AlSi_2O_6]\cdot H_2O$, or $Na_2O\cdot Al_2O_3\cdot 4SiO_2\cdot 2H_2O$. "Analcis" is the Greek for impotent. The name derives from its property of becoming only slightly electrified on rubbing.

Chemical composition (per cent): Na_2O 14.07; Al_2O_3 23.29; SiO_2 54.47; H_2O 8.17. There is also a K_2O-rich (up to 5.5%) variety of analcime. May contain minor amounts of CaO and MgO.

System, cubic; symmetry, hexoctahedral. Space group $Ia3d(O_h^{10})$. $a_0 = 13.71$. Crystallises in exactly the same forms as leucite (cf. Fig. 357). Less often in cubic crystals truncated by faces of tetragon-trioctahedron (Fig. 358). Also in granular aggregates, crystal druses in cavities, crystalline crusts and geodes.

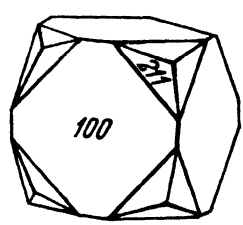


Fig. 358. Analcite crystal.

Colour. Colourless, white with greyish, reddish, or greenish tints, sometimes beef-red (iron-oxide pigmentation).

Lustre, vitreous. $n = 1.489$ to 1.479.

Hardness, 5 to 5.5. Brittle. **Cleavage**, practically absent, sometimes on {001} distinct. **Specific gravity**, 2.2 to 2.3.

Diagnostic features. Differs from the similar leucite primarily by composition, lower hardness and refractive index, and by blowpipe behaviour.

In distinction from leucite before the blowpipe, readily fuses to a transparent glass. Upon heating, readily yields water and becomes opaque (leucite does not). Decomposes completely in hydrochloric acid with the precipitation of silty silica.

Genesis and occurrence. Similarly to zeolites, analcime is usually a product of *low-temperature hydrothermal* activity during the last stages of the magmatic processes. It often forms apparently at temperatures below 100°.

In rare instances analcime may be formed as a primary mineral from a magma rich in Na and H_2O crystallising under high pressure. Being the only sodium alumosilicate present in teschenites (analcime dia-

bases), this mineral is the last to crystallise in the interstices of the earlier formed silicates. Such are the *Caucasian* teschenites. Large transparent crystals of analcime have been recorded from volcanic tuffs on the *Cyclopean Islands* near Catania (Sicily).

In *pegmatites* of sodium-rich alkaline rocks (nepheline-syenites) analcime is among the latest hydrothermal minerals, mostly replacing nepheline. Has been found in pegmatites in the *Ilmen Mountains* and elsewhere.

As a recent formation, analcime may derive from exogenous processes. It has been found, for instance, in soils forming in place of leucite rocks, occasionally in sedimentary rocks.

POLLUCITE, $Cs[AlSi_2O_6]$ (theoretical) or $Cs_4NaAl_5Si_{11}O_{32}\cdot 1.3H_2O$. The latter formula stands for a variety of pollucite richest in caesium. Synonym: pollux. Quite recently pollucite was regarded as a mineralogical rarity. By now, however, economic deposits of this mineral, the richest in caesium, are known.

Chemical composition is variable. Cs_2O 30 to 32%. An interesting case of isomorphous mixture of pollucite with analcime has been discovered. It has been demonstrated by chemical analyses, that the end member of the isomorphous series (pure pollucite, as yet not found in nature) should have the formula: $Cs[AlSi_2O_6]$, i.e., should be analogous to leucite.

Therefore, the isomorphous mixtures are formed between anhydrous and hydrous silicates: $Cs[AlSi_2O_6]$-$Na[AlSi_2O_6]\cdot H_2O$. Minor amounts of Rb_2O, K_2O, and Tl_2O are also present.

System, cubic; symmetry, hexoctahedral. Space group $Ia3d(O_h^{10})$. $a_0 = 13.69$. **Crystal structure** is similar to that of analcime. **Habit.** Well-formed crystals occur in cavities but generally are rare, and present a combination of {100} and {210}. May be as large as 2 cm across. More commonly in veinlets or massive.

Colour. Transparent, colourless. **Cleavage**, practically none. Fracture, conchoidal. **Specific gravity**, 2.86 to 2.90.

Diagnostic features. Pollucite occurs in association with lithium minerals as vitreous masses similar to quartz, from which it differs in optical properties (the powder under the microscope is isotropic). Caesium is readily established by spectral analysis. Pollucite is characteristically interspersed with numerous thin veinlets of secondary minerals which may be white, grey, or pink in colour.

Thin fragments become rounded along the edges in the blowpipe flame; the mineral fuses to a white enamel and colours the flame reddish yellow. On ignition becomes opaque (loses water). When heated in hydrochloric acid, dissolves with difficulty with the separation of pulverulent silica; its solution with platinum chloride gives an abundant precipitate of a binary chloride caesium-platinum.

Genesis and occurrence. As a hydrothermal mineral, pollucite occurs in miarolitic cavities in granite and pegmatites. Paragenetically asso-

ciates with lithium silicates (petalite, lepidolite), lithium phosphates (amblygonite), quartz, and other minerals.

Massive pollucite contains numerous white thread veinlets of kaoline-like decomposition products.

Pollucite was first discovered in cavities in granite on the Island of Elba (Italy). Large accumulations have been found in the lepidolite deposits of *Karibib* (South-West Africa). Also reported from the the deposits at *Varutresk* (Sweden), *Hebron* (U.S.A.), and elsewhere

Uses. The most important source of caesium salts which are widely used for laboratory and analytical research. Caesium is an essential material for photoelectrical devices and discharge lamps. It was not until the advent of caesium photoelements that the problem of television was practically solved.

4. NEPHELINE GROUP

This group includes alumosilicates, still more deficient in silica with a general formula: $R^{\cdot}[AlSiO_4]$, where $R^{\cdot} = Li$, Na, K, crystallising in the hexagonal system. At high temperatures $Na[AlSiO_4]$ and $K[AlSiO_4]$ form a continuous series of pseudosolutions. We shall review nepheline alone.

NEPHELINE, $Na[AlSiO_4]$, or $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$. From the Greek "nepheli" – cloud (when dissolved in strong acids, evolves cloudy silica). Often a rock-forming mineral of alkaline sodium-rich igneous rocks.

Chemical composition does not fully correspond to the formula. There is always an excess of SiO_2 (3 to 10 per cent) due to the replacement of certain sodium and aluminium ions by silicon ions as follows: $Na^{1+} + Al^{3+} = Si^{4+}$. Also contains K_2O (the $K[AlSiO_4]$ molecule content varies from 5 to 20 per cent). May also have an admixture of CaO (0.5 to 7 per cent), sometimes Fe_2O_3, Cl, and H_2O.

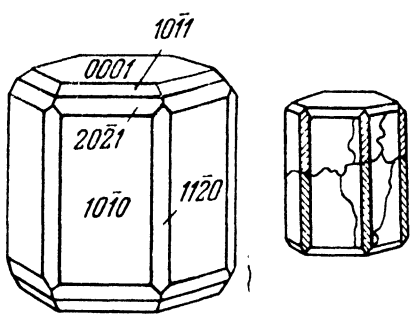


Fig. 359. Nepheline crystals.

System, hexagonal; symmetry, hexagonal pyramidal L^6. Space group $P\bar{3}c(D_3^4)$. $a_0 = 10.05$; $c_0 = 8.38$. **Crystal structure** is somewhat specific. Two-thirds of the aluminium ions are arranged differently from the remaining one-third, which has a bearing on the process of extraction of aluminium oxide from nepheline. One-third of Al passes into solution with more difficulty. It is remarkable that during natural decomposition of nepheline two-thirds of the Al ions form natrolite, while the remaining one-third forms kaolinite. **Habit**, prismatic, short-columnar (Fig. 359) or thick-tabular. The most common forms: the $\{10\bar{1}0\}$ prism and $\{0001\}$ pinacoid, and also the faces of $\{10\bar{1}1\}$ dipyramid and $\{11\bar{2}0\}$ prism. Although simple in appearance, the crystal forms

of nepheline are often twins (with irregular boundaries) as attested by etch figures and striations (Fig. 359). Crystals are rare, mostly occurring in rock cavities. **Aggregates.** Usually in irregular crystalline grains disseminated in rocks or massive, very often coarse-granular.

Colour. Colourless but more often greyish white or grey with yellowish, brownish, reddish, and greenish tints. Opaque light-coloured coarse-crystalline or massive varieties are often referred to as *eleolite*. **Lustre**, on crystal faces, vitreous; greasy on fracture surfaces. $n_y =$ $= 1.532$ to 1.547 and $n_z = 1.529$ to 1.542.

Hardness, 5 to 6. Brittle. **Cleavage**, either practically none or indistinct parallel to {0001} and {1010}. **Specific gravity**, 2.6.

Diagnostic features. Not always identifiable by the naked eye. In alkaline sodium-rich rocks it is greyish with various hues and with a typical *greasy lustre*. On the weathered surfaces, nepheline is easily recognised by thin dull coatings or crusts forming in depressions as products of chemical decomposition.

Fusible before the blowpipe, sometimes rather easily, colouring the flame yellow. Soluble in acids.

Genesis and occurrence. Nepheline occurs almost exclusively in *magmatic*, silica-poor alkaline rocks, such as nepheline-syenites and their pegmatites and phonolites. Sometimes the rocks contain schlieren which are practically solid nepheline. In silica-rich magmatic derivatives it associates with albite, and never occurs in the presence of excess silica.

In deep-seated nepheline rocks it is paragenetically associated with alkaline pyroxene (aegirine), alkaline feldspars (albite, microcline), alkaline hornblende, and often with products of hydrothermal alteration of nepheline, mainly cancrinite, sodalite, and zeolites. It is also associated, especially in pegmatites, with zirconium and titanium minerals — zircon, sphene, ilmenite, etc.

In the course of weathering nepheline is rather easily decomposed and leached. At first it develops white coatings of residual products of chemical weathering, and then cavernous cavities are formed on the surface of nepheline blocks.

Nepheline rocks often form large masses. Thus, in the U.S.S.R. very well known is a nepheline-syenite (miaskites) mass in the *Ilmen Mountains*, Southern Urals, confined to which are numerous occurrences of rare minerals. In the *Khibiny Mountains* a major apatite deposit is associated with nepheline rocks.

Uses. Massive nepheline and nepheline-bearing tails of concentration wastes (upon recovery of apatite and other economic minerals) have many industrial applications.

Small quantities of nepheline are used in making green glass without adding alkalis. Substituted for feldspar in ceramics. Owing to their high solubility in acids, nepheline-bearing tails of ore concentration may be a source of alumina (Al_2O_3 content varies from 31 to 34%), silica gel, soda, ultramarine, and other products.

5. SODALITE GROUP

The sodalite minerals, crystallising in the cubic system, closely approach in composition the nephelines but, as different from the latter, contain Cl^{1-}, S^{2-}, $[SO_4]^{2-}$ as additional anions, and correspondingly additional cations: Na^{1+} and Ca^{2+}.

SODALITE, $Na_8[AlSiO_4]_6Cl_2$, or $3Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2NaCl$. So named because of its sodium (soda) content. As the other members of the group, except lazurite, it is found in sodium-rich and silica-poor igneous rocks.

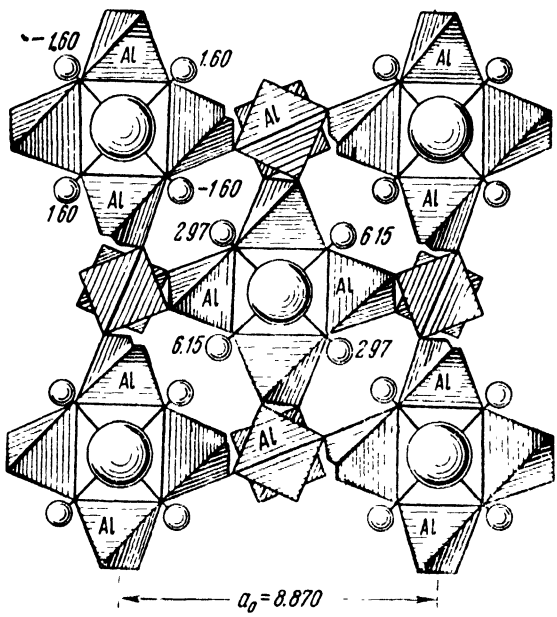


Fig. 360. Crystal structure of sodalite projected on cube face parallel to *c* axis.

Cl^{1-} ions (large balls) occur in summits of square at a height of *o* and in the middle of $^1/_2 c = 4.435$ Å. Small spheres – Na^{1+} ions (the figures indicate the relative height of the spheres). In tetrahedral framework Al stands for AlO_4 aluminium oxygen groups. For the sake of clarity, those tetrahedral summits which must be linked to upper and lower unit cells, are broken off on the drawing.

Chemical composition. Na_2O 25.5%, Al_2O_3 31.7%, SiO_2 37.1%, Cl 7.3%. Contains small amounts of K_2O.

System, cubic; symmetry, hexatetrahedral. Space group $P\bar{4}3n$ (T_d^4). $a_0 = 8.87$. **Crystal structure**, simple cubic (Fig. 360). The Cl ions occur in the corners and centres of the cube and are surrounded by the Na ions tetrahedrally. **Habit**, rhombic dodecahedral (Fig. 361) with {110} and {100} faces. Other forms are extremely rare. Twins are

frequent, with composition plane (111), i.e., the twinning axis is the threefold axis. **Aggregates.** Massive granular.

Colour. Colourless or grey with a yellowish or bluish tinge, less often blue. **Lustre**, vitreous; greasy on fracture surfaces. $n = 1.483$ to 1.490.

Hardness, 5.5 to 6. **Cleavage**, {110} distinct. Fracture, uneven. **Specific gravity**, 2.13 to 2.29.

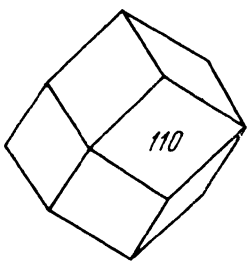


Fig. 361. Sodalite crystal.

Diagnostic features. Distinguished from the other groups of alkaline silicates by optical isotropy. Very hard to distinguish from nosean and hauyne without chemical tests. Differs from dark-coloured fluorite by high solubility in acids.

Before the blowpipe fuses with intumescence to a colourless glass. In the closed tube, its transparent varieties become opaque. Dissolves in hydrochloric acid leaving a deposit of gelatinous silica on evaporation. When HNO_3 solution is slowly evaporated on a slide, yields NaCl crystals. May also be tested with $AgNO_3$ for the presence of chlorine.

Genesis and occurrence. Sodalite is a primary mineral of igneous alkaline rocks, mostly effusives. Occasionally, is found in intrusive rocks, e.g., in sodalite syenites of *Zeravshan*, Tajikistan, or in basic rocks at Mariupol, and elsewhere. Usually associates with nepheline, cancrinite, eudialyte, and other minerals. As a late mineral, sodalite often replaces nepheline and other alumosilicates of alkalis in nepheline-syenites, e.g., in the Lovozero massif on the Kola Peninsula.

Has been found in nepheline *pegmatites* in the *Ilmen Mountains* as minor accumulations and veinlets of blue colour associated with cancrinite, sometimes as inclusions in analcime.

As all alkali-rich minerals, sodalite gradually decomposes in the zone of oxidation.

NOSEAN, $Na_8[AlSiO_4]_6[SO_4]$. System, cubic. Properties are exceedingly similar to those of sodalite.

Colour, grey with yellowish, greenish, or light-blue tinges, less often white. $n = 1.495$. Hardness, 5.5. Cleavage, (110) distinct. Specific gravity, 2.28 to 2.40. Often contains inclusions of foreign minerals, which gives the crystals a badly eroded appearance.

Occurs in alkaline igneous rocks, mostly effusives, e.g., in alkaline lavas on the Canary Islands, Cape Verde Islands, in the Minusinsk area, the Albano Mountains (Italy), etc.

HAUYNE, $Na_6Ca[AlSiO_4]_6[SO_4]$. May contain small amounts of K_2O. System, cubic. Occurs in crystals of dodecahedral or octahedral habit, but more frequently in rounded grains fused around the edges.

Colour, bright blue, sky blue, greenish blue, less often yellow and red. Lustre, vitreous; greasy on fracture surfaces. $n = 1.495$ to 1.504.

Hardness, 5.5. Cleavage, {110} distinct. Specific gravity, 2.4 to 2.5. Before the blowpipe decrepitates and fuses to a greenish-blue glass.

Has been recorded from lavas at Monte Somma (Vesuvius) associated with nepheline and leucite, the Albano Mountains (Italy), and many other places. As an exception, hauyne has been discovered in the Malo-Bystryanka lazurite deposit (Slyudyanka River, South-Baikal region) in replacement zones of pegmatites at the contact with dolomite.

HELVITE, $(Mn, Fe, Zn)_8[BeSiO_4]_6S_2$.BeO 13.6%. Contains FeO (up to 15%) and ZnO, sometimes up to tens of per cent (genthelvite).

System, cubic; symmetry, hexatetrahedral. Occurs in tetrahedral crystals or globular masses.

Colour, yellow, yellow brown, red brown, less often green. Translucent. **Lustre**, vitreous, resinous. $n = 1.746$.

Hardness, 6 to 6.5. Fracture, uneven conchoidal. **Cleavage**, {111} distinguishable parallel. **Specific gravity**, 3.16 to 3.36.

Diagnostic features. Very similar to garnet, from which it is distinguished by the presence of sulphur, easily detected by the reaction for sulphur liver. When the powdered mineral is boiled with As_2O_3 in H_2SO_4, a bright canary-yellow coating of As_2S_3 is produced.

In the blowpipe flame intumesces and fuses to yellowish-brown opaque glass. With borax gives a reaction for Mn. Dissolves in hydrochloric acid, evolving H_2S; on evaporation gives a precipitate of gelatinous silica.

Genesis and occurrence. Helvite occurs in pegmatite dikes associated with quartz, albite, and amazonite. Has been recorded from augite syenites at Langezundfjord (Norway), from some mica mines near Amelia Court (Virginia, U.S.A.) and in large masses at the *contact zones* of rhyolites and granites with limestones, in association with magnetite and fluorite at Sierra and Socorro, New Mexico.

Uses. When found in quantity may be important as a beryllium ore.

LAZURITE, $Na_8[AlSiO_4]_6[SO_4]$. The exact formula has not been established. Contains up to several per cent of CaO. The name derives from the mineral's bright-blue colour. Synonyms: lapis-lazuli, ultramarine (artificial).

Chemical composition of lazurite from the Malo-Bystryanka deposit (per cent): Na_2O 16.8, CaO 8.7, Al_2O_3 27.2, SiO_2 31.8, SO_3 11.8, S 0.34, Cl 0.25, and minor amounts of H_2O, SrO, MgO, K_2O, Fe_2O_3, and CO_2.

System, cubic. Usually in compact massive. Crystal structure similar to that of sodalite.

Colour, deep azure-blue, violet, sometimes light-blue or greenish blue. **Lustre**, vitreous. n about 1.50 (variable).

Hardness, 5.5. Brittle. **Cleavage**, {110} indistinct. **Specific gravity**, 2.38 to 2.42.

Diagnostic features. Lazurite both massive and in thin polished sections is primarily identifiable by intense bright-blue or light-blue colour. Resembles blue sodalite but its paragenetic associations are entirely different: the former associates with alkaline silicates, the latter with calcite and dolomite.

Before the blowpipe fuses readily with intumescence to a white bead. Upon heating to a dark-red glow the colour sometimes becomes more intense. Decomposes in hydrochloric acid with evolution of H_2S (recognised by odour) and on evaporation leaves gelatinous silica.

Genesis and occurrence. Rare deposits are confined to the contacts of alkaline igneous rocks (syenites, granites and their pegmatites) with carbonate rocks. Besides calcite, it is often associated with pyrite, clearly visible as fine grains in polished specimens, as well as with glaucolite and many other minerals, but never with quartz. Found occasionally in alkaline lavas (Vesuvius).

The famous *Badashkhan* deposit in Afghanistan, discovered very long ago and described already by Marco Polo (1271), contains lazurite masses of varying colour from indigo to light-blue, formed metasomatically in limestones. The deposit has not yet been studied in detail geologically. Another famous locality is at *Malo-Bystryanka* on Slyudyanka River (south of Lake Baikal), where lazurite has formed metasomatically through reactions between pegmatite and dolomite. Lazurite was first discovered in that area in 1784.

Uses. As a beautiful ornamental stone, lazurite has been known from antiquity. Mentions of this stone are found in the writings of many authors of different ages and countries. In ancient Greece and in the Roman Empire it was renowned as a material for fast and beautiful pigments.

Very well known are antique lazurite bowls, caskets, rings, statuettes, charms, and other ornamental objects. In the 17th century lazurite was used in jewelry and in inlay work in furniture and mantlepieces together with gold, bronze, and other metals. Cornflower-blue lazurites with embedded specks of pyrite were especially valued. This stone may be seen in the columns of the St. Isaac's Cathedral, on the walls of the Winter Palace, in vases and tables of the Hermitage in Leningrad, and elsewhere.

6. CANCRINITE GROUP

The minerals of the group are very close to the nephelines in many properties but differ from them in composition and by having $[CO_3]^{2-}$ and $[SO_4]^{2-}$ as additional anions.

CANCRINITE, $Na_3Ca[AlSiO_4]_3[CO_3, So_4]\cdot nH_2O$. According to the analytical data available, there may be a continuous series between *carbonatic-cancrinite* containing as an additional anion the CO_3 group

and *sulphatic-cancrinite* (wischnewite) containing additionally the SO_4 anion. No sulphate-cancrinite without any CO_3 has been found as yet.

Chemical composition is variable (per cent): SiO_2 33.7 to 34.7, Al_2O_3 29.0 to 29.4, Na_2O 15.6 to 18.9, CaO 1.2 to 4.2, K_2O 1.4 to 5.1 (increases with decreasing total Na_2O+CaO), CO_2 0.3 to 6.3, SO_3 4.6 to 6.2 (for sulphate-cancrinites), H_2O 3.9 to 7.6.

System, hexagonal; symmetry, hexagonal pyramidal L^6. Space group $C6_3(C_6^6)$. $a_0 = 12.75$; $c_0 = 5.18$. **Habit.** Crystals are very rare, usually as prisms with the faces of an obtuse dipyramid (Fig. 362). **Aggregates.** Usually massive, sometimes in the form of selvages around nepheline as a product of its alteration.

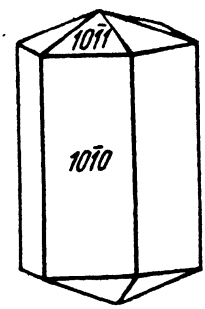


Fig. 362. Cancrinite crystal.

Colour, white, blue, grey with a yellowish or greenish tinge, sometimes reddish pink (due to microscopic Fe_2O_3 scales). Sulphate-cancrinite has a light-blue or bluish light-blue colour (colourless varieties are also known). **Lustre** on cleavage surfaces is vitreous with a pearly sheen; greasy on fracture surfaces. For carbonate-cancrinite: $n_y = 1.515$ to 1.524 and $n_z = 1.491$ to 1.502. For sulphate-cancrinite: $n_y = 1.489$ to 1.530 and $n_z = 1.488$ to 1.535.

Hardness, 5 to 5.5. Brittle. **Cleavage**, $\{10\bar{1}0\}$ perfect or distinct. **Specific gravity**, 2.42 to 2.48.

Diagnostic features. Cancrinite occurs, as a rule, in nepheline rocks. Differs from nepheline, from which it is formed, by cleavage. Sulphate-cancrinite (wischnewite) is easily recognised by bluish colour and cleavage.

Before the blowpipe flame fuses with difficulty to a blebby bead. On ignition, in contrast to nepheline, becomes opaque which may be explained by the release of CO_2. Soluble in hydrochloric acid with effervescence. Gelatinous silica begins to precipitate only on boiling and evaporation.

Genesis and occurrence. Cancrinite is formed during the postmagmatic stage under the action of carbon dioxide and sulphuric acid solutions on earlier crystallised nepheline masses. In turn, cancrinite is often altered to micas, zeolites, carbonates, etc.

In the zone of weathering cancrinite decomposes in the same way as nepheline, i.e., first giving rise to zeolites in the form of mealy crusts, and then to halloysite.

In the *Ilmen* and *Vishneviye* mountains carbonate-cancrinite and light-blue sulphate-cancrinite (wischnewite) occur in nepheline pegmatites, often associated with sodalite, calcite, zeolites, hydrargyllite, residual nepheline that survived replacement, and other minerals. In the *Tunkin* mountains, cancrinite is found in granite together with zircon, calcite, and magnetite. Outside the Soviet Union, occurs chiefly in genetic association with nepheline-syenites.

7. ZEOLITE GROUP

The zeolites are an extensive group of minerals that are essentially hydrous alumosilicates, mostly of Ca and Na, partly of Ba, Sr, K, and very seldom of Mg and Mn. Judging by the elements entering into their composition, these minerals are chemically directly related to the anhydrous alumosilicates reviewed above.

Although the total number of elements entering into their composition is not great, the mineral species of this group are very numerous and differ from each other by intercationic ratio, which often defies expression by simple chemical formulas, rather than by water content. The general chemical formula may be written as follows: $A_mX_pO_{2p}\cdot nH_2O$, where X = Si, Al. No definite alkali-to-silica ratio has been established for different minerals of this group.

We have not yet obtained any clearly defined concepts of the various types of anionic radicals that are characteristic for the minerals of this group. Yet the zeolites have a number of very peculiar common properties; and there is not the slightest of doubt that they constitute a separate group.

According to X-ray studies, their crystal structures consist of frameworks of alumosilicon-oxygen tetrahedra which differ from other types of frameworks in that the "ducts" are somewhat wider. This open-type rigid framework contains loosely attached water molecules. Upon gradual heating the water may be removed without disturbing the crystal structure as a whole. It is noteworthy that the water thus lost may be completely re-absorbed, or replaced by molecules of different substances (hydrogen sulphide, ethyl alcohol, ammonia, etc.). During this process the crystalline environment remains homogeneous and only the optical properties are altered. Consequently, the water content of zeolites is variable and depends on the temperature and water-vapour pressure in the environment. The so-called zeolite water differs from crystallisation water in that on heating it evolves from the mineral gradually, not abruptly at definite temperatures.

Another characteristic property of the zeolites is the easy exchange of the cations that balance the negative charge of the crystal lattice framework for those in the surrounding water solution. Some cations in the solution are capable of replacing those located in the voids of the zeolite framework without altering their structure. This property is made practical use of in softening water by means of permutite, or artificial zeolite.

In contrast to the more "closed" framework structures of feldspars where all the "empty" cells are occupied by cations, in the zeolite frameworks not all the empty spaces are occupied. A comparison of the analytical and structural data reveals two types of cationic exchange: the conventional feldspar exchange with the total charge, number, and volume of ions preserved (for instance, $NaSi \rightleftarrows CaAl$ or

$KSi \rightleftarrows BaAl$), and the zeolite exchange ($Ca \rightleftarrows Na_2$, $Ba \rightleftarrows K_2$, and $NaCa_2 \rightleftarrows Na_3Ca$).

In these two cases, the total charge of the replaced cations equals that of the replacing, roughly equidimensional, cations, but the number of ions will be different. The crystal structures of the zeolites evidently have a certain "reserve" space for such substitutions.

As compared with anhydrous alumosilicates, the zeolites are distinguished by lower hardness, specific gravity and refractive indices, and are more readily attacked by acids. Most of them swell before the blowpipe, and hence their name: "zeo", the Greek for boiling up.

Zeolites are formed under very similar conditions. *Endogenously* they are formed under low pressure in the latest low-temperature stages of hydrothermal process, being mostly associated with calcite, chalcedony, quartz, hydrargyllite, and other minerals. They are generally found in hydrothermally altered magmatic rocks, in cellular effusives (mandelstones), very often in basalts (resulting from submarine eruptions), in pegmatites (being formed last either in cavities or metasomatically from the earlier-formed minerals, such as feldspars, nepheline, etc.), in hydrothermal ore deposits, and in certain recent hot spring deposits.

Zeolites are also widespread in *exogenous* environment. Thus, there are some indications of their being formed in soils. As recent formations, zeolites occur in young sediments.

CHABAZITE, $(Ca, Na_2)[AlSi_2O_6]_2 \cdot 6H_2O$. From the word "chabasios", a stone eulogised by the Greek poet Orpheus.

Chemical composition is variable even for specimens from the same deposit, but in most cases conforms to the formula. Contains small amounts of Ba and Sr.

System, trigonal. **Habit**, rhombohedral, almost cubic (Fig. 363). Penetration twins are frequent, often with trihedral angles protruding on the edges. More commonly in crystalline druses, crusts, secretions, and massive aggregates.

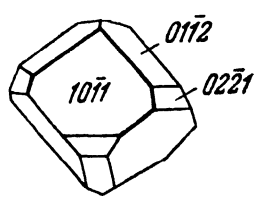


Fig. 363. Chabazite crystal.

Colour, white with a reddish or brownish tinge. **Lustre**, vitreous. $n_x = 1.480$ to 1.490 and $n_y = 1.478$ to 1.485.

Hardness, 4 to 5. Brittle. **Cleavage**, parallel to rhombohedron, distinct. **Specific gravity**, 2.08 to 2.16.

Diagnostic features. Identifiable by rhombohedral crystals and cleavage, with the faces of the rhombohedron meeting at almost right angles. These features make it easily distinguished from almost all other zeolites. Similar calcite has lower hardness and reacts differently with hydrochloric acid.

Swells before the blowpipe and fuses with difficulty to a blebby translucent enamel. Soluble in hydrochloric acid with the separation of slimy silica.

Occurrence. Chabazite occurs mostly as amygdules in spherical cavities of vesicular basalts, phonolites, and other effusives, often in association with phillipsite, calcite, etc. Has been found in Iceland in fossilised shells. Forms abundantly around some hot springs.

NATROLITE, $Na_2[Al_2Si_3O_{10}]\cdot 2H_2O$. Name given by Klaproth, means sodium stone.

Chemical composition. Na_2O 16.3%, Al_2O_3 26.8%, SiO_2 = 47.4%, H_2O 9.5%. Contains occasionally Fe_2O_3 and K_2O.

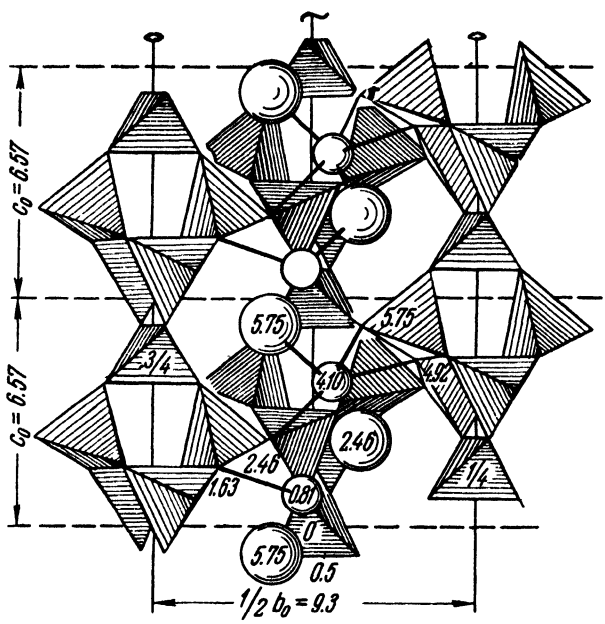


Fig. 364. Crystal structure of natrolite.
Projection of a portion of the framework on (100). Two unit cells are shown along the vertical. Median vertical chain of linked tetrahedra located beyond plane of drawing is shown in a darker shade. Large spheres – H_2O molecules, small spheres – Na^{1+} ions.

System, orthorhombic; symmetry, pyramidal $L^2 2P$. Space group Fdd (C_{2v}^{19}). a_0 = 18.3; b_0 = 18.6; c_0 = 6.57. **Crystal structure.** The unit cell is the $[Al_2Si_3O_{10}]$ group, or a ring of four $[Al_2Si_2O_8]$ tetrahedra with an additional SiO_4 tetrahedron or with an alternating AlO_4 (Fig. 364). These rings occur as continuous chains parallel to the *c* axis and are interlinked by sharing free apexes of the (Si, Al)O_4 tetrahedra. Four such chains are arranged around a spiral axis (Fig. 364 does not show only the chain above the plane of drawing). The H_2O molecules form a zigzag chain parallel to the *c* axis around each double spiral axis. The Na^{1+} ions are surrounded by four O^{2-} ions and two H_2O molecules. As in other zeolites, the Na ions in natrolite may be replaced by other cations from the surrounding solutions. **Habit**, commonly columnar.

Crystals are simple, the most common are prism faces {110}, sometimes pinacoidal {010}, {100}, and dipyramidal {111} (Fig. 365). Twins on (110), and also on (100). **Aggregates.** Often in radial aggregates or crystalline crusts, and compact spherulitic and fibrous masses.

Colour. Colourless or white with yellowish, greenish, and reddish tinges. **Lustre,** vitreous; silky for fibrous masses. n_x = 1.485 to 1.493, n_y = 1.476 to 1.482, and n_z = 1.473 to 1.480.

Hardness, 5 to 5.5. Brittle. **Cleavage,** {110} distinct. **Specific gravity,** 2.2 to 2.5.

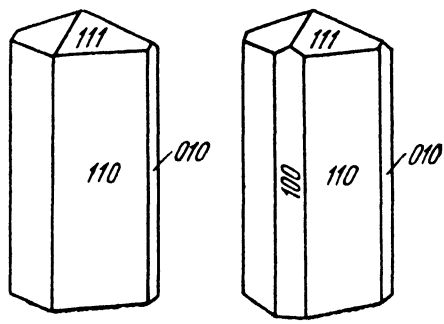


Fig. 365. Natrolite crystals.

Diagnostic features. Outwardly natrolite is hard to distinguish from other zeolites of similar form and mode of occurrence. Positive identification depends on optical constants, X-ray or chemical analyses.

Before the blowpipe fuses readily without swelling to a transparent bead. At 300° almost completely loses its water, which is re-absorbed upon cooling. Dissolves in hydrochloric acid with separation of gelatinous silica.

Occurrence. Natrolite frequently occurs in amygdules and geodes of effusive igneous rocks (basalt). Has been found in nepheline-syenite pegmatites in the *Vishneviye* and *Ilmen* mountains as a hydrothermally altered product of nepheline, and also in radially-fibrous aggregates.

SCOLECITE, $Ca[Al_2Si_3O_{10}]\cdot 3H_2O$. "Scolex" is the Greek for worm. So named because it curls like a worm before the blowpipe.

Chemical composition (per cent): CaO 14.3, Al_2O_3 26.0, SiO_2 45.9, H_2O 13.8.

System, monoclinic; domatic *P*. Space group $Cc(C_s^4)$. a_0 = 5.67; b_0 = 6.54; c_0 = 18.44. Pseudotetragonal. **Habit,** columnar with faces {110}, {111}, and also {010}. In crystal habit indistinguishable from natrolite. Twins on (100) with striations on the {010} faces. **Aggregates,** acicular, radially-fibrous. Also in fibrous spherulitic masses.

Colour. Colourless or white. **Lustre,** vitreous, silky for fibrous masses. n_x = 1.519, n_y = 1.518, and n_z = 1.512.

Hardness, 5 to 5.5. Brittle. **Cleavage,** {110} distinct. **Specific gravity,** 2.2 to 2.4.

Diagnostic features. Scolecite cannot be distinguished from natrolite without chemical analyses and blowpipe tests.

Before the blowpipe swells and curls worm-like (natrolite does not). Fuses to a blebby glass. Decomposes in hydrochloric acid with separation of gelatinous silica.

Occurrence. In the U.S.S.R., occurs in pegmatites in the *Vishneviye* mountains (the Urals), in the North Caucasus, and elsewhere. Common in vesicular basalt lavas as amygdules and geodes, especially in *Iceland* and *Colorado* U.S.A. Large crystals occur at *Puna*, south-west of Bombay (India).

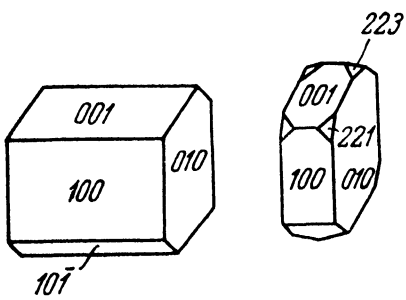


Fig. 366. Heulandite crystals.

HEULANDITE,
$(Ca, Na_2)[AlSi_3O_8]_2 \cdot 5H_2O$. **Chemical composition.** CaO 9.2 %, Al_2O_3 16.8%, SiO_2 59.2%, H_2O 14.8%. Usually contains Na_2O, often SrO (sometimes up to 3.6%), K_2O, and BaO.

System, monoclinic symmetry, monoclinic prismatic. **Crystal structure** with elements of layered arrangement. **Habit**, isometric or tabular (Fig. 366); crystals usually isolated. Predominant forms: {010}, {001}, {100}, and {101}. **Aggregates.** Fairly often in foliated masses with a parallel intergrowth of the foliae, and also in radial foliated aggregates as secretions in cavities.

Colour. Colourless or white, yellow, brick-red (owing to microscopic inclusions of Fe_2O_3). **Lustre**, vitreous, pearly on cleavage surfaces. $n_x = 1.505$, $n_y = 1.499$, and $n_z = 1.498$.

Hardness, 3.5 to 4. Brittle. **Cleavage**, {010} perfect. **Specific gravity**, 2.18 to 2.22.

Diagnostic features. Heulandite is distinguished from the other zeolites by characteristic platy crystal habit, perfect cleavage, which causes a pearly chatoyancy, and platy-granular aggregates.

Before the blowpipe decrepitates and fuses with swelling to a white enamel. Easily decomposes in hydrochloric acid with separation of gelatinous silica.

Occurrence. Heulandite occurs in cavities of effusive rocks (basalts, etc.), e.g., in Iceland. Sporadically has been recorded from silver vein deposits at Andreasberg, Harz (Germany), Kongsberg (Norway), and elsewhere.

PHILLIPSITE, $(K_2, Ca)[Al_2Si_4O_{12}] \cdot 4.5H_2O$.

Chemical composition. SiO_2 44 to 48%, Al_2O_3 22 to 24%, CaO 3 to 8%, K_2O 4 to 11%, H_2O 15 to 17%. Also contains Na_2O (up to 6%).

System, monoclinic; symmetry, monoclinic prismatic. **Habit**, columnar, parallel to the *a* axis. Simple crystals are rare. Usually in twins,

often with rhombic or square cross section, and also in fourlings (Fig.367), sometimes of cruciform cross section with striations on {010} parallel to the edge between *b* (010) and *m* (110). More complex twin intergrowths are also known.

Colour. Colourless or white with greyish, yellowish, and reddish tinges. **Lustre**, vitreous. $n_x = 1.503$, $n_y = 1.500$, and $n_z = 1.498$.

Hardness, 4 to 4.5. Brittle. **Cleavage**, {001} and (010) rather distinct. **Specific gravity**, 2.2.

Diagnostic features. Identifiable by twinning forms. Very similar to less common harmotome and desmine but differs from them in optical constants.

Crumbles intensely before the blowpipe, partly swells and then fuses to a white enamel. Dissolves in hydrochloric acid with the separation of flocculent or gelatinous silica.

Occurrence. As many other zeolites, occurs in cavities in effusive, particularly basic, rocks (leucite basalts, etc.) as amygdules and secretions on the walls of cavities, for instance, in lavas at Vesuvius, in Sicily, Iceland, and elsewhere. Phillipsite is also formed in recent deep-sea sediments of the Pacific, probably as a decomposition product of volcanic ash (up to 20 to 30 per cent of the entire sediment mass).

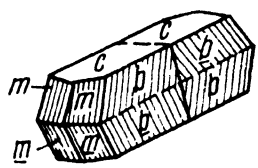


Fig. 367. Phillipsite fourling.

HARMOTOME, $(K_2, Ba)[Al_2Si_5O_{14}]\cdot 5H_2O$. System, orthorhombic. Very characteristic are twins of cruciform section elongated parallel to the *a* axis, similar to phillipsite twins (Fig. 368).

Colour, white with greyish or yellowish tinges, also brown and red. $n_x = 1.508$, $n_y = 1.505$, and $n_z = 1.503$.

Hardness, 4.5. Cleavage, {010} distinct; {001} imperfect. Specific gravity, 2.44 to 2.50. Before the blowpipe whitens, crumbles, and fuses with difficulty but without swelling to a white translucent bead. Decomposes in hydrochloric acid with the separation of pulverulent silica.

Occurs in conditions similar to those for other zeolites, chiefly in effusive igneous rocks, sometimes in gneisses and in some hydrothermal ore deposits: Andreasberg, Harz (Germany) with galena, sphalerite, quartz, etc.; near Stroncian (Scotland) with calcite, galena, etc.

DESMINE, $(Na_2, Ca)[Al_2Si_6O_{16}]\cdot 6H_2O$. Synonym: stilbite.

System, monoclinic. Occurs frequently in twins (Fig. 368) and in fourlings of cruciform section like phillipsite and harmotome. Such complex twinned crystals are usually found in sheaf-like aggregates (Fig. 369) that gave the mineral its name ("desme" is the Greek for sheaf).

Colour, white with a yellowish or reddish tinge. Lustre, vitreous, pearly on cleavage surfaces. $n_x = 1.500$, $n_y = 1.489$, and $n_z = 1.493$.

Hardness, 3.5 to 4. Cleavage, {010} perfect; {100} distinct. Specific gravity, 2.09 to 2.20. Before the blowpipe exfoliates, swells and

assumes fan-like and vermicular forms and finally fuses to a white enamel. Decomposes in hydrochloric acid with the separation of pulverulent silica.

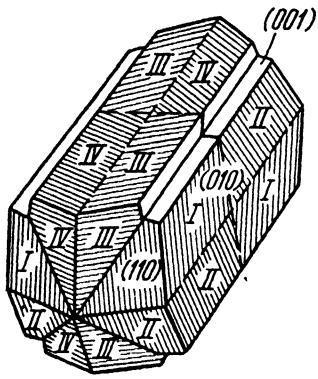


Fig. 368. Cruciform fourling of harmotome.

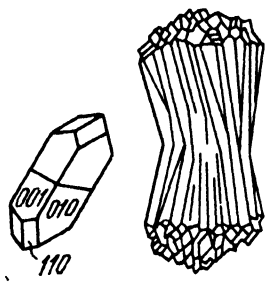


Fig. 369. Desmine.
Left: penetration twin with twinning plane (001); right: sheaf-like aggregate of twinned individuals.

Desmine occurs in cavities and fissures as secretions, chiefly in effusive igneous rocks, but sometimes in hydrothermal ore veins. Some localities in the U.S.S.R. are at Karagach near Simpheropol (the Crimea), near Borzhomi (Georgia), along the Angara River near Village Chyornaya, and elsewhere.

Part Three

Chapter I. MINERALS OF THE EARTH'S CRUST

Quantitative distribution of the different types of chemical compounds in the earth's crust. As many as 6,000 names of minerals are mentioned in the old and modern geological literature. However, with a critical approach to the establishment of mineral species and varieties, the vast majority of these names should be discarded for various reasons. First, many of them, as shown by modern accurate methods of examination, are mechanical mixtures. A very considerable number of names proved to be synonyms referring to the same mineral substances that differ from each other either in the degree of dispersion of the crystal phase or in certain external features (shades of colour, form of individual crystals, etc.), or by minor variations in chemical composition (this concerns especially the names of varieties).

If the synonyms are discarded and the mineral mixtures stricken off the list of minerals, the number of true mineral species will be at present just under 1,500. Moreover, there will be retained about 200 names of varieties. It should be noted, on the other hand, that some of the actually existing varieties have no names as yet.

According to the principal types of chemical compounds the mineral species are distributed as follows (per cent):

1. Silicates and alumosilicates	25.8
2. Phosphates and their analogues	18.0
3. Sulphides and their analogues	13.3
4. Oxides and hydroxides	12.7
5. Sulphates	9.4
6. Halides	5.8
7. Carbonates	4.5
8. Native elements	4.3
9. Borates	2.9
10. Others	3.3

The greatest number of mineral species is found among the silicates, phosphates, oxides, sulphides, and sulphates, which comprise about 80 per cent of the total.

In terms of weight percentages, however, the picture is entirely different. According to the data on the clarkes as calculated by V. I. Vernadsky, A. Y. Fersman, and others for the principal types of chemical compounds in the part of the earth's crust that is known to us, weight percentages of the following order are obtained:

1. Silicates—about 75% (with 55% going to the share of feldspars).
2. Oxides and hydroxides—about 17% (quartz with chalcedony and opal 12.6%, iron oxides and hydroxides 3.6%).
3. Carbonates (chiefly calcite and dolomite)—about 1.7%.
4. Phosphates and their analogues (chiefly apatite)—about 0.7%.
5. Chlorides and fluorides—about 0.5% (the most common chloride is halite, the most common fluoride, fluorite).
6. Sulphides and sulphates—0.3 to 0.4% (the predominant sulphide is that of iron, i.e., pyrite).
7. Native elements—about 0.1%; this includes nitrogen 0.04% and 0.01% oxygen.

Thus, the silicates and quartz alone comprise some 87% of the earth's crust by weight while the phosphates with their analogues, sulphides, sulphates, oxides (without quartz and iron hydroxides) which are represented in nature by numerous mineral species make up only a very small part of the total composition of the earth's crust by weight. Nevertheless it should be emphasised that it is these types of chemical compounds that contain many valuable metals so important for the mining, metallurgical, chemical, and other industries.

Certain specific features of the composition and distribution of minerals in the earth's crust. Although the natural reactions are incomparably greater, the total number of natural compounds (minerals) is much smaller than of those which can be artificially obtained in the laboratory. In recent decades relatively few new minerals have been discovered each year (10 on the average), in spite of the powerful perfect modern research tools. The total number of minerals, i.e., natural inorganic compounds is 1,500, whereas the number of artificial compounds obtained so far runs into hundreds of thousands, and keeps rapidly increasing with the modern advances in the synthesis techniques.

The question concerning the quantitative distributions of minerals of diverse composition in natural formations of various genetic types in the earth's crust could be answered as follows, on the basis of analysis of factual data.

Among endogenous formations, the fewest mineral species are found in effusive rocks developing at high temperatures and pressures. In postmagmatic, especially hydrothermal deposits, the number of mineral species of most diverse types of compounds is incomparably greater. But richest in various minerals are exogenous formations developing at low temperatures and pressures in aqueous-atmospheric

environment, i.e., at high partial oxygen pressure, and, finally, under the conditions of extensively developed organic life on earth. But even so, the total number of minerals is negligible in comparison with what can be obtained in laboratories and factories.

This is due to various reasons. Thus, as Vernadsky had noted long ago, natural compounds contain *by far not all the ions* that may be obtained for any given element in the laboratory. For instance, in nature, manganese in minerals is di-, tri-, and tetravalent; in the laboratory one can easily obtain compounds of hexa- and heptavalent manganese, and also metallic manganese and various intermetallic compounds. In nature, tungsten is known only as a hexavalent ion, whereas in the laboratory di-, tri-, tetra-, and pentavalent tungsten compounds can be obtained. Natural metals of the platinum group occur mostly native and almost never form any ions (apart from rare sulphides and arsenides), whereas in the laboratory they form typical ionic compounds with valences of 2, 3, 4, and, in the case of Ru and Os, even 6 and 8. That is why so far only 30 minerals of the platinum group are known as compared with many hundreds of artificial compounds.

It is quite obvious that in the course of mineral formation in the earth's crust which occurs in a complex multicomponent environment within a comparatively narrow range of oxidation-reduction potentials the conditions for the formation of ions of different valences are very restricted. Therefore, *the number of possible combinations* of ions in the formation of minerals *is also sharply reduced.*

Another important circumstance noted already by A. Y. Fersman is that many elements characterised by *low clarkes* do not form separate minerals in nature. This can happen only when the ions of these elements approach in size and chemical properties the ions of the elements that are abundant in the particular environment and are therefore capable of becoming isomorphously admixed to the principal minerals crystallising from the given melt or solution (isovalent and heterovalent isomorphism). Thus hafnium may be "concealed" in the zirconium minerals; rhenium in molybdenite; gallium in the aluminium minerals, and partly in the zinc minerals; bromine in the chlorine minerals; samarium, holmium and lutecium in the yttrium minerals scandium in the magnesium and iron minerals; etc. In the laboratory on the other hand, it is possible to create artificially any concentration of these elements, and not only obtain artificially most diverse chemical compounds but also obtain many of them in the metallic state.

Such "concealment" is also observed in the case of elements with higher clarkes. A good example is an isomorphous admixture of nickel (up to 0.2%) to magnesium in silicates (olivine and its derivate serpentine). It is in this way that enormous quantities of nickel are scattered throughout olivine and serpentinite rock masses (hundreds of billions of tons in terms of metal), whereas ore deposits of nickel sulphides and arsenides, such as at Sudbury and Schneeberg, contain hardly over 10 per cent of the total nickel in the earth's crust. The sam

is true of endogenous formations in which manganese is isomorphously admixed either to the iron or the calcium of the silicates and other types of compounds. Indeed, many iron- and calcium-rich minerals contain considerable manganese of an isomorphous admixture (fayalite, hedenbergite, diopside, biotite, apatite, ankerite, siderite, etc.). The total amount of manganese thus concealed is very great. The same holds for titanium, vanadium, cobalt, the rare earths, strontium, etc.

The rare elements which form either too small or too large ions (Be, B, C, Rb, Cs, Nb, P, Ta, U, etc.) as compared with the principal elements of magmatic rock constituents, for instance, are concentrated, according to geological data, in *residual* solutions from which, during the postmagmatic stage as they become supersaturated and as a result of chemical reactions, special minerals containing volatile components or a higher percentage of rare elements begin to crystallise (tourmaline, beryl, lithium micas, monazite, apatite, etc.). These minerals often form economic ore deposits of important metals either in magmatic rock masses themselves or in the enclosing rocks nearby.

Similarly, the ions which differ essentially in chemical properties from the basic ions (for instance, those with an 18-electron outer shell: Cu, Ag, Au, Zn, Pb, Bi, etc., and also some of the iron-group elements are often transported in residual solutions *far beyond* the magmatic masses and form the so-called hydrothermal deposits of heavy metals, mostly sulphides and oxides, and are often accompanied by carbonates and sulphates of the petrogenic elements.

Similar phenomena of differentiations of ions giving rise to different mineral groups are also observed in the products of exogenous processes (in the crust of weathering and in sedimentary formations).

Thus, geological processes in the earth's crust result in *regular spatial distribution* of chemical elements and hence of the minerals in the various products of these processes. It is this distribution that, on the one hand, results in the formation of vast *rock masses* of relatively simple mineralogical composition (igneous, sedimentary, and metamorphic) that constitute the bulk of the earth's crust and, on the other hand, in the formation of genetically closely related *economic mineral deposits* which substantially differ, however, from the former in composition, and are subject to the same geological laws and develop through the same geological processes. These deposits, especially of metallic minerals, although greatly inferior in size to rock masses, are so different from the latter in chemical composition and economic importance that they inquestionably must be regarded as independent geologic bodies, taking part in the general structure of the earth's crust, along with the rock masses.

It is this that underlies the common division of all the chemical elements into petrogenic (rock-forming) and metallogenic (ore-forming). According to Mendeleyev's periodic classification, the former are arranged in the left-hand part of the table, and the latter in the

right-hand part and at the bottom. This principal feature of the spatial distribution of chemical elements in the earth's crust is due to the chemical properties of the elements, and in particular to their atomic structure. Indeed, the most characteristic chemical elements of rocks (Na, K, Mg, Ca, Al, Si) under natural conditions form ions with an 8-electron outer shell, while typical metallogenic elements with high atomic weights are characterised by ions with an 18-electron outer shell which are somewhat less symmetrical in the configuration of internal electronic spheres (ions of the middle part of the table: triades of group VIII, then Mn, Cr, V, Mo, W, Nb, Ta, U, Th).

Chapter II.

MINERAL ASSOCIATIONS IN ROCKS AND ORE DEPOSITS

A brief survey of the processes of mineral formation in the earth's crust was made under *Concepts and Definitions* (cf. *Part One*, p. 117). In accordance with these processes we shall review mineral associations characteristic of different rocks and the economic mineral deposits genetically related to them under the following headings:

Minerals of endogenous formations

1. Minerals of plutonic igneous rocks of diverse composition, and of magmatic ore deposits.
2. Principal mineral associations in pegmatites.
3. Mineral associations in contact-metasomatic formations.
4. Minerals of hydrothermal deposits of economic minerals.
5. Minerals of effusive rocks and products of fumarole activity.

Minerals of exogenous formations

1. Minerals of the crust of weathering.
2. Minerals of sedimentary rocks and of economic deposits.

Minerals resulting from regional metamorphism

1. Minerals of metamorphosed rocks and ore deposits.

Minerals of plutonic igneous rocks, and of magmatic ore deposits. Primary minerals of intrusive (plutonic) igneous rocks and of magmatic deposits crystallise at high temperatures and pressures.

As distinct from effusives, *intrusive rocks* are holocrystalline mineral aggregates. Among the rock-forming minerals, as among all the other rocks, there are distinguished the principal ones, or those that form the bulk of the rock, and accessory ones, often visible only under the microscope. Besides primary minerals, often there are also present secondary, or later, minerals deriving from the former during the post-magmatic stage of mineral formation. Of the numerous intrusive rocks of diverse chemical and mineralogical composition which are studied in detail in petrography, we shall consider only the most representative ones (ultrabasic, basic, medium acidic and acidic, and alkali-

rich rocks) in the order in which they are given in Fig. 50, i.e., beginning with the silica-poor intrusives.

Ultrabasic rocks (dunite, peridotite, pyroxenite) consist almost exclusively of ferro-magnesian silicates (olivine, pyroxenes). Unaltered dunite is a monomineral rock composed of *olivine*, while the peridotites

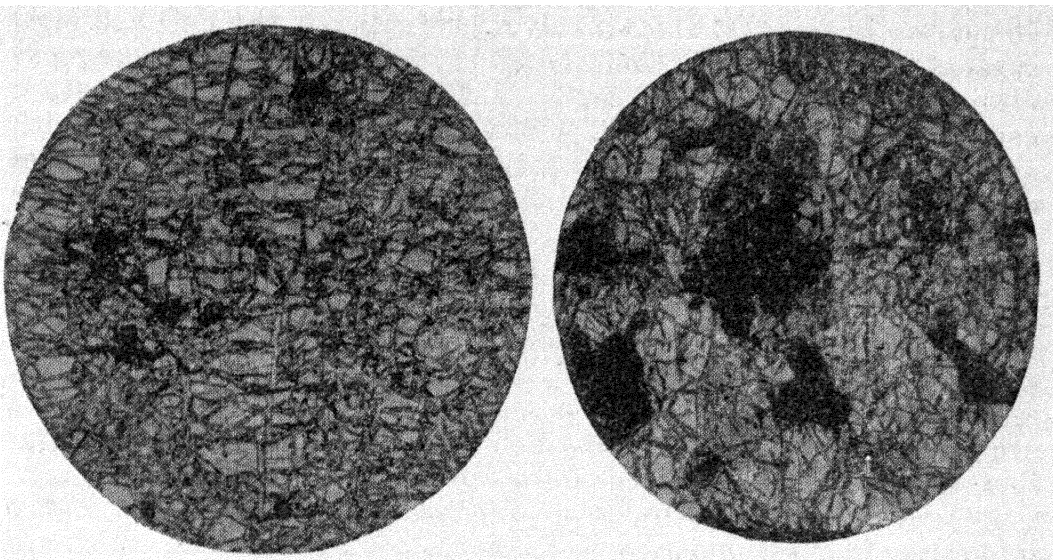


Fig. 370. Partly serpentinised dunite in transparent polished section under the microscope.

Left: photograph with one nicol. Light-coloured grains—olivine; network of threads—serpentine formed from olivine. Black grains—accessory chromespinellid. Right: photograph with crossed nicols. Differently oriented olivine grains show different colours in polarised light.

contain orthorhombic or monoclinic *pyroxene* in addition. The most common accessory minerals in these rocks are *chrome-spinellids*. Diallagites—the most widespread pyroxenites—contain accessory titanomagnetite and occasionally green spinel. The most easily formed secondary minerals of ultrabasic rocks are *serpentine*, deriving from olivine (Fig. 370), *breunnerite* (ferro-magnesian carbonate), sometimes *talc*, *amphiboles* (usually deriving from pyroxenes), etc.

The *basic* rocks (gabbro family), richer in SiO_2 and alkalis than the ultrabasic rocks, essentially differ from the latter in chemical composition, especially in respect to Al_2O_3, MgO, and FeO (cf. Fig. 50). Mineralogically these rocks are characterised by the fact that along with such ferro-magnesian silicates as *pyroxenes*, *amphiboles*, sometimes *biotite* and *olivine*, they contain large amounts of *basic plagioclases* (labradorite, bytownite, anorthite). Typical gabbro rocks contain approximately 50 per cent of dark-coloured minerals (ferro-magnesian silicates). Their most common accessories are *titanomagnetite*, often in considerable quantities, *apatite*, *ilmenite* and sometimes *sulphides* of Fe, Ni, Cu, etc. In altered gabbro rocks basic plagioclases may be replaced by an intimate mixture of zoisite or epidote with albite

recognisable under the microscope; whereas olivine may be replaced by serpentine.

The *medium acidic* and *acidic* intrusive rocks (diorite, granodiorite, granite) are richer in silica and thus belong to the class of definitely quartz-bearing rocks (only diorites do not always contain quartz). The quantity of dark-coloured minerals is much smaller (only 5 to 10 per cent in granites) which involves a reduction in the FeO and MgO content (cf. Fig. 50). The composition of the *plagioclases* of these rocks also changes; they become more acidic (andesine, oligoclase) with a corresponding decrease in CaO and increase in Na_2O. Granites, which are the most widespread igneous rocks, contain considerable quantities of potassium feldspars, such as *orthoclase* and *microcline*, and their *quartz* content may exceed 20 per cent. *Biotite* is the most widespread dark-coloured mineral. Granites have the greatest variety of accessory minerals; *apatite*, *zircon*, *sphene*, *magnetite*, *hematite*, sometimes *monazite*, *orthite*, while the greisenised mica-quartz portions contain *topaz*, *fluorite*, *lithium micas*, *cassiterite*, *wolframite*, *arsenopyrite*, *tourmaline*, *axinite*, etc. In the process of greisenisation the feldspars are decomposed and replaced by light-coloured micas, topaz, tourmaline, and other aluminous minerals.

Alkali-rich intrusive rocks are silica-poor quartzless rocks highly interesting from the mineralogical standpoint. The syenites, which are poorest in alkalis, in mineralogical composition closely approach the rocks of the granite family (but do not contain quartz). The nepheline-syenites, in addition to orthoclase, microline and albite, contain *nepheline*, and dark-coloured minerals: *alkaline pyroxenes* (aegirine, aegirine-augite), *alkaline amphiboles* (hornblende, arfvedsonite, etc.), and dark *micas* (biotite, lepidomelane). They also often contain *sodalite*, which not infrequently replaces nepheline, and more seldom nosean hauyne, cancrinite, and analcime. Their constant accessories are *zircon* and *apatite*, often *sphene*, less often fluorite. In other petrogenetic provinces there are observed complex silicates of titanium and zirconium: eudialyte, lamprophyllite, astrophyllite, lovchorrite, etc. In certain varieties of these rocks, alkaline silicates are associated with pyrochlore, loparite, titanomagnetite, ilmenite, etc.

Economic mineral deposits of magmatic origin are usually enclosed *in parent igneous rocks* as rich accumulations of ore minerals in the form of pockets, veins and sheet-like bodies. They are composed for the most part of minerals which are present in the rocks as accessories or minor segregations.

An important contribution to the branch of geological science studying the dependences that determine the formation of magmatic deposits, as well as to the classification of these deposits, has been made by Soviet scientists (Academician A. N. Zavaritsky and others). According to the modern concepts, the segregation and accumulation of ores may proceed in different ways and at different stages of the magma crystallisation. In some cases, ore minerals, especially chrome-spinel-

lids, are the first to crystallise from the magma, occasionally forming impregnated ores known as schlieren. More often the ore material accumulates in residual melts, i.e., during the late stages of the magmatic process proper, and forms ore bodies that show some features of their epigenetic relationship to the enclosing parent rocks. Such, for instance, are the typical chromite and titanomagnetite deposits.

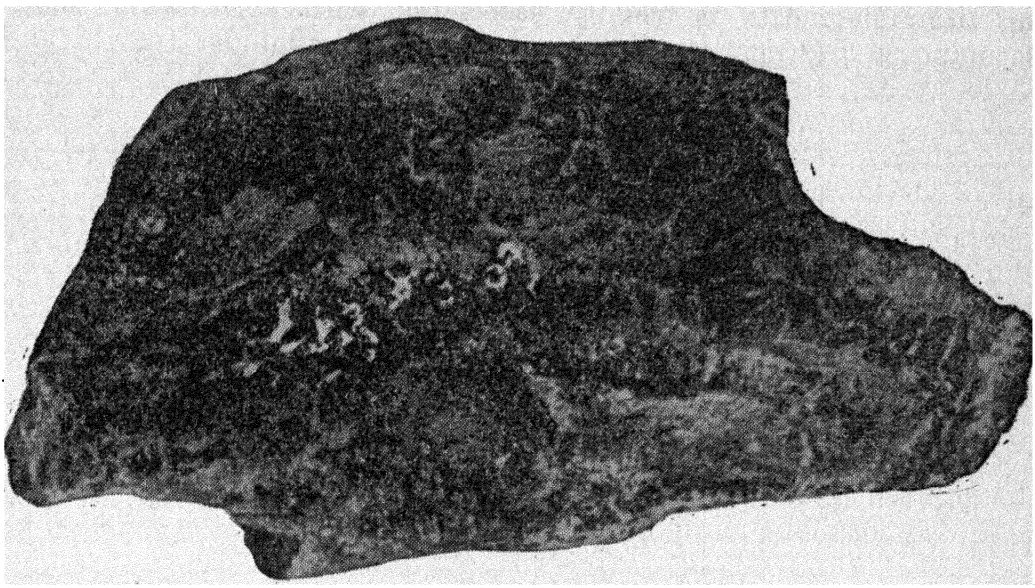


Fig. 371. Segregations of native platinum (white) in close paragenetic association with masses of chromespinellids (black). Grey mass—serpentinised dunite. Polished specimen.

Lastly there are known certain deposits (in particular those of copper-nickel sulphides) whose ore material according to a number of geological characteristics must have separated from the magma already in the liquid state (by liquation) and sunk due to its higher specific gravity towards the bottom of the magmatic chamber. However the relationship between the ore bodies and the host rocks shows that these sulphide melts crystallised after the crystallisation of the parent rocks.

A detailed analysis of the age relationships of mineral associations in ore bodies often reveals that at the final stages of the formation of magmatic minerals there develop, though in minor quantitites, lower-temperature associations which more probably correspond already to the hydrothermal stage of ore formation. Ore bodies generally are later formations than the parent rocks.

In ultrabasic rocks (dunites and peridotites) there occur *chromite deposits*, often composed of almost solid *chrome-spinellids*, forming pocket-like lenticular, and columnar ore bodies. In miarolitic cavities and in fissures there are observed sometimes low-temperature formations of *uvarovite*, *chrome-diopside*, *chrome-chlorites*, and other chromium-bearing hydrosilicates. In certain ultrabasic rock provinces, chrome-spinellids are paragenetically and closely associated with minerals of

the *platinum* (Fig. 371) and *osmiridium* (the Middle and Northern Urals) groups. Confined to the kimberlites of South Africa are *diamond* deposits.

Widespread in pyroxenites and gabbros are *titanomagnetite deposits* in the form of closely impregnated ores (Kachkanar) and massive vein-like occurrences (Kusinsk in the Urals). In these ores, vanadium-bearing titanomagnetite is usually associated with *hornblendes*, semi-decomposed *feldspars*, negligible quantities of sulphides (pyrite and chalcopyrite), sometimes with apatite, and with secondary minerals: *chlorites*, *epidote*, *zoisite*, etc.

Certain basic rocks, chiefly gabbronorites, (orthorhombic pyroxene), and sometimes the ultrabasic rocks are associated with *deposits of copper-nickel sulphide ores* composed predominantly of *pyrrhotite* and, of subordinate amounts, of cobalt-bearing *pentlandite*, *chalcopyrite*, and *magnetite*. As more recent formations they also contain *millerite*, nickel- and cobalt-bearing *pyrites*. Platinum minerals, such as *palladioplatinum* and *sperrylite*, occasionally laurite, etc., are also often present.

Thus, in the ultrabasic and basic intrusive rocks, ore deposits are formed by the iron-group elements: Ti, V, Cr, Fe, Co, Ni, together with the adjacent platinum group, and also Cu. Manganese is disseminated as an isomorphous admixture to iron and calcium in oxides and silicates.

No considerable deposits of heavy metals are known in acidic intrusives. Na_2O-rich nepheline-syenites may enclose as an exception large *deposits of apatite*, with such accessories as *nepheline*, in smaller amounts aegirine, alkaline amphiboles, sphene, titanomagnetite, etc. *Loparite* deposits are also known.

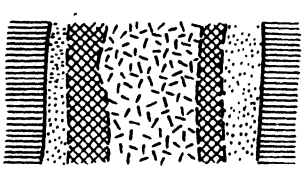


Fig. 372. Diagrammatic representation of a pegmatite dike of symmetrical structure.

1—quartz zone; *2*—zone of coarse-crystalline pegmatite composed of feldspar and muscovite; *3*—fine-grained pegmatite; *4*—gneiss.

Principal mineral associations in pegmatites. The bulk of pegmatite formations originating at great depths are related to *granites* and *nepheline-syenites*. They occur mostly as rather small bodies of heterogenous, often banded structure (cf. Fig. 51) and of later formation than the parent rocks. They often occur as typical veins (dikes), and sometimes as columnar or lenticular bodies.

Pegmatite formations may occur either as bodies with a symmetrical distribution of bands in respect of the marginal rock (Fig. 372) or with an asymmetrical banded structure.

Pegmatites have long interested mineralogists because their cavities sometimes contain druses of well-formed crystals of smoky quartz, topaz, tourmaline, beryl, and other gems and semi-precious stones. Of special interest are graphic intergrowths of feldspar and quartz (Fig. 373) whose origin is still uncertain.

Pegmatites usually are composed of the same minerals as the parent rocks, but are represented by very coarse-grained aggregates. Many pegmatite formations, however, contain small quantities of other minerals of most diverse composition with rare elements (Li, Be, Sr, Rb, Cs, Y, rare earths, Nb, Ta, Zr, Hf, Th, U, W, etc.), and also volatile elements (F, B, Cl, etc.).

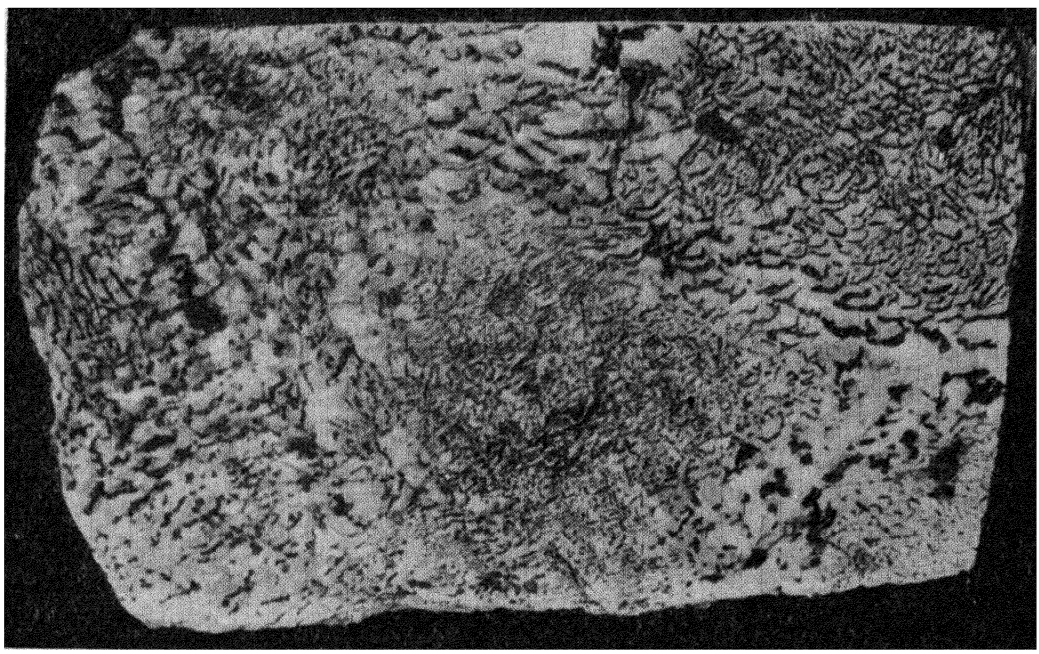


Fig. 373. Portion of large specimen showing graphic intergrowth of quartz (dark-grey) with feldspar (white). Reduced.

Different parts of specimen have different structure. The most coarse-grained intergrowths of quartz with feldspar are observed at the boundaries between these parts.

Characteristically, in granite pegmatites most of the rare minerals are confined to the albitised portions, i.e., to places where coarse-grained masses of potassium feldspars are replaced by albite, sometimes to the point of conversion to fine-grained albitites. These metasomatic phenomena are related to the later, hydrothermal, stage of mineral formation.

The problem of the origin of pegmatites still awaits solution despite the vast amount of factual material on their composition reviewed by Academician A.Y. Fersman in his monograph *Pegmatites*. Fersman's conception is that pegmatites have formed from residual silicate melts enriched with volatile compounds. The process of mineral formation is complex and occurs within a wide temperature range (700° to 100°). This is believed to be responsible for the wide diversity of mineral composition and the complex structure of many pegmatites. Recently proceeding from physical and chemical considerations, Acad-

emician A. N. Zavaritsky rejected the Vogt-Niggli theory, and came to the conclusion that pegmatites did not form by crystallisation from residual melts, but through recrystallisation of rocks under the action of residual gaseous solutions which accumulated at definite places and were at equilibrium with the minerals of the given rock.

A detailed division of *granite* pegmatites into types has been given by A. Y. Fersman in his monograph. The extremely variable quantitative ratios of mineral associations does not allow, however, to draw definite boundaries between the types. Therefore, we shall dwell only on the types that are most important economically and most interesting mineralogically.

1. The *topaz-beryl* pegmatites. In the central portions of these pegmatites in the druse cavities (cf. Fig. 51), whose walls are formed by faces of large crystals of *microcline* and smoky *quartz*, there are found excellent crystals of pale tinted *topaz*, sometimes of *beryl*, or in other cases, aquamarine (the two minerals seldom occur together), "cockscombs" of platy crystals of *albite* (cf. Fig. 348), crystals of *lepidolite*, *tourmaline*, occasionally of cassiterite, of Nb and Ta minerals, etc. Crystals of *muscovite*, *tourmaline*, and sometimes of biotite occur closer to the selvages in the zones of graphic granite.

2. The *tourmaline-muscovite* pegmatites (Mamsk-Vitim Area), though important economically, are rather poor in minerals and have no miarolitic cavities. Muscovite pegmatites often found in gneisses and mica schists may contain besides *feldspars* (acid plagioclases, microcline), *quartz*, and considerable quantities of *muscovite*, also *tourmaline*, *apatite*, *garnet*, *orthite*, *monazite*, *rutile*, *sulphides*, etc. Pegmatites rich in black tourmaline apart from ordinary feldspars, muscovite, and chloritised biotite (in spots composed of a grey quartz mass) may carry minor amounts of beryl, apatite, and other rarer minerals.

3. *Pegmatites with rare elements* (Ytterbi in Sweden) are characterised by a wide variety of "black" minerals of Nb, Ta, Fe, Ti, Zr, Th, U, Y, the rare earths, Sn, W, etc., such as *columbite*, *tantalite*, *ilmenite*, *rutile*, *ilmenorutile*, *zircon*, *thorite*, *gadolinite*, *fergussonite*, *samarskite*, *euxenite*, *aeschynite*, cassiterite, uraninite, monazite, xenotime, orthite, etc. These pegmatites may also contain apatite, garnet, tourmaline, beryl, chrysoberyl, phenacite, helvite, topaz, fluorite, carbonates, sulphides, etc.

4. *Pegmatites with lithium minerals* contain accumulations of such minerals as *spodumene*, *lepidolite*, sometimes *lithium phosphates* (amblygonite, lithiophilite, tryphylite); pink, red (rubellite), blue or green tourmalines; colourless, pink beryl (vorobyevite); spessartine, manganous green apatite, cassiterite, pollucite, zircon, monazite, manganocolumbite, fluorite, etc. Thus, this type of pegmatites is characterised by increased content of Li, Mn, Ca, and also Cs.

Besides the above "pure-bred" pegmatites, Fersman distinguishes "*cross breeds*" deriving from the reaction of pegmatitic solutions with

the enclosing rocks of a different composition. These reactions materially alter both the chemical and mineralogical composition of the pegmatites themselves and of the contact zones of their host rocks. Thus, when silica-rich granite pegmatite solutions act upon silica-poor ultrabasic rocks (serpentinites), the pegmatites thus formed are much poorer in silica and potassium oxide, which may be seen from the fact that the pegmatites contain no quartz but do contain basic plagioclases (poorer in SiO_2, but richer in CaO and Al_2O_3), sometimes in paragenetic association with corundum. On the other hand, the serpentinites in the contact zones are replaced by biotite, talc, actinolite, and chlorites, i.e., minerals richer in SiO_2 as compared with serpentine.

The far less common *nepheline-syenitic pegmatites* (the Ilmen mountains), in contrast to the granite pegmatites, do not contain quartz and usually are composed of *microline*, *nepheline*, frequently are enriched with *biotite* and lepidomelane; contain smaller quantities of aegirine, albite, sodalite, cancrinite, zircon, apatite, sometimes sphene, ilmenite, the pyrochlore group minerals, fluorite, hydrargyllite, zeolites, calcite. In other alkaline-rock provinces, pegmatite formations, besides the usual alkaline silicates, sometimes also contain complex silicates of Zr, Ti, TR, Ca, Na, Nb, Ta (eudialyte, lamprophyllite, rinkolite), the perovskite-group minerals (loparite), etc.

Mineral associations in contact-metasomatic formations. The most intense metasomatic reactions (skarn formation) are confined to the contacts of intrusive masses of mostly medium-acidic quartz diorites, granodiorites, monzonites (cf. Fig. 52) with carbonate wall rocks (limestones and sometimes dolomites). According to recent data D.S. Korzhinsky), the contact aureoles forming at comparatively shallow depths where postmagmatic (pneumatolytic-hydrothermal) solutions impregnate the rocks in the contact zone, represent the scene of chemical reactions between the intrusive rock and limestones. In this process, not only are the limestones altered (exocontact metamorphism), but so are also the solidified intrusive rocks (endocontact metamorphism).

Thus, the process of skarn formation postdates the crystallisation of magmatic rocks. The assimilation of invaded rock by the intruding magma involves little or no change in the composition of the skarn-formation products and of the resulting ore minerals.

The intensity of the skarn-formation processes depends not only on the composition of magmatic emanations, not only on the shape, size, mode, and depth of occurrence of the parent intrusives, but also on the composition and tectonics of the invaded rocks. It has been established that the above processes develop mostly along the contacts or rocks differing in physical properties and composition (granitoids and carbonate rocks), as well as along the bedding planes in the invaded heterogenous sedimentary series and along the fractured zones in the country rock (Fig. 374), and sometimes within the granitoids themselves. The thickest portions of skarn bodies often occur at junctions of

tectonic dislocations. In particular, scheelite-rich quartz veins (Fig. 375) are often confined to such junctions.

The early stages of *exocontact* metamorphism are expressed in the formation from limestones of so-called skarns, i.e., calcium-rich silicates of Mg, Fe, Al: garnets, mainly *andradite*, pyroxenes—*salite*, *hedenbergite*, as well as *magnetite* and *hematite* (often in the form of muschketowite). There may also be formed *wollastonite*, *datolite*, *scapolite*,

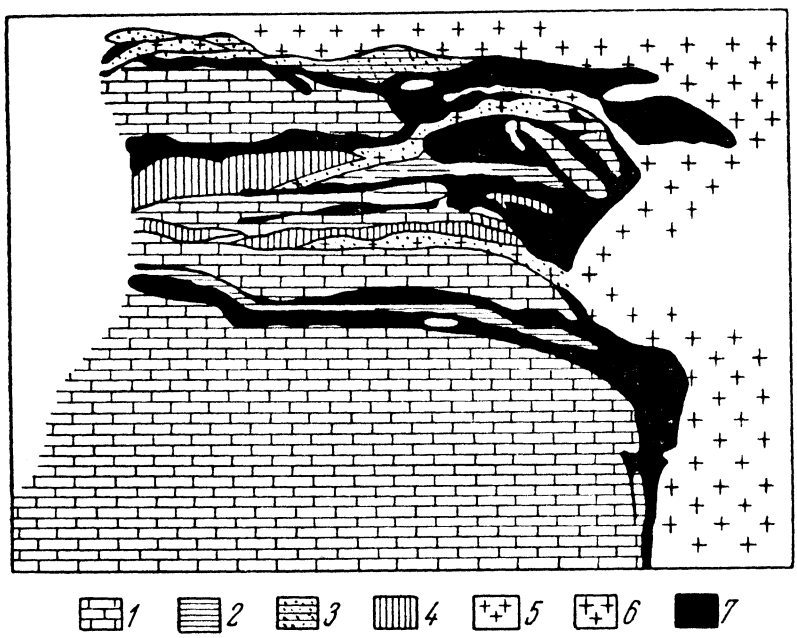


Fig. 374. Diagram of the localisation of skarn formations at contact of an acid igneous intrusive with enclosing rocks.

1—limestone; *2*—clay shale; *3*—sand-clay shale; *4*—hornfels; *5*—granodiorite; *6*—altered granodiorite; *7*—skarn.

scheelite, *helvite*, *ilvaite*, etc. Skarns often have complex structure and are tens of metres thick. Sometimes no skarns develop and the intrusive rocks come into direct contact with limestones.

Endocontact metamorphism is expressed in the formation of non-ferruginous but calcium-rich and silica-poor silicates, viz., *plagioclases* (including anorthite), *diopside* (after hornblende), *grossular*, *vesuvianite*, etc.

By comparing the composition of the resulting minerals it may be easily seen that there has been an influx mainly of Ca and a partial outflow of Si, Al, and Fe, which participate in the exocontact metamorphism of limestones. However, most of the iron of the magnetite, hematite, andraditic and hedenbergitic skarns, as well as magnesium, is obviously brought in by solutions in the form of some highly soluble, most likely chlorous, compounds. The intensity of metamorphism is probably due to the high chemical activity of the solutions, which, in

turn, is determined by the minerallising agents dissolved in them (Cl, F, B, etc).

During the later stage of contact metamorphism which corresponds to a typical hydrothermal stage, the skarns decompose, forming *epidote*, *chlorites* accompanied by *quartz*, *calcite*, *fluorite*, and often such sulphides as pyrrhotite, chalcopyrite, pyrite, sometimes cobaltite, molybdenite, etc.

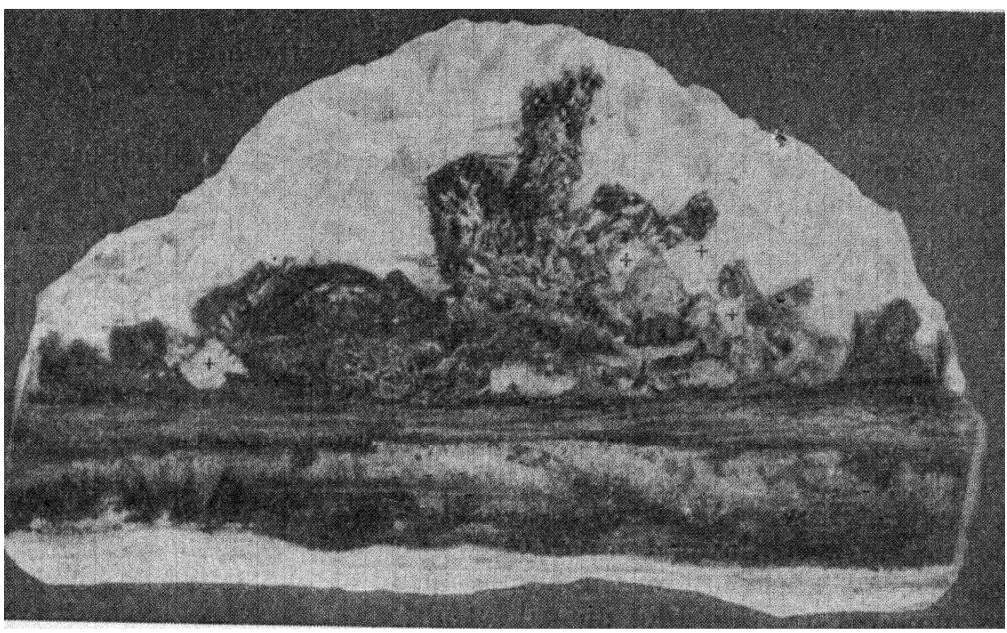


Fig. 375. Portion of quartz vein (top white) with semi-decomposed prismatic crystals of hedenbergite (middle and sides) and coarse grains of scheelite (marked by crosses). Dark band below—garnet mass in marbled limestone (white).

Genetically related to the exoskarns are large deposits of *magnetite* (mounts Magnitnaya and Vysokaya) *tungsten* and *molybdenium* (scheelite and molybdenite), *copper*, occasionally *lead-zinc*, and other ores. The formation of sulphide deposits corresponds to a lower-temperature stage which often overlaps the earlier processes of formation of magnetites and skarns.

The contact action of acidic intrusions on invaded rocks containing little or no calcium (clay shales, marls, tuffs, sandstones, etc.), usually gives rise to close-grained, compact, non-schistose metamorphic rocks known as hornfels. Depending on the initial composition of these rocks under the microscope they show paragenetic associations of the following minerals: plagioclases, pyroxenes, garnets, cordierite, sillimanite, andalusite, spinel, quartz, epidote, chlorites, topaz, tourmaline, scapolite, fluorite, apatite, sometimes cassiterite, magnetite, sulphides, etc.

Contact formations rarely occur in limestones and dolomites in association with *basic* intrusive rocks. The Nazyam and Shishim mining districts near Zlatoust (Southern Urals) offer a remarkable examples of this type of formations. Thus, at the contact aureole of gabbros with carbonate rocks, there have been mostly formed in marbles, garnet-pyroxenes, and talc-chlorites, silicates of Ca, Mg, Fe, Al, and Ti. In cavities in metamorphic rocks there occur excellent crystals of *garnets* (from grossular to andradite), and also crystals (which attracted the attention of mineralogists already in the last century) of such minerals as *diopside*, *sphene*, *actinolite*, *vesuvianite*, *humite*, *chondrodite*, *epidote*, *clinochlore*, *xanthophyllite* (of the group of brittle micas), *perovskite*, *ilmenite*, *apatite*, *chlorospinel*, *magnetite*, *magnesioferrite*, *hematite*, *hydrargyllite*, etc.

Economic minerals of hydrothermal deposits. The bulk of hydrothermal deposits (cf. Fig. 53) are genetically related to the intrusives of acid igneous rocks and are formed at medium and shallow depths. These deposits usually occur as typical veins (cf. Fig. 54) in rocks greatly varying in genesis and composition. Metasomatic bodies are less frequent and occur generally in limestones or as impregnations in other for the most part hydrothermally altered rocks.

It is assumed that in the case of the most high-temperature formations the segregation of minerals from solutions began at about 400° and that only in the case of deposits which had "roots" directly in the parent intrusives. Most of the hydrothermal deposits, however, have formed at much lower temperatures as far as we can judge from the scanty available data on the homogenisation of gas-liquid inclusions in minerals (cf. Fig. 190) upon heating*.

A characteristic feature of many hydrothermal vein deposits is the multistage nature of their mineralisation, i.e., repeated resumption of the circulation of the mineralising solutions due to the re-opening of fissures. The superposition of new mineralisation stages is expressed in the formation of veinlets of different ages, sometimes intersecting each other, in the earlier deposited material (Fig. 376), or of breccias in which fragments of earlier mineral formations are cemented by later ones, or, lastly in the intersection of veins. The quite frequent changes in mineral composition show that there must have been variations in the composition of the successive solutions. This is attributed by Academician S.S. Smirnov to the intermittent activity of hydrothermal solutions that penetrated either along the same fissures or along new ones developing in the given metalliferous area due to repeated fracturing.

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* Individual minerals have long been overrated as "geological thermometers". A study of paragenetic ratios for various types of ores shows that most minerals of hydrothermal deposits will precipitate from solutions within a wide range of temperatures (down to the very lowest). The former concept that each mineral has a definite formation temperature is not true for postmagmatic formations.

Widespread in hydrothermal deposits are minerals of such economically important elements (cf. Fig. 53) as nonferrous metals: Cu, Pb, Zn, (Cd), (In), (Ge); rare metals: W, Sn, Mo, Ni, Co, Bi, As, Sb, Hg, Te; noble metals: Au and Ag; radioactive metals: U; certain rare earths, and sometimes ferrous metals: Fe, Mn. Some hydrothermal deposits are

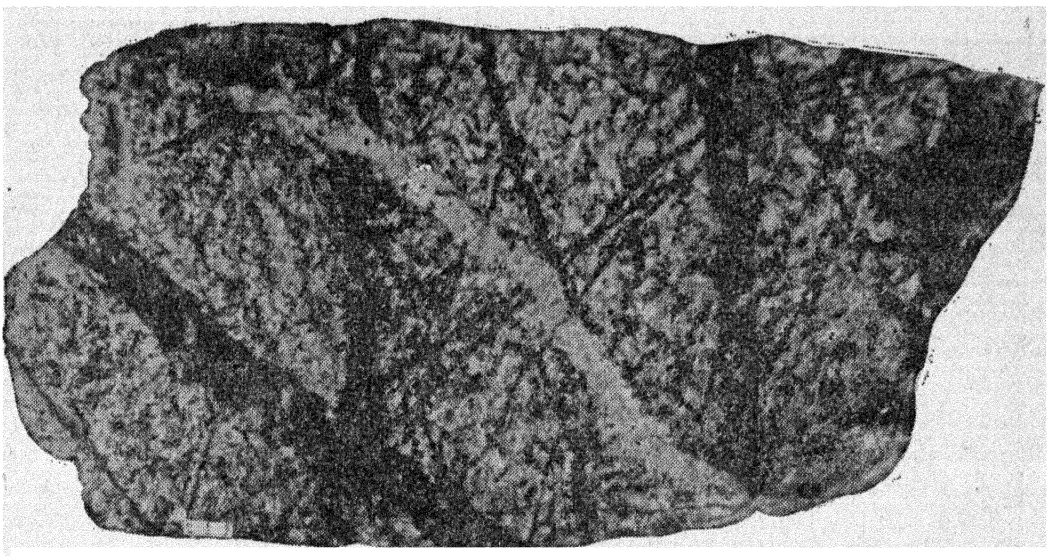


Fig. 376. Intersection of quartz-molybdenite and quartz-pyrite veinlets (dark) by aplite-porphyry veinlet (light band). In turn, aplite-porphyry is intersected by thread veinlets of ore-free quartz (barely visible on the photograph).

associated with accumulations of nonmetallic minerals, such as talc, asbestos, fluorite, barite, magnesite, Iceland spar, alunite, etc.

Most metallogenic elements in hydrothermal deposits occur as *sulphides*, *arsenides*, more rarely as *native metals* (Au, Ag, Cu, Bi, As, Sb, Te) and sometimes as *oxygen compounds* (Sn, W, Fe, Mn, etc.). All these are elements of the right-hand part of the periodic table (drawn up on the principle of long periods), characterised by ions with an 18-electron shell; and the adjacent elements on the left with asymmetrical structure of ions. Overwhelmingly important among the petrogenic elements typical of hydrothermal deposits is Si occurring mostly as quartz and sometimes as silicates (e.g., tourmaline, chlorite, talc, etc.); less important are Ca and Mg usually as carbonates, and less often as silicates (Mg), fluorite (Ca), etc. Aluminium is not a typical element of the minerals deposited from hydrothermal solutions; the Al minerals, such as chlorites, micas, and alunite derive mostly from the alteration of aluminous wall rocks. Alkalis also occur only as recent formations in hydrothermally-altered wall rocks (micas, sericite), as well as in gas-liquid inclusions (cf. Fig. 190) in ore-forming minerals. Barium characteristically occurs in certain hydrothermal deposits as a sulphate (barite), occasionally as a carbonate (witherite).

The bulk of hydrothermal veins is composed of almost solid quartz often outcropping as blocks (Fig. 377) located either at the site of the primary deposit or exhibiting slight downhill creep. The sulphide-bearing quartz masses contain numerous leaching cavities and cracks filled with sulphide oxidation products (limonite, copper-blue, copper-green, etc.).

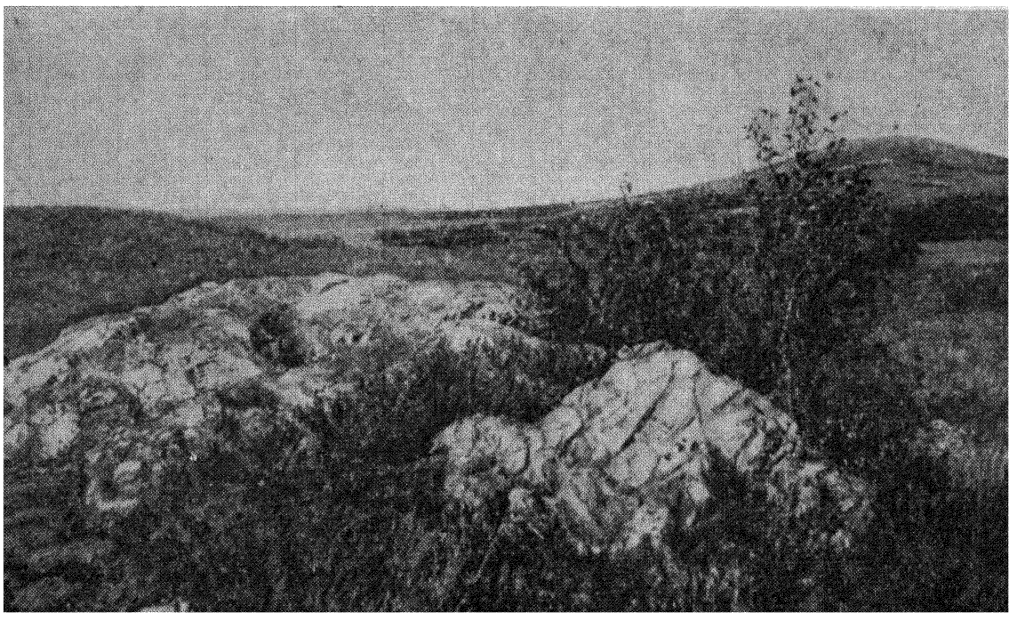


Fig. 377. Outcropping quartz blocks (white in the foreground).

Hydrothermal ore deposits are notable for a wide variety of mineral associations, which it seems is due primarily to the composition of the solutions themselves and of the wall rocks which often react with the solutions as far as one can gather from the changes in them.

The paragenetic ratios of minerals in ores is definitely affected by the state of sulphur and oxygen in solution, which largely depends on the depth at which the deposits are formed*.

Sometimes, with diminishing distance to the parent intrusive rock (cf. Fig. 53) obvious alterations are observed in the composition of mineral associations. And, finally, the diversity of paragenetic mineral associations in ores is often due to superimposition of fresh portions of solutions of varying composition or else to gradual facies changes in the mineral composition of the ores caused by the physico-chemical conditions of mineralisation.

Without discussing the entire range of mineral associations in hydrothermal deposits (which are considered in detail in the course in

* The partial pressure (or concentration) of oxygen in the earth's crust gradually increases towards the surface.

ore deposits), we shall confine ourselves only to a few characteristic examples.

1. *Quartz wolframite, quartz-cassiterite,* and *quartz-molybdenite* veins usually occur very close to or even within the parent intrusives of acidic igneous rocks. The veins are composed principally of a quartz mass some of which may have, mostly at the margins, impregnated

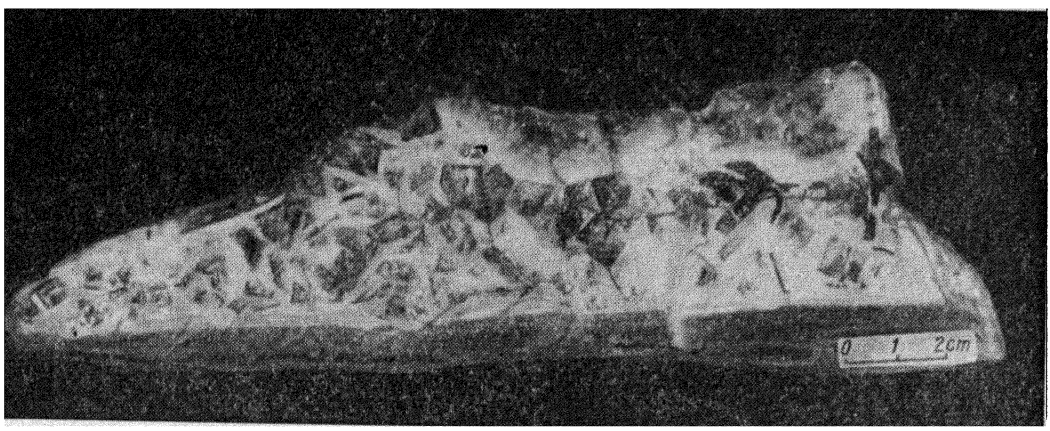


Fig. 378. Wolframite (black elongated crystals) and fluorite (grey crystals of square section) in fine-grained quartz groundmass (white). Dark-grey selvage (below) also consists of fine-grained quartz.

crystals of *wolframite* (Fig. 378) which are often quite large, others contain *cassiterite,* or *molybdenite* as fine scales (cf. Fig. 376) or as coarse-scaly selvages along the sides of the veins. These minerals may also occur together in the same vein. Scheelite, arsenopyrite, native bismuth, pyrrhatite, pyrite, sphalerite, chalcopyrite appear in places as admixtures. Their veins may contain feldspars, micas, occasionally fluorite, topaz, beryl, tourmaline, etc. Alterations of the immediate wall rock are frequently observed, either in the form of *greisenisation* of granite accompanied by recent formations of *quartz, muscovite, lithium mica, fluorite,* less often of *topaz, tourmaline,* etc., or the formation of mica and quartz gouges deriving from the sedimentary or metamorphic wall rocks.

2. *Auriferous quartz* veins usually contain no admixtures of other minerals. However, native gold may be associated paragenetically generally with negligible, but sometimes with appreciable (Beryozovsk, Darasun deposits) quantities of ordinary sulphides such as *pyrite, galena* (Fig. 379), *sphalerite, chalcopyrite, arsenopyrite, grey ores*; besides quartz there may be present nonmetallic minerals such as *calcite, dolomite* and *barite.* The distribution of gold through the veins is usually very uneven.

Quartz-tourmaline and quartz-scheelite veins may also contain gold. In rare instances deposits formed in near-surface conditions contain tellurides of gold and silver.

3. *Sulphide ore deposits are the most widespread* among hydrothermal formations. Their composition is extremely variable. According to their content of the principal economic metals they are classified as copper, lead-zinc, polymetallic, arsenic, antimony, and other ores. The most frequent nonmetallic minerals are quartz and carbonates, less often barite, chlorite, etc.

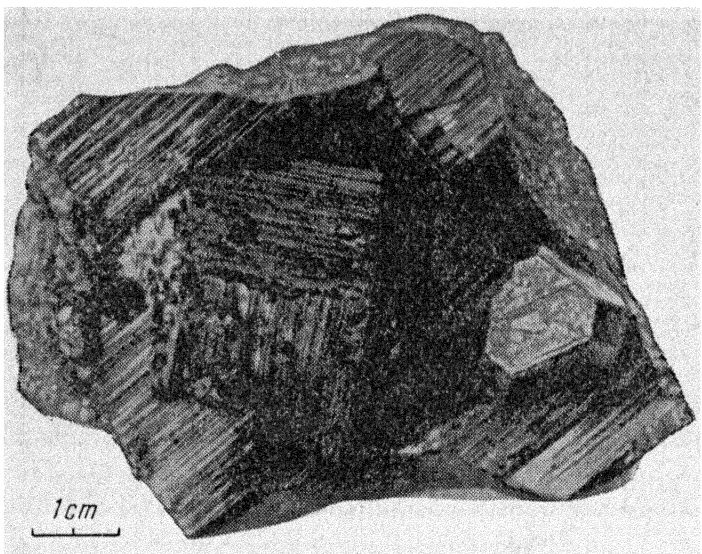


Fig. 379. Large pyrite crystals and a galena crystal (right) in a druse cavity of auriferous quartz vein.

(a) Vein-type copper deposits, such as the one at Zangezur, are usually composed of *pyrite*, *chalcopyrite*, *grey ores*, sometimes *bornite*, endogenous *chalcosine*, *enargite*, occasionally accompanied by molybdenite, bismuth, etc. Also known are large deposits of the disseminated type confined to the hydrothermally-altered apical parts of intrusives and granitoids of porphyritic appearance.

(b) The principal constituents of lead-zinc veins (Sadon) or metasomatic sheet-like bodies in limestones (Kan-Sai) are *sphalerite* and *galena* which often contains silver and sometimes bismuth. The most common accessories of these ores are pyrite, chalcopyrite, grey ores, arsenopyrite; less often pyrrhotite, stannite, cassiterite; also boulangerite, jamesonite, bournonite, proustite, pyrargillite, stephanite, etc.

The structure of galena-sphalerite and of many other sulphide veins is often extremely nonhomogenous. Ore minerals occur either as impregnations, or as continuous irregular portions, or as bands and zones, or fill the spaces between fragments in breccias (Fig. 380), etc. Some hydrothermal deposits in near surface conditions show a symmetrical banded structure of the veins (Fig. 381).

(c) Polymetallic deposits, i.e., those containing several metals in commercial quantities, may be of most diverse composition. Thus the Altai polymetallic ores contain Zn, Pb, Cu, Ag, and Au in the form of

sphalerite, *galena*, *pyrite*, *chalcopyrite*, *tetrahedrite*, sometimes *arsenopyrite*, *native gold*, and occasionally *tellurides* of Pb and Ag. Nonmetallic minerals, such as quartz, barite, ankerite, sericite are usually present in these ores in minor amounts. The alteration of wall rocks as for many other sulphide deposits, is expressed in the form of keratinisation (silicification), sericitisation or chloritisation.

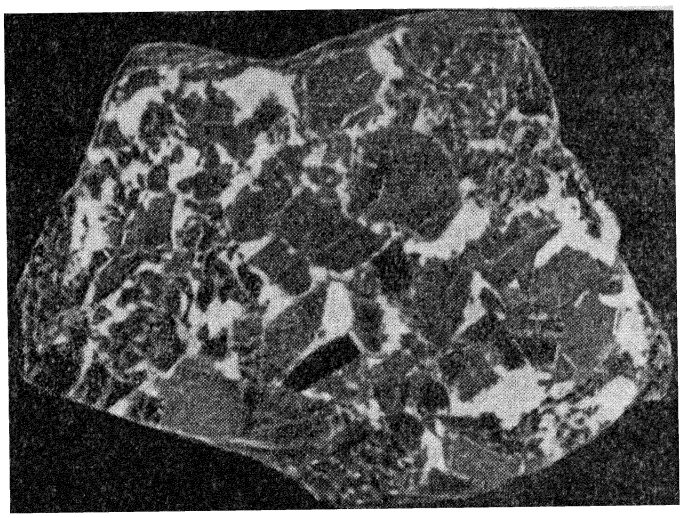


Fig. 380. Black sharply angular fragments—limestone. The cementing mass is calcite (white) and sphalerite (grey fringes around fragments). Natural size.

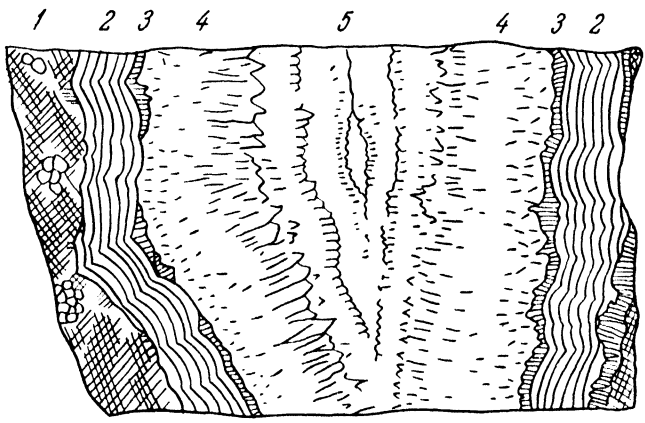


Fig. 381. Vein of symmetrical banded structure.

1—chlorite, quartz, sphalerite, and galena; *2*—thinly-banded crustification quartz; *3*—sphalerite of late generation; *4*—bands of amethyst; *5*—comb quartz; *6*—druse cavity.

(d) Arsenic deposits occur either as *arsenopyrite* ores, which sometimes contain gold or bismuth (usually as bismuthinite), or else as *realgar-auripigment* ores with quartz and calcite, and also marcasite, antimonite, etc., as impurities. The formation conditions for these two types of ores are substantially different. The realgar-auripigment ores,

in contrast to the first type, are formed at low temperatures and pressures.

(e) Antimony deposits occur as typical *quartz-antimonite* veins containing negligible quantities of pyrite and other sulphides, occasionally gold.

(f) In mercury deposits, *cinnabar* is practically the only mineral of mercury. It is often associated with *antimonite*, sometimes with admixtures of marcasite, pyrite, and arsenopyrite. The most common nonmetallic minerals in these typically low-temperature hydrothermal deposits are *quartz*, *chalcedony*, *calcite*, *fluorite*, and *barite* (Khaidarkan).

4. Mention should be also made of rare deposits of *arsenide* ores of nickel and cobalt, which are very peculiar in composition, with native bismuth and silver (Schneeberg, Saxony). These deposits contain the arsenides of nickel and cobalt such as niccolite, chloanthite-smaltite, rammelsbergite-safflorite, skutterudite, often associated with native arsenic, bismuth, and silver.

Some deposits of this type also contain uraninite and rare sulphides (pyrite, marcasite, metacolloidal sphalerite, galena, grey ore, gersdorffite, millerite, argentite, proustite, pyrargyrite, dyscrasite, etc.). The nonmetallic minerals in these deposits are quartz and ankerite or dolomite.

5. *Fluorite* deposits are also typical hydrothermal formations. As an accessory mineral, fluorite occurs in many types of pneumatolytic-hydrothermal deposits, from greisens and certain tin ore deposits to low-temprature cinnabar deposits. However, fluorite frequently, especially at low temperatures and pressures, form accumulations large enough to be of economic importance on their own. Depending on the mode of formation, the accumulations occur as vein or metasomatic deposits in limestones. Associated with fluorite are minor amounts of pyrite, marcasite, chalcopyrite, galena, quartz, calcite, sometimes hematite, berite, chalcedony, adular, etc. Massive fluorite may occur as concentrically-banded aggregates of radial-fibrous structure with bands and crystals of different colours (violet, green, pink, milk-white). It also occurs as perfectly colourless transparent crystals.

6. *Barite* hydrothermal deposits are usually formed at low temperatures near the earth's surface. Besides the predominant barite, they contain in some cases minor quantities of sulphides (most often pyrite, chalcopyrite, galena, sphalerite) as well as siderite, quartz, and zeolites, and in other cases, iron oxides (hematite). The former mineral paragenesis indicates that the veins were formed in relatively reducing conditions, whereas the latter clearly points to an oxidising environment. Typical barite vein deposits are found in several localities in Georgia where the veins show a symmetrical banded structure due to intermittent filling of the fissure cavities from the walls to the centre.

Minerals of effusion rocks and products of volcanic exhalations. The most common effusive are basalts or diabases, andesites or por-

phyrites deriving from basic magmas; liparites and quartz porphyries, which are the products of acidic, or more rarely of alkaline (leucitophyres) magmas. A characteristic feature of these rocks is the presence of volcanic glass or its decomposition products in varying amounts.

The mineral composition of *effusive rocks* may be established positively only under the microscope. However, in effusives of porphyritic structure it is possible to detect with the naked eye impregnated crystals of green *olivine* in black olivine basalt, *feldspars* in dark-grey porphyrites and in light-coloured acid quartzless porphyries, *hornblende* in hornblende porphyrites, *quartz* in light-coloured quartz porphyries and of *leucite* in leucitophyres.

Amygdaloidal rocks, i.e., blister lavas whose spherical cavities are filled with mineral matter, often contain later depositions of hydrothermal origin, chiefly *chalcedony*, *quartz*, sometimes *calcite*, *zeolites*, less often tridymite, and other minerals. The larger amygdules known as geodes (cf. Figs. 42, 191) frequently contain chalcedony-quartz mass of concentrical banded structure (agates). The amygdules and geodes mostly occur in such silica-poor effusives as basalts, melaphyres, and pyroxene-porphyrites.

As products of volcanic exhalations in cavities on the walls of craters and in cracks, there may occur minerals of different composition, viz., *ammonium chlorite*, *halite*, *silvine*, occasionally chlorides of Fe, Cu, Mn, Al, Mg, etc., and also *sassolite*, *carbonates*, *native sulphur*, *marcasite*, *covellite*, *realgar*, *auripigment*, etc., and in places high-temperature minerals: *hematite*, *magnesioferrite*, *spinel*, *tridymite*, *quartz*, sometimes *leucite*, *pyroxenes*, *feldspars* (sanidine, anorthite), *topaz*, etc.

In the areas of solfataric activity where the emissions of hydrogen sulphide and its oxidation products (sulphurous and sulphuric acids) penetrated along fissures in the effusives, the wall rocks are strongly leached and bleached, and recent formations are deposited. The rocks in this process are enriched with SiO_2, Al_2O_3, and with SO_3 due to the removal of the more soluble constituents. The rocks are usually kaolinised, with the formation of iron sulphide and sulphate impregnations, the most common of the sulphates being *gypsum*, *alunite*, and *ammonia* and *potash alums*. In rare instances, ammonium and potassium silicofluorides and other unstable minerals are also found.

Economic mineral deposits related genetically to effusive volcanic activity are much less common and varied than those associated with plutonic intrusives. Hypabyssal (not deep-seated) acidic effusive masses of Tertiary or Quaternary age sometimes contain typical veins of solid *pyrite-marcasite* ores. The ore mass in cavities in the kaolinised fractured zones is reniform in appearance.

Pyrite deposits, widespread in the Urals, are rich in sulphides (chiefly iron pyrite and less chalcopyrite, sphalerite, etc.) but *poor in nonmetallic minerals*, are spatially confined to the old, sometimes strongly metamorphosed, series of volcanogenic Silurio-Devonian effusives. They are evidently genetically related to subvolcanic intru-

sives. Very characteristic of nonmetamorphosed pyrite deposits are colloform accumulations (Fig. 382) which besides the minerals mentioned above contain marcasite and wurtzite, which points to the acidic nature of solutions.

An interesting phenomenon is the formation of large masses of *native sulphur* in the areas of contemporary volcanic activity. Thus a

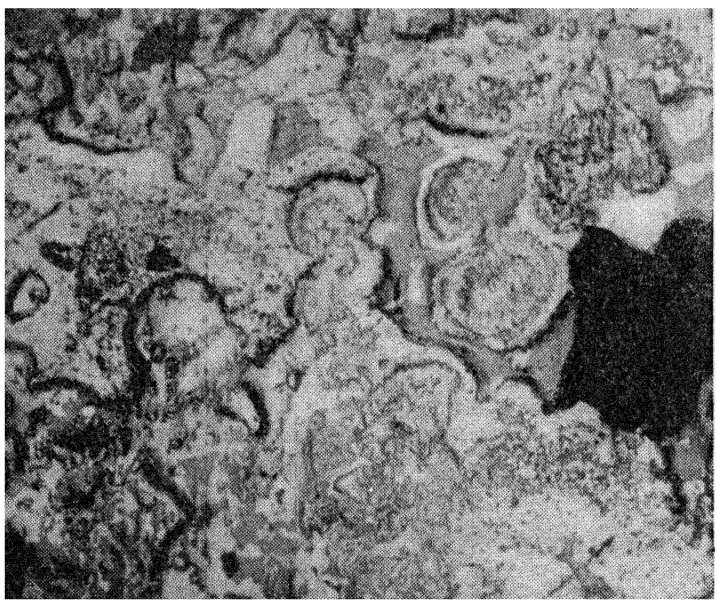


Fig. 382. Pyritic ore composed of pyrite (white with shading) chalcopyrite (white), and grey ore (grey). Black—a cavity. Polished section. Photographed in reflected light. × 90.

geyser in the crater of the Iosan volcano (Japan) after a long period of quiet solfataric activity began ejecting intermittently superheated steam and pure molten sulphur. The latter overflowed from the crater into a valley and solidified. Native sulphur had evidently been accumulating at certain depth in the course of the solfataric activity under conditions of incomplete hydrogen sulphide oxidation.

Mention should be also made of the numerous cold and hot mineral springs in areas of extinct volcanic activity.

Minerals of the crust of weathering. A considerable contribution to the mineralogy of the crust of weathering, of the rocks and of the oxidised zones of ore deposits has been made by Soviet scientists (Academician V. I. Vernadsky, Academician S. S. Smirnov, I. I. Ginzburg, F. V. Chukhrov, and others).

Thanks to their work, modern concepts of the processes in the crust of weathering have become much broader. During exogenous processes in general and weathering processes in particular, a great variety of finely-dispersed mineral formations are formed developing through

complex reactions with the atmospheric O_2, CO_2, and H_2O as well as from the life activity of microorganisms which play a tremendous role in the decomposition of many minerals. Most easily decomposed are those primary minerals that contain elements which are either low in valency (Fe^{2+} in siderite, S^{2-} in sulphides, etc.) or are capable of forming with CO_2 highly-soluble bicarbonates (Na, K in feldspars, Mg in olivine, and serpentine, etc.). A major role in the formation of colloidal sediments belongs to hydrolysis of the soluble salts developing during oxidation, a process involving the precipitation of hydroxides of strongly polarising cations with small ionic radii (Fe^{3+}, Al^{3+}, Si^{4+}, Mn^{4+}, etc.).

Thus, the composition of the mineral formations accumulating in the crust of weathering greatly depends on that of the primary rocks and ores. The chemically inert minerals not susceptible to decomposition by the surface agents are mechanically concentrated in the products of weathering, and upon their erosion by water, pass into placers (cf. Fig. 56). These minerals are *quartz*, *magnetite*, *hematite*, *corundum*, *spinel*, *chromespinellids*, *ilmenite*, *rutile*, *cassiterite*, *apatite*, *monazite*, *scheelite*, *zircon*, *topaz*, *tourmaline*, *disthene*, *andalusite*, *cinnabar*, *native gold*, *osmiridium*, *platinum*, *diamond*, etc.

Most intensive processes of chemical decomposition of minerals take place in the zone of oxidation of sulphide deposits (cf. Fig. 55). The most important characteristic of chemical reactions in that zone is that all the sulphides during oxidation pass through the so-called *sulphate stage*, i.e., they are first converted into sulphates ($FeS \rightarrow FeSO_4$, $PbS \rightarrow PbSO_4$, etc.). This is important for understanding the phenomena of the migration of metals in the zone of oxidation, since *the solubility of sulphates differs from metal to metal.* The mineral associations developing in the course of oxidation of sulphide deposits could be best considered according to the types of primary ores.

In *copper-sulphide* deposits, rich in pyrite, chalcopyrite, and other sulphides of copper, abundant iron hydroxides (*limonite*, *goethite*) are formed in the zone of oxidation (gossan). This is due to the fact that in the presence of oxygen the $FeSO_4$ sulphate formed from the iron of the sulphide alters readily to the Fe^{3+}, $Fe_2[SO_4]_3$ sulphate, which is immediately hydrolised to insoluble iron hydroxides. The copper in the form of highly-soluble sulphate migrates with percolating water down to the ground-water table, and the zone of oxidation is strongly depleted of copper. Vice versa, the ores of the zone of secondary sulphide enrichment (cf. Fig. 55) are enriched in copper due to the formation of secondary copper-rich sulphides, such as *covellite*, *chalcosite*, and sometimes *bornite*, developing in the place of the primary sulphides through the reactions of the latter with cupriferous solutions. Thus, when the gossan contains even traces of *malachite*, *azurite*, chrysocolla, and other copper-oxygen compounds, it may be safely assumed that below the ground-water table there is a copper-enriched zone of secondary sulphides.

In areas of a hot arid climate with little rainfall some sections of the zone of oxidation of the sulphide deposits may consist of semi-oxidised ores. Under the microscope such copper-sulphide ores usually show a combination of hydroxides or oxysalts with secondary sulphides, mostly covellite and chalcosine (Fig. 383).



Fig. 383. Stringers of limonite with dark fringes of covellite in tetrahedrite (white groundmass), from semi-oxidised ore. Polished section. Photographed in reflected light. ×80.

Cuprite and *native copper* often derive from the oxidation of sulphur-poor chalcosine ores. More seldom there occur copper phosphates and arsenates: *libethenite*, *olivenite*, etc., occasionally silicates: *dioptase* and *chrysocolla*. Hydrous and basic sulphates of copper such as *chalcanthite*, *brochantite*, as well as those of iron, such as *melanterite* and *jarosite*, usually occur in countries with a hot arid climate.

Lead-zinc deposits rich in sphalerite and galena contain large amounts of secondary lead minerals in addition to the iron hydroxides forming after the ubiquitous pyrite. The poorly soluble *anglesite*, $PbSO_4$, the first alteration product of galena, often coats the remaining pure galena with a thin crust and thus prevents its further decomposition. Only at the surface anglesite alters to *cerussite* whose solubility in water is also low (Fig. 384). The deposits may contain other lead oxysalts in minor amounts: molybdates, such as *wulfenite*; phosphates, such as *pyromorphite*; arsenates, such as *mimetesite*; vanadates, such as *vanadinite*; occasionally chromates, such as *crocoite*, etc. Considering that the divalent Pb^{2+} cation is rather large (cf. Fig. 206), no wonder that in the zone of oxidation it forms chemically stable compounds

with such large anionic radicals as SO_4, PO_4, AsO_4, VO_4, MoO_4, and CrO_4.

The behaviour of zinc is entirely different. Sphalerite decomposes readily, and zinc in the form of a *water-soluble* sulphate is almost completely removed from the zone of oxidation. If the zinc-sulphate solutions encounter limestones in the lower horizons of the zone (in wall

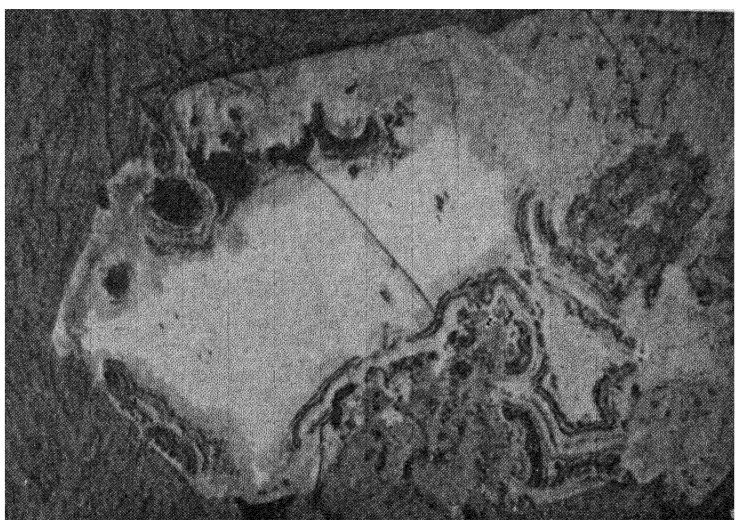


Fig. 384. Replacement of galena (white) by anglesite and cerussite (light-grey). Dark-grey background—barite. Polished section. Photographed in reflected light. ×17.

rocks) *smithsonite* ores are formed through exchange reactions (cf. Fig. 224). If wall rocks are schists or other chemically inert rocks, the zinc sulphate percolates to the ground-water table and escapes from the deposit in the efflux zone (zinc does not produce secondary sulphide enrichment). Sometimes, the oxidising zone may contain Zn silicates, such as *calamine*, *willemite*, occasionally phosphates, arsenates, etc.

Thus, lead and zinc intimately associated in the form of sulphides in endogenous deposits, separate in the zone of oxidation. This may serve as a guide to the prospector (the absence of zinc in samples of oxidised lead ores does not always signify the absence of sphalerite in the primary ores).

Silver, often found in lead-zinc deposits behaves in a different manner. In the lower parts of the zone of oxidation it may occur native in association with *argentite*. In countries with a hot arid climate it often passes into stable halides, such as *cerargyrite*, etc.

Ores rich in arsenopyrite and other iron arsenides form in the zone of oxidation *scorodite* masses which are often interspersed with iron hydroxides. Nickel arsenides in the same conditions give *annabergite*, cobalt arsenides—*erythrite*. Antimony sulphides change to oxides, such as kermesite (Sb_2S_2O), valentinite (Sb_2O_3), and stibiconite

(Sb_3O_6OH). Bismuth sulphides usually yield a basic carbonate, such as *bismuthite*. Molybdenite on exposure to weathering alters to *powellite* and *ferrimolybdite*, etc.

Carbonates containing Fe^{2+} and Mn^{2+} are easily decomposed forming hydroxides. In general, the minerals containing low-valent manganese (rhodonite, manganite, braunite, hausmannite, etc.) readily

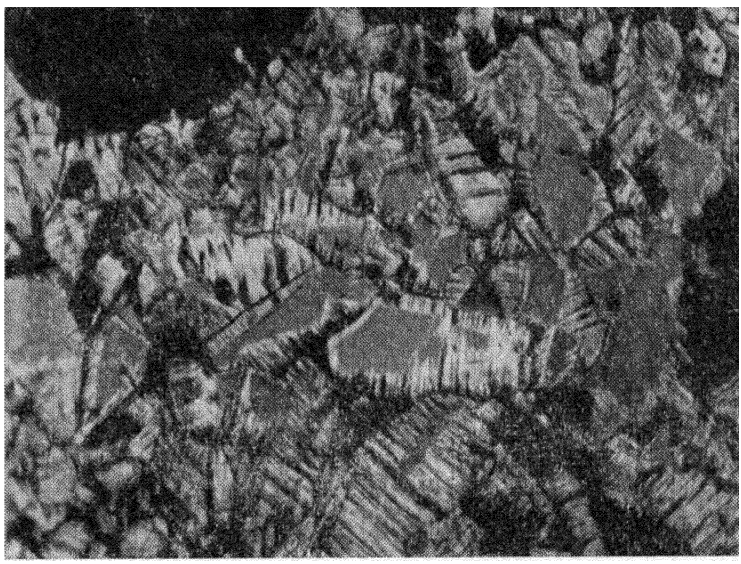


Fig. 385. Replacement of manganite (grey) by pyrolusite (white fringes with cleavage). By external features this ore is identified as pyrolusite. Polished section. Photographed in reflected light. ×165.

decompose in the zone of oxidation into oxides and hydroxides of Mn^{4+}, such as *vernadite*, *pyrolusite* (Fig. 385), and *psilomelanes* forming manganese hats. Silicates of *iron* (serpentine, chlorites, garnets, pyroxenes, etc.) are similarly decomposed by intensive weathering, forming friable *brown iron* ores in place of the rocks rich in these silicates (e.g., skarns).

Intensive weathering of *silicate rocks* may give rise to new deposits of economic minerals from the residual products. In temperate climate in place of *acid* igneous rocks, poor in iron but *rich in alumina*, there are formed *kaolin deposits*; on the other hand, laterite weathering in hot and humid climate gives rise to *bauxites* composed mainly of aluminium hydroxides, such as *hydrargillite*, *boehmite*, and *diaspore*.

Of particular interest are the thick crusts of weathering of *ultrabasic* magnezia-rich rocks, chiefly serpentinites, which give rise to nickel silicate ores containing *revdinskite*, *garnierite*, nickel-bearing *halloysites*, etc. (deposits in the Southern Urals). In the course of chemical weathering of silicates, the bulk of magnesium combines with the CO_2 dissolved in waters, percolates to the lower parts of the crust

of weathering, and precipitates there as *magnesite* (Fig. 386). The iron, on the contrary, accumulates at the surface as friable hydroxides. As the silicate crystal structures break down, the liberated silica passes into colloidal solution, partly forming new minerals (below the gossan), such as *nontronite* and halloysites, and partly precipitating as *opal* and *chalcedony* which often develop metasomatically in place of the primary rocks of the lower horizons. Nickel hydrosilicates are formed in the zone of nontronite development. There also occur manganese hydroxides called *asbolans*, containing cobalt and nickel.

In addition to the above minerals, the crusts of weathering may contain numerous other new formations, such as *gypsum*, *aragonite*, *calcite*, *jarosite*, *native sulphur* (deriving from the decomposition of gypsum), and various phosphates, whereas in arid regions there also appear efflorescences of saltpetre, alums, and other well-soluble sulphates, carbonates, and halides of various elements.

Minerals of sedimentary rocks and of economic mineral deposits. Important contributions to the mineralogy of sedimentary formations have been made by Soviet scientists (Academician A.D. Archangelsky, B. P. Krotov, G.M. Strakhov, L.V. Pustovalov, and others). Most noteworthy is the work of Soviet scientists in establishing the dependences governing the facies changes of sediments determined by the physico-chemical conditions of mineral formation. Stratified sedimentary rocks and ores are formed predominantly in lacustrine and marine basins and fall into two main groups: (1) *clastic* rocks chiefly composed of products of mechanical destruction of igneous rocks and crystalline schists, and (2) *chemical* sediments — crystalline, colloidal, and also those of organic origin.

Typical clastic sedimentary rocks (mechanical sediments) are sands and sandstones composed chiefly of rounded quartz grains, sometimes with a considerable admixture of *feldspars*. Occasionally they contain shell fragments, *glauconite*, and as accessories *magnetite*, *zircon*, *rutile*, *apatite*, *tourmaline*,

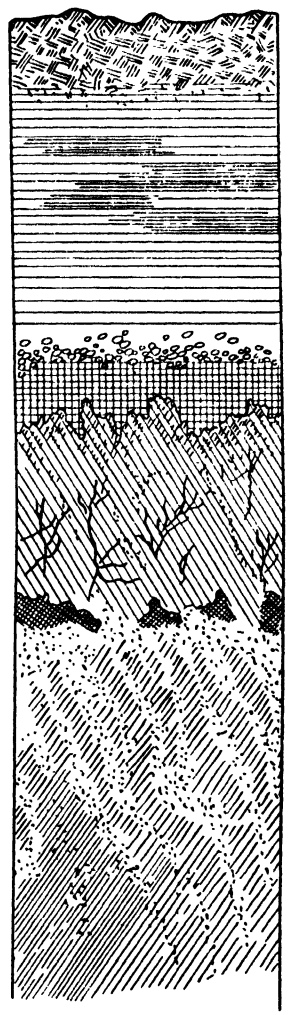


Fig. 386. Diagrammatic section of ancient crust of weathering in ultrabasic rocks, preserved under more recent sediments.

1—contemporary soil; *2*, *3*, and *4*—Mesozoic sand-clay sedimentary rocks burying eroded old weathering crust; *5*—uppermost layer of old crust of laterite weathering, composed of ferruginous ochres; *6*—nontronitised zone with hydrosilicates of nickel and hydroxides of manganese; *7*—zone of magnesite and hydromagnesite development; *8*—primary rocks (serpentinites).

etc. The fragments in sandstones are usually cemented together by argillaceous matter, seldom by carbonates (calcite), and still more seldom by iron and manganese hydroxides. In coarse-grained sandstones and conglomerates the clastic material are pebbles of rocks. When deposits and rocks containing chemically inert economic minerals (diamond, gold, platinum, cassiterite, etc.) are eroded by running water, the mechanical sediments are enriched through rewashing with valuable minerals, which gives rise to river or marine near-shore placers (cf. Fig. 56).

The most characteristic feature of *chemical* processes that give rise to sedimentary rocks is that in the course of dissociation of rock-forming silicates and alumosilicates of alkalis and divalent metals (Ca, Mg, Fe, Mn) which compose igneous and, in part, metamorphic rocks, these elements *are separated*, the hydrosilicates of Al (clay) being deposited in one place, the siliceous sediments in another, the compounds of Ca in a third, Al, Fe, and Mn in a fourth, Na, K, Mg in a fifth place and so on.

Clays, slates, and shales which often form thick series are composed of redeposited products of chemical weathering: in some cases of *kaolinite*, and in others of *beidellite* and *montmorillonite*. The most frequent admixtures are clastic *quartz*, often in considerable quantities (sandy clays), micas, organic remains, finely-dispersed carbonates (marls), and also opal, iron hydroxides, melnikovite, concretions of marcasite and pyrite, carbonaceous or bituminous matter, etc.

The siliceous (cherty) sediments consisting in part of chemically deposited silica, are composed of *opal*, *chalcedony*, and partly of *quartz*. Some rocks contain abundant fragments of siliceous spiculae of sponges (spongiolites), other rocks contain radiolarians (dense jaspers), still others diatomic skeletons (friable tripolis). Light finely porous opal-chalcedony rocks without organic remains are called gaizes. The most frequent impurity in them is argillaceous matter (kaolinite), sometimes glauconite, fragments of quartz and of other minerals.

Carbonate rocks (limestones and dolomites) often found as huge outcropping masses, consist of almost solid *calcite* or *dolomite* or of a mixture of the two minerals. They contain frequently some argillaceous matter, clastic quartz, glauconite, sometimes chalcedony-quartz nodules (flints), phosphorite concretions, occasionally accumulations of celestite, barite, gypsum, as well as of bitumens and gases (hydrogen sulphide). Many limestones contain a certain amount of various organic remains: fragments of mollusk shells, brachiopods, foraminifera, coral fragments, etc. (Fig. 387). Certain varieties of limestones (oölitic) show signs of colloidal chemical precipitation.

Chemically precipitated *iron-rich* colloidal sediments (iron-ore deposits) occur in some fresh-water lakes (as well as in bogs) in northern regions. According to geological data, large sedimentary deposits are confined to lagoons or near-shore zones of marine basins (the Kerch deposit).

The principal minerals of sedimentary iron-ore deposits are hydroxides of trivalent iron: *limonite* and *goethite* (often as oxidation products of siderite and iron hydrosilicates). Occasionally they are associated with *opal*, *vivianite*, *barite*, *manganese oxides*, etc. Farther offshore facies are composed of oölitic iron hydrosilicates (leptochlorites) such as *chamosite*, *thuringite*, and other chlorites rich in divalent iron



Fig. 387. Organogenic limestone. Polished specimen. Natural size.

and often associated with *siderite* (Fig. 388) which also forms beds of its own (Ayat and other deposits in the Urals). Frequent admixtures to siderite are *sulphides* (pyrite, and occasionally pyrrhotite) which rarely form any large accumulations.

In the case of *manganese* deposits, which are mostly confined to series of siliceous or siliceous-argillaceous sedimentary rocks, the most thorough study has been made of *the sequence of facies* differing in composition. Closer to the shore, the ores are chiefly composed of such tetravalent-manganese compounds as *pyrolusite* and *psilomelanes*, accompanied by friable or compact opal and argillaceous matter. Farther from the coast, in deep sea zones, under conditions of oxygen deficiency, these ores give place to *manganite* ores in which some of the manganese is divalent (Mn^{2+}), often in association with glauconite (in the siliceous layers). Still farther from the coast, come solid carbonate ores composed of *rhodochrosite* and *manganocalcite* (i.e., minerals with divalent manganese only) associated with opal, marcasite, pyrite,

occasionally with barite, etc., which clearly points to reducing conditions of hydrogen-sulphide fermentation and decomposition of the organic remains with the liberation of CO_2. Such are the dependences governing the changes of facies in sedimentary manganese deposits at Chiatury, Polunochny, and elsewhere.

Phosphorite deposits in the form of concretions (cf. Fig. 43), nodules and oölites confined to the deeper parts of a shelf, occur in carbonate rocks or glauconitic sandstones. Calcium phosphates accumulations

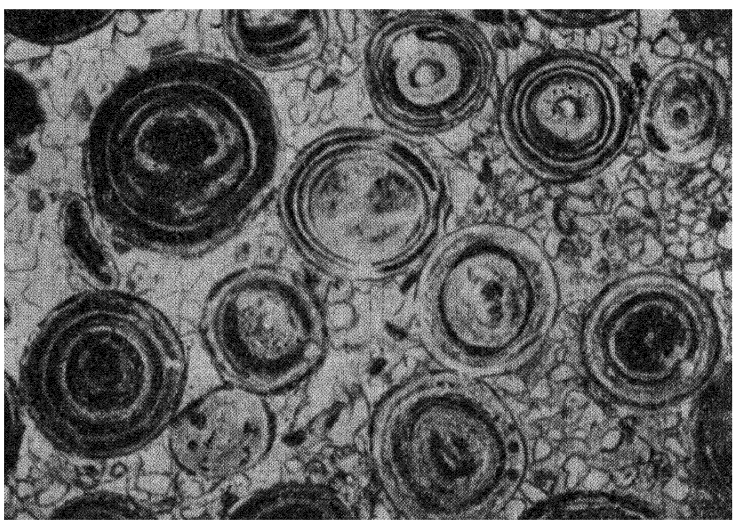


Fig. 388. Oölites of goethite-chlorite composition. Some contain quartz particles in the centre. The cementing mass is chlorite and siderite with abundant inclusions of rounded quartz fragments. Transparent polished section. ×46

often contain grains of quartz, *glauconite*, sometimes *pyrite*, and other minerals. According to the latest conceptions (V.A. Kazakov), the principal agent which causes phosphates of dead marine organisms to pass into solution is carbon dioxide, whose content in the water below the phytoplankton zone increases due to the oxidation of the dead organic matter. This is why sea water at a depth of 500 to 1500 m is enriched in CO_2 and phosphorus. When the CO_2- and P-enriched water is transported by the rising bottom currents to the shallow near-shore zone, some of the carbon dioxide passes into the phytoplankton zone. Consequently, the water becomes supersaturated with phosphorus, and this results in the precipitation of colloidal phosphates as phosphorite nodules.

Salt deposits forming as crystalline sediments in the conditions of hot arid climates in drying lakes or in partly isolated sea basins, chiefly contain chlorides, such as *halite*, less often *silvite*, *carnallite*, etc.; sulphates, such as *mirabilite*, *thenardite*, *astrakhanite*, *epsomite*, *kieserite*, *kainite*, *polyhalite*, *gypsum*, *anhydrite*, etc. Observations and physico-chemical studies of the sequence of strata carried out by Van

Hoff, Academician N. S. Kurnakov, and others show that the precipitation of salts from sea water occurs in a definite order: poorly soluble salts (carbonates and sulphates of Ca) are precipitated first, and well soluble salts (sulphates, and especially chlorides of Mg and K) last. However the order of precipitation also largely depends on the *concentration ratio* of salts in solution. Thus, certain highly concentrated salts may precipitate first in spite of their higher solubility.

In the ideal case the precipitation of salts from the sea water would proceed in this order: (1) gypsum, anhydrite; (2) halite associated with gypsum, anhydrite, and polyhalite; (3) kieserite with halite, kainite, polyhalite, etc.; (4) carnallite with halite, kieserite, etc.; (5) bishofite with carnallite, halite, and other well soluble salts.

It follows from the above that salts of potassium and magnesium are precipitated at the very last stages of the drying-up of salt basins. In nature, however, due to specific conditions the precipitation of crystalline salts does not always occur in a strict order. The observed alternations and repetitions in the deposition of sediments and the occasional absence of certain salt-bearing rocks from a geological column indicate changes that had occurred, for some reason or other, in the regimes of the given drying basin, in particular, in the concentration ratio of salts in solutions.

Salt-bearing deposits may also contain calcite, dolomite, and boric compounds (boracite). Occasionally borates form beds of their own containing *hydroboracite*, *colemanite*, *pandermite*, *boronatrocalcite*, *borax*, *ascharite* (as secondary formations), etc. An example is the Inder deposit. Lastly, soda lakes are also known. Large deposits of *native sulphur* (cf. Fig. 57) are sometimes confined to the salt-bearing series of gypsum and anhydrite, accompanied by bituminous dolomitised limestones and rock salt. Frequently associated with the native sulphur are calcite, aragonite, dolomite, gypsum, sometimes celestite, barite, opal, chalcedony, solid and liquid bitumens.

Furthermore, *gypsum* and *anhydrite* form very thick series of their own all over the world.

Sedimentary deposits also include such highly important industrial minerals as *caustobioliths*, i.e., coals, petroleum, and their associates: combustible gases and solid bitumens, and also peat sapropels. All of them are *biochemical* formations that have derived from plant and in part from animal life. Inorganic minerals occurring in coal measures, besides clastic material, include iron sulphides—*pyrite*, *marcasite*, and very rarely galena, sphalerite, and carbonates. Carbonaceous-argillaceous sediments often contain sheet-like accumulations of *sphero-siderite* concretions, occasionally with some sulphides which on weathering turn to brown iron ores.

Minerals of metamorphosed rocks and ore deposits. As stated earlier (p. 131), the so-called regional metamorphism strongly changes the composition, structure, and physical properties of endogenous, and especially of exogenous, rocks and ores. Depending on the physico-

chemical conditions of metamorphism—depth (pressure), temperature, and the composition of initial rocks and the metamorphosing postmagmatic solutions—there are formed crystalline schists of most diverse composition (Fig. 58): feldspar-rich gneisses, mica schists, amphibolites, talc and chlorite schists, as well as serpentinites, marbles, and other metamorphic rocks. Without listing all the associations in these numerous rocks we shall review only certain specific features of the metamorphic processes, with special reference to the typical minerals occurring besides the usual rock-forming constituents.

To begin with, it should be pointed out that the composition of metamorphic rocks deriving from sedimentary formations has some peculiar features. We have already said that most sedimentary rocks (clays, siliceous sediments, limestones, etc.) differ greatly in composition and that they derive from the differentiation of compounds liberated from endogenous rocks by weathering. Metamorphosis of clays and shales, almost entirely devoid of alkaline earths, gives rise to quite extraordinary rock-forming minerals, aluminium silicates: *disthene*, *sillimanite*, *andalusite*, *staurolite*, and *brittle micas*. Only when dissolved alkalis from external sources are brought in, the clays are altered to sericite and mica schists. Siliceous sediments are metamorphosed into dense quartz-chalcedony rocks (jaspers) or quartzites. D. S. Korzhinsky has demonstrated that upon metamorphism of essentially carbonate rocks at shallow depths, the Ca silicates (*wollastonite*, *grossularite*, and *diopside*) associated with calcite and dolomite may remain stable. At greater depths, however, wollastonite is less stable than the quartz-calcite association, and still deeper grossularite also becomes unstable, being decomposed by CO_2, the partial pressure of which increases with depth.

Salt-bearing sediments (chlorides and sulphates of K, Na, Mg) as well as gypsum, anhydrite, alunite, and other sulphates *completely disappear* in the conditions of deep regional metamorphism, as do the deposits of native sulphur and phosphorites. Evidently, the elements of these compounds migrate with postmagmatic solutions.

Sedimentary deposits of iron and manganese also undergo material alterations during metamorphism. The colloidal hydroxides, stable in an exogenous environment, are altered to anhydrous compounds; thus, limonite and goethite turn into *hematite* and *magnetite*; iron hydrosilicates into a *quartz-magnetite* mixture or anhydrous silicates; psilomelanes and manganite into *braunite* (Fig. 389) and *hausmannite*, and, in the presence of silica, into the Mn silicates: *rhodonite*, *tephroite*, *manganous garnets*, etc.

Many metamorphosed deposits usually retain the stratified structure of ores. Unilateral dynamic stress results in fine folding (Fig. 390). Many crystalline schists often contain new formations, such as *garnets* (almandite, pyrope, etc.) usually in well-formed rather large crystals, *cordierite*, various *pyroxenes* and *amphiboles*, *spinel*, *magnetite*, *rutile*, *graphite*, etc.

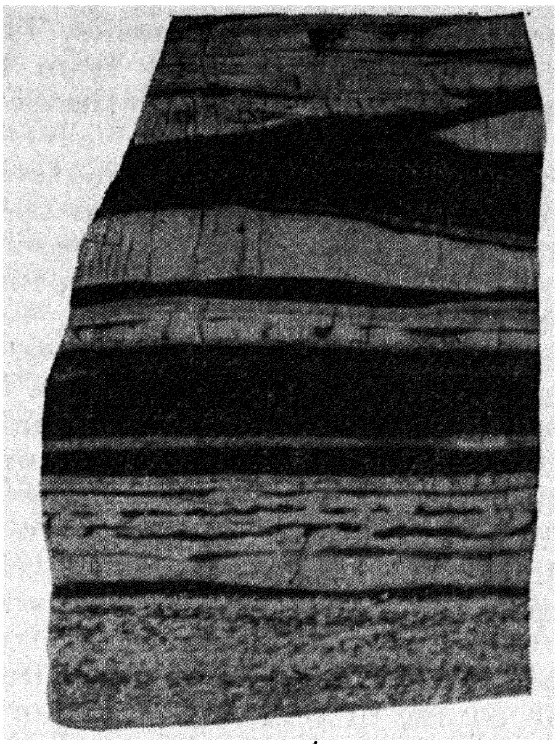


Fig. 389. Laminated braunite ore. Light bands—braunite. Black—carbonates impregnated with red iron oxide. Lowermost band—sandstone. Polished ore specimen. Photographed in reflected light.

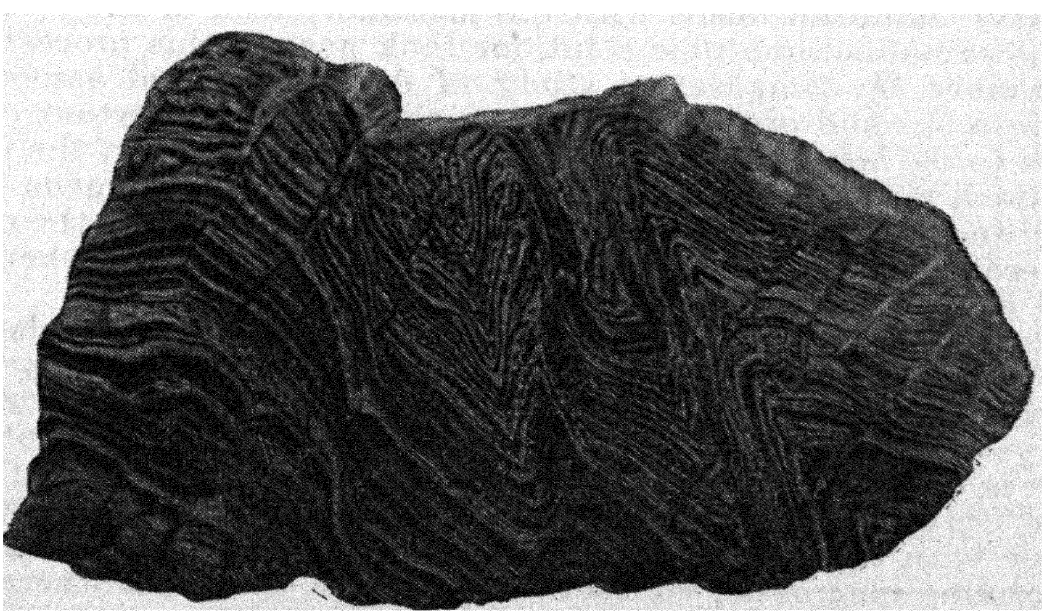


Fig. 390. Plicated hematite ore. Light bands—hematite; black—quartzite. Polished section. Photographed in reflected light.

Minerals of metamorphic economic deposits. This group as stated above (p. 133), includes minerals *deriving* from the metamorphism of rocks and other formations which prior to that were of no economic importance.

An example are deposits of *disthene*, a material for refractories. These deposits are composed of crystalline schists rich in this mineral and have derived from alumina-rich rocks. Associated with disthene in these deposits are *micas*, *andalusite*, *staurolite*, sometimes *corundum*, rutile, tourmaline, etc.

Of the same origin are some deposits of *garnet* (almandite), used as a material for abrasives, found in mica schists. In addition to mica (usually biotite) and garnet these schists usually contain *quartz*, *disthene*, staurolite, sometimes rutile, zircon, tourmaline, etc.

No less characteristic are the deposits of *graphite* deriving by metamorphosis from coals. Graphite in this case is a new mineral which is no longer combustible because of the complete loss of original properties. The vegetal imprints on its parting planes are sufficient proof that the graphite of these deposits has derived from coals.

The so-called Alpine clefts (cf. Fig. 60), confined to the ruptures that developed in the course of regional metamorphism, are of great mineralogical and economic interest. In swelled portions of these clefts, large druse cavities contain excellent *rock crystals* (cf. Fig. 41) possessing piezoelectric properties and also crystals of *chlorite*, *epidote*, *actinolite*, *adular*, *albite*, *brookite*, *rutile*, *anatase*, *sphene*, *calcite*, etc. A characteristic feature is that the minerals developing in these veins are the same that occur as rock-forming constituents in the enclosing metamorphic rocks. This shows that they had formed in the expanding cracks simultaneously with the metamorphism of the rocks and that the same metamorphic solutions took part in this process.

Summary. A comparative study of diverse mineral associations found in rocks and ores of different origin leads to important conclusions as to *the history of migration* of chemical elements in the earth's crust. Each stage in the development of geological phenomena has its own dependences determining the behaviour of elements in the process of mineral formation in strict conformity with the laws of chemistry, crystal chemistry, and physical chemistry.

Indeed, whereas at the early magmatic stage all chemical elements, both petrogenic and metallogenic, were rather uniformly distributed throughout the common mass, during the period of differentiation and crystallisation of the magma, particularly at great depth, the picture is quite different. The *metallogenic* elements (Pt, Cu, Fe, Au, Ag, Zn, Pb, Bi, etc.) have a pronounced tendency to concentrate and, together with the volatiles, to separate spatially from the petrogenic ones forming magmatic, contact-metasomatic, and hydrothermal *ore* deposits. The *petrogenic* elements, on the contrary, remain rather uniformly distributed during the formation of the igneous rocks, becoming only slightly enriched during magmatic differentiation. Only

the elements with small or very large ionic radii (as compared with common petrogenic elements) are capable of accumulating in appreciable amounts in pegmatites.

Quite the *opposite* phenomena occur during exogenous processes. These processes deriving their energy from the sun and occurring in a strongly oxidising environment have a destructive effect on the products of endogenous mineral formation and in the end give rise to enormously thick series of sedimentary rocks. In this process most* *metallogenic* elements are *dispersed* through the sedimentary rocks. True, initially at the very surface of the lithosphere we still observe concentration of certain metallogenic elements in the zones of oxidation and of secondary sulphide enrichment of deposits (Pb, Cu). However, their negligible importance in the total mass of exogenous formations and their subsequent inevitable dispersion in the process of sedimentation make them appear sporadic indeed. Contrary to this, the *petrogenic* elements (Na, K, Mg, Ca, Al, C, Cl, B, S, P, etc.) during exogenous processes manifest a strong tendency to accumulate with the formation of many nonmetallic economic minerals (limestones, gypsums, salt-bearing lacustrine deposits, bauxites, phosphorites, coals, petroleums, etc.).

In fact, regional metamorphism does not result in considerable concentration of chemical elements, and is confined mainly to transformation of the mineral products endogenous processes.

* With the exception of Fe and Mn which, in properties, occupy an intermediate position between the petrogenic and the metallogenic elements.

LIST OF THE MOST IMPORTANT MINERALS GROUPED ACCORDING TO PRINCIPAL METALS (ELEMENTS)

The list below includes groups of some minerals containing appreciable quantities of important economic metals (or compounds extracted in the course of ore processing, e.g., boric acid from borates). Moreover, the list includes some natural chemical compounds that are not important in their own right, as accessories to the principal minerals since they may be an additional source of the metal or the compound extracted in ore treatment.

The principal minerals of a given metal or a compound are printed in **bold type.**

Economic minerals that are used in their natural state, not as sources of metals, are marked with an asterisk(*).

In each group the minerals are arranged in classes of compounds according to the classification adopted in this book (from native elements to silicates).

ALUMINIUM

*Cryolite—Na_3AlF_6
*Corundum—Al_2O_3
*Spinel—$MgAl_2O_4$
Hydrargillite—$Al[OH]_3$
Boehmite—$AlOOH$
Diaspore—$HAlO_2$
*Alum—$KAl[SO_4]_2 \cdot 12H_2O$
Halotrichite—$FeAl_2[SO_4]_4 \cdot 22H_2O$
Alunite—$KAl_3[SO_4]_2[OH]_6$
*Topaz—$Al_2[SiO_4][F,OH]_2$
*Disthene—Al_2SiO_5
*Andalusite—Al_2SiO_5
*Sillimanite—Al_2SiO_5
*Dumortierite—$Al_8BSi_3O_{19}$ [OH]
*Garnets (aluminiferous)—$R_3Al_2[SiO_4]_3$
Cordierite—$Al_3(Mg,Fe)_2[AlSi_5O_{18}]$
*Palygorskite minerals: complex hydrosilicates of Mg and Al
*Pyrophyllite—$Al_2[Si_4O_{10}][OH]_2$
*Muscovite—$KAl_2[AlSi_3O_{10}][OH]_2$
Chloritoid—$Fe_2Al_2[Al_2Si_2O_{10}][OH]_4$
Margarite—$CaAl_2[Al_2Si_2O_{10}][OH]_2$
Amesite—$(Mg,Fe)_4Al_2[Al_2Si_2O_{10}][OH]$
*Kaolinite—$Al_4[Si_4O_{10}][OH]_8$
*Halloysite—$Al_4[Si_4O_{10}][OH]_8 \cdot 4H_2O$
*Beidellite—$Al_2[Si_4O_{10}][OH]_2 \cdot nH_2O$
Albite-anorthite—$Na[AlSi_3O_8]$-$Ca[Al_2Si_2O_8]$
*Orthoclase, microcline—$K[AlSi_3O_8]$
*Scapolite—$(Na,Ca)_4[(Si,Al)_4O_8]_3[Cl,SO_4,CO_3]$
Leucite—$K[AlSi_2O_6]$
Nepheline—$Na[AlSiO_4]$
*Zeolites: hydrous alumosilicates

BARIUM

Witherite—$BaCO_3$
Barytocalcite—$BaCa[CO_3]_2$
Barite—$BaSO_4$
Hyalophanes—$K[AlSi_3O_8]$—$Ba[Al_2Si_2O_8]$
Celsian—$Ba[Al_2Si_2O_8]$

BERYLLIUM

Bromellite—BeO
Chrysoberyl—$BeAl_2O_4$
Swedenborgite—$NaBe_4SbO_7$
Beryllonite—$NaBePO_4$
Herderite—$BeCaPO_4[F,OH]$
Hambergite—$Be_2BO_3[OH]$

Phenacite—Be_2SiO_4
Euclase—$Be_2Al_2Si_2O_8[OH]_2$
Eudidymite—$NaBeSi_3O_7[OH]$
Epididymite—$NaBeSi_3O_7[OH]$
Gadolinite—$Y_2FeBe_2Si_2O_{10}$
Bertrandite—$Be_4Si_2O_7[OH]_2$
Barylite—$Be_2BaSi_2O_7$
Beryl—$Be_3Al_2[Si_6O_{18}]$
Milarite—
$K(Be,Al)_3Ca_2[Si_{12}(O,OH)_{30}]$
Bavenite—$Ca_4BeAl_2Si_9O_{25}[OH]_2$
Trimerite—$(Ca,Mn)_2Be_3Si_3O_{12}$
Leucophanite—$CaNaBeSi_2O_6F$
Helvite—$(Mn,Fe)_4[BeSiO_4]_6S_2$
Danalite—$Fe_4[BeSiO_4]_6S_2$
Chkalovite—$Na_2BeSi_2O_6$
Karpinskyite—
$(Na,K)_2(Be,Zn,Mg)Al_2Si_6O_{16}[OH]_2$

BORON

Sassolite—$B[OH]_3$
Jeremeyevite—$AlBO_3$
Dioptase—$MgHBO_3$
Ludwigite—$(Mg,Fe)_2Fe[BO_3]O_2$
Boracite—$Mg_6B_{14}O_{26}Cl_2$
Borax—$Na_2B_4O_7\cdot 10H_2O$
Boronatrocalcite—$HaCaB_5O_9\cdot 8H_2O$
Inderite—$Mg_2B_6O_{11}\cdot 15H_2O$
Kurnakovite—$Mg_2B_6O_{11}\cdot 13H_2O$
Inderborite—$MgCaB_6O_{11}\cdot 11H_2O$
Hydroboracite—$MgCaB_6O_{11}\cdot 6H_2O$
Inyoite—$CaB_6O_{11}\cdot 13H_2O$
Collemanite—$Ca_2B_6O_{11}\cdot 5H_2O$
Pandermite—$Ca_4B_{10}O_{19}\cdot 7H_2O$
Datolite—$CaBSiO_4[OH]$
Danburite—$CaB_2[SiO_4]_2$
Axinite—$Ca_2(Mn,Fe)Al_2BSi_4O_{15}[OH]$
*Tourmaline—
$(Na,Ca)\ (Mg,Al)_6[B_3Al_3Si_6(O,OH)_{30}]$
Fluoborite—$Mg_5B_{10}O_{17}[OH]_6$
Warwickite—$(Mg,Fe)_3Ti[BO_4]_2$
Serendibite—
$(Ca,Mg)_5Al_4BSi_3O_{18}[OH]$
Calcioborite—$Ca_5B_8O_{17}$
Garrelsite—$H_6(Ba,Ca,Mg)SiO_2B_6O_{20}$
Ridmedjerite—$Na_2B_2Si_6O_{16}$

VANADIUM

Patronite—VS_2?
Sulvanite—Cu_3VS_4
Colusite—$Cu_3(As,Sn,V)S_4$
Coulsonite—$(Fe,V)_3O_4$
Titanomagnetite (vanadiferous)—
$(Fe,Ti)_3O_4$
Minasragrite—$V_2O_4\cdot SO_4\cdot 16H_2O$
Pucherite—$BiVO_4$
Vanadinite—$Pb_5[VO_4]_3Cl$
Descloizite—$(Zn,Cu)Pb[VO_4][OH]$
Cuprodescloizite—
$(Cu,Zn)Pb[VO_4][OH]$
Volborthite—$CuCa[VO_4][OH]$
Brackebuschite—
$Pb_2(Mn,Fe)[VO_4]_2\cdot H_2O$
Pyrobelonite—$MnPb[VO_4][OH]$
Turanite—$Cu_5[VO_4]_2[OH]_4$
Uzbekite—$Cu_3[VO_4]_2\cdot 3H_2O$
Carnotite—$K_2[UO_2]_2[VO_4]_2\cdot 3H_2O$
Fervanite—$Fe[VO_4]\cdot 2H_2O$
Rossite—$CaV_2O_6\cdot 4H_2O$
Metarossite—$CaV_2O_6\cdot 2H_2O$
Corvusite—$V''''V_6O_{17}\cdot nH_2O$
Roscoelite—$KV_2[AlSi_3O_{10}][OH]_2$
Navajoite—$V_2O_5\cdot H_2O$

BISMUTH

Native bismuth—Bi
Tellurobismuthite—Bi_2Te_3
Tetradymite—Bi_2Te_2S
Bismuthinite—Bi_2S_3
Guanajuatite—$Bi_2(Se,S)_3$
Galena (Bi-containing)—PbS
Matildite—$AgBiS_2$
Emplectite—$CuBiS_2$
Wittichenite—Cu_3BiS_3
Klaprothite—$Cu_6Bi_4S_9$
Alaskaite—$(Ag,Cu)_2PbBi_4S_8$?
Benjaminite—$(Cu,Ag)PbBi_2S_4$
Hammarite—$Cu_2Pb_2Bi_4S_9$?
Beegerite—$Pb_6Bi_2S_9$
Hoongarrite—$Pb_4Bi_2S_7$
Lillianite—$Pb_3Bi_2S_6$
Cosalite—$Pb_2Bi_2S_5$
Galenobismuthite—$PbBi_2S_4$
Pavonite—$AgBi_3S_5$
Schirmerite—$Ag_4PbBi_4S_9$
Aikinite—$CuPbBiS_3$
Lindströmite—$CuPbBi_3S_6$
Gladite—$CuPbBi_5S_9$
Rezbanyite—$Cu_2Pb_3Bi_{10}S_{19}$
Bismite—Bi_2O_3
Sillenite—Bi_2O_3
Russellite—$(Bi_2W)O_3$
Daubreelite—BiOCl
Bismutite—$Bi_2CO_3[OH]_4$
Pucherite—$BiVO_4$
Rooseveltite—$BiAsO_4$
Atelestite—$Bi_3[AsO_4][OH]_2O_2$
Eulytite—$Bi_4[SiO_4]_3$

TUNGSTEN

Tungstenite—WS_2
Tungstite (meymacite)—H_2WO_4

Hubnerite—$MnWO_4$
Wolframite—$(Mn,Fe)WO_4$
Ferberite—$FeWO_4$
Scheelite—$CaWO_4$
Stolzite—$PbWO_4$
Raspite—$PbWO_4$
Chillagite—$Pb(Mo,W)O_4$
Ferritungstite—$Fe_2[WO_4][OH]_4 \cdot 4H_2O$

GALLIUM

Gallite—$CuGaS_2$
Germanite—Cu_3GeS_4?

GERMANIUM

Germanite—Cu_3GeS_4?
Argyrodite—Ag_8GeS_6
Canfieldite—$Ag_8(Sn,Ge)S_6$

IRON

Pyrrhotite[1]—$Fe_{1-x}S$
Pyrite[1]—FeS_2
Marcasite—FeS_2
Löellingite[2]—$FeAs_2$
Arsenopyrite[2]—$FeAsS$
Hematite—Fe_2O_3
Maghemite—Fe_2O_3
Smithite—Fe_3S_4
Ilmenite—$FeTiO_3$
Magnetite—$FeFe_2O_4$
Magnomagnetite—$(Fe,Mg)Fe_2O_4$
Goethite—$HFeO_2$
Limonite—$HFeO_2 \cdot aq$
Lepidocrocite—$FeOOH$
Siderite—$FeCO_3$
Melanterite—$FeSO_4 \cdot 7H_2O$
Fibroferrite—$FeSO_4[OH] \cdot 4{,}5H_2O$
Coquimbite—$Fe_2[SO_4]_3 \cdot 9H_2O$
*Jarosite—$KFe_3[SO_4]_2[OH]_6$
Römerite—$FeFe_2[SO_4]_4 \cdot 14H_2O$
Craftonite—$(Fe,Mn)_3[PO_4]_2$
Vivianite—$Fe_3[PO_4]_2 \cdot 8H_2O$
Scorodite[2]—$FeAsO_4 \cdot 2H_2O$
Strengite—$FePO_4 \cdot 2H_2O$
Phosphosiderite—$FePO_4 \cdot 2H_2O$
Fayalite—$FeSiO_4$
*Almandite—$Fe_3Al_2[SiO_4]_3$
Andradite—$Ca_3Fe_2[SiO_4]_3$
Hypersthene—$(Mg,Fe)_2[Si_2O_6]$
Hedenbergite—$CaFe[Si_2O_6]$
Aegirine—$NaFe[Si_2O_6]$
Grunerite—$Fe_7[Si_4O_{11}]_2[OH]_2$
Lepidomelane—
$KFe_3[Si_3(Al,Fe)O_{10}][OH]_2$
Glauconite hydrosilicate—Chamosite—
$Fe_4Al[AlSi_3O_{10}][OH]_6 \cdot nH_2O$
Thuringite—
$Fe_{3,5}(Al,Fe)_{1,5}[Si_{2,5}Al_{1,5}O_{10}][OH]_6 \cdot \cdot nH_2O$
Ferrihalloysite—
$(Fe,Al)_4[Si_4O_{10}][OH]_8 \cdot 4H_2O$
Nontronite—
$(Fe,Al)_2[Si_4O_{10}][OH]_2 \cdot nH_2O$

GOLD

Native gold—Au
Electrum—(Au,Ag)
Aurostibite—$AuSb_2$
Petzite—$(Ag,Au)_2Te$
Calaverite—$AuTe_2$
Krennerite—$AuTe_2$
Sylvanite—$AuAgTe_4$
Nagyagite—$Pb_5Au(Te,Sb)_4S_{5-8}$?

YTTRIUM AND RARE EARTHS (CERIUM GROUP)

Cerianite—CeO_2
Fluocerite—$(La,Ce\ldots)F_3$
Yttrocerite—$(Ca,Y,Ce)F_{2-3}$
Yttrofluorite—$(Ca,Y)F_{2-3}$
Yttrocalcite—$(Ca,Y)F_{2-3}$
Knopite—$(Ca,Ce)(Ti,Fe)O_3$
Dysanalyte—$(Ca,Ce,Na)(Ti,Fe,Nb)O_3$
Loparite—$(Na,Ce,Ca\ldots)(Nb,Ti)O_3$
Pyrochlore—$(Na,Ca,Ce\ldots)_2Nb_2O_6F$
Fergusonite—
$(Y,Er,Ce\ldots)(Nb,Ta,Ti)O_4$
Formanite—$(Y,Er,Ca\ldots)(Ta,Nb)O_4$
Fersmite—
$(Ca,Ce)(Nb,Ti,Fe,Al)_2(O,OH,F)_6$
Euxenite—$(Y,Ce,Ca\ldots)(Nb,Ta,Ti)_2O_6$
Polycrase—
$(Y,Ce,Ca\ldots)(Ti,Nb,Ta)_2O_6$
Aeschynite—$(Ce,Ca,Th)(Ti,Nb)_2O_6$
Priorite—$(Y,Er,Ca,Th)(Ti,Nb)_2O_6$
Chlopinite—$(Y,U,Th)(Nb,Ti,Fe)_2O_6$?
Samarskite—$(Y,Er\ldots)_4(Nb,Ta)_6O_{21}$
Yttrotantalite—
$(Fe,Y,U\ldots)_4(Ta,Nb)_6O_{21}$?
Bastnäsite—$(Ce,La\ldots)[CO_3]F$
Synchysite—$Ca(Ce,La\ldots)[CO_3]_2F$
Parisite—$Ca(Ce,La\ldots)_2[CO_3]_3F_2$
Cordylite—$Ba(Ce,La\ldots)_2[CO_3]_3F$
Ambatoarinite—$Sr(Ce,La\ldots)_2[CO_3]_3O$
Ancylite—
$Sr_3(Ce,La\ldots)_4[CO_3]_7[OH]_4 \cdot 3H_2O$
Lanthanite—
$(La,Pr,Ce\ldots)_2[CO_3]_3 \cdot 8H_2O$
Tengerite—$Y_3Ca[CO_3]_4[OH]_3 \cdot 3H_2O$
Monazite—$(Ce,La\ldots)PO_4$

[1] Is used as raw material for sulphuric acid production.
[2] Is a source of arsenic.

Xenotime—YPO_4
Abukumalite—
$(Y,Ca,Th)_{10}[PO_4SiO_4AlO_4]_6[F,O]$
Britholite—
$(Ce,Ca,Na)_5[SiO_4,PO_4]_3[F,OH]$
Florencite—$CeAl_3[PO_4]_2[OH]_6$
Churchite—$(Ce,Ca)PO_4 \cdot 2H_2O$?
Weinschenkite—$(Y,Er)PO_4 \cdot 2H_2O$
Hagatalite—(zircon variety containing TR)
Yttrotitanite—$(Ca,Y,Ce)Ti[SiO_4]O$
Tornebomite—
$(Ce,La\ldots)_3[SiO_4]_2[OH]$
Lessingite—
$Ca(Ce,Y,La)_4[SiO_4]_3[OH,F]_4$
Rinkolite—
$(Ca,Na,Ce)_7Ti[SiO_4]_4[F,OH]_2$?
Thalenite—$Y_2Si_2O_7$
Thortveitite—$(Sc,Y)_2Si_2O_7$
Yttrialite—$(Y,Th)_2Si_2O_7$
Cerite—$(Ce,Y,Pr\ldots)_2Si_2O_7 \cdot H_2O$
Rowlandite—$(Y,Ce,La)_4Fe[Si_2O_7]_2F_2$
Cenosite—
$Ca_2(Ce,Y)_2Si_4O_{12}[CO_3] \cdot H_2O$
Orthite—
$(Ca,Ce)_2(Al,Fe)_3Si_3O_{12}[O,OH]$
Nagatelite—
$(Ca,Ce)_2(Al,Fe)_3(Si,P)_3O_{12}[O,OH]$
Magnesioorthite—
$(Ca,Ce)_2Mg_2AlSi_3O_{10}[O,F,OH]_3$

CADMIUM

Greenockite—CdS
Hauleite—CdS
Sphalerite(Cd-containing)—ZnS
Monteponite—CdO
Otavite—$CdCO_3$

POTASSIUM

Sylvite—KCl
Carnallite—$MgCl_2 \cdot KCl \cdot 6H_2O$
Potassium nitrate—KNO_3
Kalicinite—$KHCO_3$
Taylorite—$(K,NH_4)_2SO_4$
Langbeinite—$K_2Mg_2[SO_4]_3$
Schoenite (pycromerite)—
$K_2Mg[SO_4]_2 \cdot 6H_2O$
Leonite—$K_2Mg[SO_4]_2 \cdot 4H_2O$
Polyhalite—$K_2MgCa_2[SO_4]_4 \cdot 2H_2O$
Kainite—$KMg[SO_4]Cl \cdot 3H_2O$
Alunite—$KAl_3[SO_4]_2[OH]_6$
Potash alum—$KAl[SO_4]_2 \cdot 12H_2O$
Kaliborite—$KMg_2B_{11}O_{19} \cdot 7H_2O$
Micas (muscovite, phlogopite, biotite)
*Glauconite—potassium hydrosilicate
Apophyllite—$KCa_4[Si_4O_{10}]F \cdot 8H_2O$
Potassium feldspars (orthoclase microcline)
Hyalophanes
Leucite—$K[AlSi_2O_6]$
Phillipsite—
$(K_2,Ca)[Al_2Si_4O_{12}] \cdot 4,5H_2O$
Harmotome—$(K_2,Ba)[Al_2Si_5O_{14}] \cdot 5H_2O$

CALCIUM

Fluorite—CaF_2
*Perovskite group—$CaTiO_3$
Pyrochlore group—
$(Na,Ca)_2(Nb,Ti)_2O_6[F,OH]$
***Calcite**—$CaCO_3$
Aragonite—$CaCO_3$
*Dolomite—$CaMg[CO_3]_2$
Anhydrite—$CaSO_4$
*Gypsum—$CaSO_4 \cdot 2H_2O$
Belovite-arsenate—
$Ca_2(Ca,Mg)[AsO_4]_2 \cdot 2H_2O$
Scheelite—$CaWO_4$
Powellite—$CaMoO_4$
Apatite—$Ca_5[PO_4]_3[F,Cl]$
Colemanite—$Ca_2B_6O_{11} \cdot 5H_2O$
Inyoite—$Ca_2B_6O_{11} \cdot 13H_2O$
Hydroboracite—$CaMgB_6O_{11} \cdot 6H_2O$
Inderborite—$CaMgB_6O_{11} \cdot 11H_2O$
Larnite—Ca_2SiO_4
Garnet group
Vesuvianite—$Ca_3Al_2[SiO_4]_2[OH]_4$
Sphene—$CaTi[SiO_4]O$
Axinite—$Ca_2(Mn,Fe)Al_2BSi_4O_{15}[OH]$
Datolite—$CaB[SiO_4][OH]$
*Wollastonite—$CaSiO_3$
Pyroxene group
Amphibole group
Epidote group
Pumpellyite (lotrite)—
$Ca_2Al_3Si_3O_{11}[OH]_3$
Prehnite—$Ca_2Al_2Si_3O_{10}[OH]_2$
Margarite—$CaAl_2[Al_2Si_2O_{10}][OH]_2$
Plagioclases (basic)
Scapolite group
Zeolite group (Ca minerals)

COBALT

Linneite—Co_3S_4
Bornhardite—$CoSe_4$
Siegenite—$(CoNi)_3S_4$
Carrollite—$CuCo_2S_4$
Cattierite—CoS_2
Troughtalite—$CoSe_2$
Cobaltpyrite—$(Fe,Co)S_2$
Cobaltite—CoAsS
Glaucodote—(Co,Fe)AsS
Safflorite—$CoAs_2$

Skutterudite—$CoAs_3$
Smaltite—$CoAs_{3-2}$
Stainerite—$HCoO_2$
Asbolan—$m(Co,Ni)O \cdot MnO_2 \cdot nH_2O$
Spherocobaltite—$CoCO_3$
Cobaltsmithsonite—$(Zn,Mg,Co)CO_3$
Bieberite—$CoSO_4 \cdot 7H_2O$
Erythrite—$CO_3[AsO_4]_2 \cdot 8H_2O$
Forbesite—$(Ni,Co)HAsO_4 \cdot 4H_2O$

LITHIUM

Cryolithionite—$3NaF \cdot 3LiF \cdot 2AlF_3$
Triphylite—$Li(Fe,Mn)PO_4$
Lithiophilite—$Li(Mn,Fe)PO_4$
Amblygonite—$LiAlPO_4F$
Fremontite—$(Na,Li)AlPO_4[OH,F]$
Sicklerite—$Li_{<1}(Mn,Fe)PO_4$
Spodumene—$LiAl[Si_2O_6]$
Lepidolite—
$KLi_{1.5}Al_{1.5}[Si_4O_{10}][F,OH]_2$
Zinnwaldite—
$KLiFeAl[Si_3AlO_{10}][Fe,OH]_2$
Cookeite—$LiAl_5[Si_3AlO_{10}][OH]_8$
Petalite—$(Li,Na)AlSi_4O_{11}$
Eucryptite—$LiAlSiO_4$

MAGNESIUM

Sellaite—MgF_2
Carnallite—$KCl \cdot MgCl_2 \cdot 6H_2O$
Bishofite—$MgCl_2 \cdot 6H_2O$
Tachhydrite—$2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$
Periclase—MgO
Geikielite—$MgTiO_3$
*Spinel group—$MgAl_2O_4$
*Magnesioferrite—$MgFe_2O_4$
Brucite—$Mg[OH]_2$
Hydrotalcite—
$Mg_6Al_2[OH]_{10}[CO_3] \cdot 4H_2O$
Pyroaurite—$Mg_6Fe_2[OH]_{10}[CO]_3 \cdot 4H_2O$
***Magnesite**—$MgCO_3$
Dolomite—$MgCa[CO_3]_2$
Ankerite—$(Mg,Fe)Ca[CO_3]_2$
Artinite—$Mg_2[CO_3][OH]_2 \cdot 3H_2O$
Hydromagnesite—
$Mg_5[CO_3]_4[OH]_2 \cdot 4H_2O$
*Epsomite—$MgSO_4 \cdot 7H_2O$
Hexahydrite—$MgSO_4 \cdot 6H_2O$
*Kieserite—$MgSO_4 \cdot H_2O$
Wagnerite—Mg_2PO_4F
Bobierrite—$Mg_3[PO_4]_2 \cdot 8H_2O$
Hoernesite—$Mg_3[AsO_4]_2 \cdot 8H_2O$
Dioptase—$MgHBO_3$
Kotoite—$Mg_3[BO_3]_2$
Boracite—$5MgO \cdot MgCl_2 \cdot 7B_2O_3$
Fluoborite—$Mg_3[BO_3][F,OH]_3$
Ludwigite—$(Mg,Fe)_2Fe[BO_3]O_2$
Pinnoite—$Mg[BO_2]_2 \cdot 3H_2O$
Sulphoborite—
$4MgHBO_3 \cdot 2MgSO_4 \cdot 7H_2O$
Forsterite—Mg_2SiO_4
*Olivine—$(Mg,Fe)_2SiO_4$
Norbergite—$Mg_3[SiO_4][OH,F]_2$
Chondrodite—$Mg_5[SiO_4]_2[OH,F]_2$
Humite—$Mg_7[SiO_4]_3[OH,F]_2$
Clinohumite—$Mg_9[SiO_4]_4[OH,F]_2$
*Pyrope—$Mg_3Al_2[SiO_4]_3$
Enstatite—$MgSiO_3$
Anthophyllite—
$(Mg,Fe)_7[Si_4O_{11}]_2[OH]_2$
Cupfferite—$Mg_7[Si_4O_{11}]_2[OH]_2$
Cummingtonite—
$(Mg,Fe)_7[Si_4O_{11}]_2[OH]_2$
Tremolite—$Ca_2Mg_5[Si_4O_{11}]_2[OH]_2$
Actinolite—
$Ca_2(Mg,Fe)_5[Si_4O_{11}]_2[OH]_2$
Sepiolite—$Mg_3[Si_4O_{11}]H_2O \cdot nH_2O$
*Palygorskite-hydrosilicates of Mg and Al of complex composition
*Talc—$Mg_3[Si_4O_{10}][OH]_2$
Phlogopite—$KMg_3[AlSi_3O_{10}][F,OH]_2$
Biotite—$K(Mg,Fe)_3[AlSi_3O_{10}][F,OH]_2$
Pennine—$(Mg,Fe)_5Al[AlSi_3O_{10}][OH]_8$
Clinochlore—
$(Mg,Fe)_{4.75}Al_{1.25}[Al_{1.25}Si_{2.75}O_{10}][OH]_8$
*Vermiculite—
$(Mg,Fe)_3[(Si,Al)_4O_{10}][OH]_2 \cdot 4H_2O$
*Serpentine—$Mg_6[Si_4O_{10}][OH]_8$
Cerolite—$Mg_4[Si_4O_{10}][OH]_4 \cdot 4H_2O$
*Saponite—$Mg_3[Si_4O_{10}][OH]_2 \cdot nH_2O$

MANGANESE

Alabandite—MnS
Hauerite—MnS_2
Manganosite—MnO
Hausmannite—Mn_3O_4
Jacobsite—$MnFe_2O_4$
Braunite—Mn_2O_3
Bixbyite$(Mn,Fe)_2O_3$
Pyrolusite—MnO_2
Pyrochroite—$Mn[OH]_2$
Manganite—$Mn^{\cdot\cdot}Mn^{\cdot\cdot\cdot\cdot}O_2[OH]_2$
Vernadite—$MnO_2 \cdot nH_2O$
Psilomelane—$mMnO \cdot MnO_2 \cdot nH_2O$
Romanechite—$BaMnMn_8O_{16}[OH]_4$
Rancieite—$m(Mn,Ca)O \cdot MnO_2 \cdot nH_2O$
Cryptomelane—
$K_2O \cdot MnO \cdot 15MnO_2 \cdot nH_2O$
Coronadite—$PbMnMn_6O_{14}$
Hollandite—$BaMnMn_6O_{14}$
Crednerite—$CuMn_2O_4$
Rhodochrosite—$MnCO_3$
Manganocalcite—$(Mn,Ca)CO_3$
Mallardite—$MnSO_4 \cdot 7H_2O$
Szmikite—$MnSO_4 \cdot H_2O$

Hubnerite—$MnWO_4$
Purpurite—$(Mn,Fe)PO_4$
Laueite—$MnFe_2PO_4[OH]_2 \cdot 8H_2O$
Natrophylite—$NaMnPO_4$
Lithiophilite—$Li(Mn,Fe)PO_4$
Manganapatite—
$(Ca,Mn)_5[PO_4]_3[F,OH]$
Arsenoclasite—$Mn_5[AsO_4]_2[OH]_4$
Allactite—$Mn_7[AsO_4]_2[OH]_8$
Stewartite—$Mn_3[PO_4]_2 \cdot 4H_2O$
Reddingite—$(Mn,Fe)_3[PO_4]_2 \cdot 3H_2O$
Sussexite—$MnHBO_3$
Tephroite—Mn_2SiO_4
Spessartine—$Mn_3Al_2[SiO_4]_3$
*Rhodonite—$MnSiO_3$
Bustamite—$(Mn,Ca)SiO_3$
Pyroxmangite—$(Mn,Fe)SiO_3$
Piedmontite—$Ca_2(Al,Mn,Fe)_3Si_3O_{12}[OH]$
Coupletskite—$(K,Na)_2(Mn,Fe)_4TiSi_4O_{14}$

COPPER

Native copper—Cu
Domeykite—Cu_3As
Chalcosite—Cu_2S
Chalcopyrite—$CuFeS_2$
Bornite—Cu_5FeS_4
Covellite—CuS
Cubanite—$CuFe_2S_3$
Carrollite—$CuCo_2S_4$
Tennantite—Cu_3AsS_3
Tetrahedrite—Cu_3SbS_3
Enargite—Cu_3AsS_4
Famatinite—Cu_3SbS_4
Sulvanite—Cu_3VS_4
Chalcostibite—$CuSbS_2$
Emplectite—$CuBiS_2$
Klaprothite—$Cu_6Bi_4S_9$
Wittichenite—Cu_3BiS_3
Seligmannite—$CuPbAsS_3$
Bournonite—$CuPbSbS_3$
Aikinite—$CuPbBiS_3$
Atacamite—$CuCl_2 \cdot 3Cu[OH]_2$
Cuprite—Cu_2O
Tenorite—CuO
Delafossite—$CuFeO_2$
***Malachite**—$Cu_2[CO_3][OH]_2$
Azurite—$Cu_3[CO_3]_2[OH]_2$
Rosasite—$(Cu,Zn)_2[CO_3][OH]_2$
Pisanite—$(Fe,Cu)SO_4 \cdot 7H_2O$
Boothite—$CuSO_4 \cdot 7H_2O$
Chalcanthite—$CuSO_4 \cdot 5H_2O$
Dolerophanite—$Cu_2[SO_4]O$
Brochantite—$Cu_4[SO_4][OH]_6$
Langite—$Cu_4[SO_4][OH]_6 \cdot H_2O$
Vernadskite—$Cu_4[SO_4]_3[OH]_2 \cdot 4H_2O$
Cyanotrichite—
$Cu_4Al_2[SO_4][OH]_{12} \cdot 2H_2O$
Lindgrenite—$Cu_3[MoO_4]_2[OH]_2$
Libethenite—$Cu_2[PO_4][OH]$
Olivenite—$Cu_2[AsO_4][OH]$
Volborthite—$CuCa[VO_4][OH]$
Cuprodescloizite—
$(Cu,Zn)Pb[VO_4][OH]$
Dihydrite—$Cu_5[PO_4]_2[OH]_4$
Erinite—$Cu_5[AsO_4]_2[OH]_4$
Turanite—$Cu_5[VO_4]_2[OH]_4$
Pseudomalachite—$Cu_5[PO_4][OH]_3$
Clinoclasite—$Cu_3[AsO_4][OH]_3$
Uzbekite—$Cu_3[VO_4]_2 \cdot 3H_2O$
*Turquoise—$CuAl_6[PO_4]_4[OH]_8 \cdot 5H_2O$
Chalcosiderite—
$CuFe_6[PO_4]_4[OH]_8 \cdot 4H_2O$
Tagilite—$Cu_2[PO_4][OH] \cdot H_2O$
Ehlite—$Cu_5[PO_4]_2[OH]_4 \cdot H_2O$
Tyrolite—$Cu_9Ca_2[AsO_4]_4[OH]_{10} \cdot 10H_2O$
Chalcophyllite—
$Cu_4[AsO_4][OH]_5 \cdot 9H_2O$
Bandylite—$Cu[BO_2]Cl \cdot 2H_2O$
Dioptase—$Cu_6[Si_6O_{18}] \cdot 6H_2O$
Chrysocolla—$CuSiO_3 \cdot nH_2O$

MOLYBDENUM

Molybdenite—MoS_2
Ilsemanite—$Mo_3O_8 \cdot nH_2O$?
Powellite—$CaMoO_4$
Chillagite—$Pb(Mo,W)O_4$
Wulfenite—$PbMoO_4$
Ferrimolybdite—$Fe_2[MoO_4]_3 \cdot 7H_2O$

ARSENIC

Native arsenic—As
Allemontite—AsSb
Realgar—AsS
Auripigment—As_2S_3
Löllingite—$FeAs_2$
Arsenopyrite—FeAsS
Tennantite[1]—Cu_3AsS_3
Enargite[1]—Cu_3AsS_4
Arsenolite—As_2O_3
Claudetite—As_2O_3
Symplesite—$Fe_3[AsO_4]_2 \cdot 8H_2O$
Scorodite—$FeAsO_4 \cdot 2H_2O$
Pharmacosiderite—
$Fe_5[AsO_4]_3[OH]_6 \cdot 6H_2O$
Ferrisymplesite—
$Fe_3[AsO_4]_2[OH]_3 \cdot 6H_2O$

SODIUM

Halite—NaCl
Villiaumite—NaF

[1] Source of arsenic sublimate in copper-ore smelting.

Cryolite—Na_3AlF_6
Loparite—$(Na,Ce,Ca)(Nb,Ti)O_3$
Pyrochlore group
Sodium nitrate—$NaNO_3$
Soda—$Na_2CO_3 \cdot 10H_2O$
Trona—$NaH[CO_3]_2 \cdot 2H_2O$
Thenardite—Na_2SO_4
Mirabilite—$Na_2SO_4 \cdot 10H_2O$
Glauberite—$Na_2Ca[SO_4]_2$
Natrophylite—$NaMnPO_4$
Beryllonite—$NaBePO_4$
Borax—$Na_2B_4O_7 \cdot 10H_2O$
Boronatrocalcite—$NaCaB_5O_9 \cdot 8H_2O$
Elpidite—$Na_2ZrSi_6O_{15}[OH]_6$
Eudialyte—
$Na_4Ca_2ZrSi_6O_{17}[Cl,OH]_2$?
Catapleite—$Na_2ZrSi_3O_9 \cdot 2H_2O$
Jadeite—$NaAlSi_2O_6$
Aegirine—$NaFeSi_2O_6$
Arfvedsonite—
$Na_3(Fe,Mg)_4(Fe,Al)[Si_4O_{11}]_2[OH]_2$
Glaucophane—
$Na_2(Mg,Fe)_3Al_2[Si_4O_{11}]_2[OH]_2$
Riebeckite—
$Na_2Fe_3Fe_2[Si_4O_{11}]_2[O,OH]_2$
Albite and acidic plagioclases
Scapolite group
Analcite—$Na[AlSi_2O_6] \cdot H_2O$
*Nepheline—$NaAlSiO_4$
Sodalite—$Na_8[AlSiO_4]_6Cl_2$
Nosean—$Na_8[AlSiO_4]_6[SO_4]$
Hauyne—$Na_6Ca[AlSiO_4]_6[SO]_4$
*Lazurite—$Na_8[AlSiO_4]_6[SO_4]$?
Cancrinite—$Na_6Ca[AlSiO_4]_6[CO_3,SO_4]$
Natrolite—$Na_2[Al_2Si_3O_{10}] \cdot 2H_2O$
Desmine—$(Na_2,Ca)[Al_2Si_6O_{16}] \cdot 6H_2O$

NICKEL

Melonite—$NiTe_2$
Dinerite—Ni_3As
Maucherite—Ni_3As_2
Heazlewoodite—Ni_3S_2
Pentlandite—$(Fe,Ni)_9S_8$
Millerite—NiS
Polydymite—Ni_3S_4
Violarite—$FeNi_2S_4$
Vaesite—NiS_2
Bravoite—$(Ni,Fe)S_2$
Nicolite—$NiAs$
Breithauptite—$NiSb$
Chloanthite—$NiAs_{2-3}$
Rammelsbergite—$NiAs_2$
Gersdorffite—$NiAsS$
Ullmannite—$NiSbS$
Bunsenite—NiO
Trevorite—$NiFe_2O_4$
Zaratite—$Ni_3[OH]_4CO_3 \cdot 4H_2O$
Morenosite—$NiSO_4 \cdot 7H_2O$
Rötgersite—$NiSO_4 \cdot 6H_2O$
Forbesite—$(Ni,Co)HAsO_4 \cdot 4H_2O$
Annabergite—$Ni_3[AsO_4]_2 \cdot 8H_2O$
Cabrerite—$(Ni,Mg)[AsO_4]_2 \cdot 8H_2O$
Schuchardite—
$(Ni,Fe,Al)_6[(Si,Al)_4O_{10}][OH]_8$
Connarite—$(Ni,Fe)_6[(Si,Fe)_4O_{10}][OH]_8$
Rewdinskite—$(Ni,Mg)_6[Si_4O_{10}][OH]_8$
Garnierite—$Ni_4[Si_4O_{10}][OH]_4 \cdot 4H_2O$

NIOBIUM AND TANTALUM

Ilmenorutile—$(Ti,Nb,Fe)O_2$
Mossite—$Fe(Nb,Ta)_2O_6$
Tapiolite—$Fe(Ta,Nb)_2O_6$
Columbite—$(Fe,Mn)Nb_2O_6$
Tantalite—$(Fe,Mn)Ta_2O_6$
Loparite—$(Na,Ce,Ca)(Nb,Ti)O_3$
Pyrochlore—
$(Na,Ca\ldots)_2(Nb,Ti\ldots)_2O_6[F,OH]$
Microlite—
$(Na,Ca\ldots)_2(Ta,Ti\ldots)_2O_6[F,OH]$
Stibiocolumbite—$SbNbO_4$
Stibiotantalite—$SbTaO_4$
Thoreaulite—$SnTa_2O_7$
Other minerals of the fergusonite-euxenite-samarskite group

TIN

Stannopalladinite—Pd_3Sn_2
Herzenbergite—SnS
Teallite—$SnS \cdot PbS$
Stannite—Cu_2FeSnS_4
Colusite—$Cu_3(As,Sn,V)S_4$
Canfieldite—Ag_8SnS_6
Franckeite—$Pb_5Sn_3Sb_2S_{14}$
Cylindrite—$Pb_3Sn_4Sb_2S_{14}$
Cassiterite—SnO_2
Thoreaulite—$SnTa_2O_7$
Arandisite—$Sn_3[SiO_4]_2[OH]_2$
Stokesite—$CaSn[Si_3O_9] \cdot 2H_2O$
Nordenskiöldine—$CaSn[BO_3]_2$
Hulsite—
$12(Mg,Fe)O \cdot 2Fe_2O_3 \cdot SnO_2 \cdot 3B_2O_3 \cdot 2H_2O$?

PLATINOIDS

Platinum—Pt
Polyxene—(Pt,Fe)
Ferroplatinum—PtFe
Cuproplatinum—(Pt,Fe,Cu)
Nickelplatinum—(Pt,Fe,Ni,Cu)
Palladioplatinum—(Pt,Pd)
Palladium—Pd
Allopalladium—Pd

Potarite—(Pd,Hg)
Porpezite—(Au,Pd)
Stibiopalladinite—Pd_3Sb
Stannopalladinite—Pd_3Sn_2
Platiniridium—(Ir,Pt)
Osmirid—(Ir,Os)
***Nevyanskite**—(Ir,Os)
Syssertskite—(Os,Ir)
Cooperite—PtS
Bröggite—(Pt,Pd,Ni)S
Sperrylite—$PtAs_2$
Laurite—RuS_2
Palladinite—PdO

RARE EARTHS

(cf. Yttrium)

MERCURY

Native mercury—Hg
Cinnabar—HgS
Metacinnabarite—HgS
Tiemannite—HgSe
Coloradoite—HgTe
Livingstonite—$HgSb_4S_7$
Montroydite—HgO
Calomel—HgCl
Eglestonite—$3HgCl \cdot HgO$?
Terlinguaite—$HgCl \cdot HgO$

SELENIUM

Naumannite—Ag_2Se
Aguilarite—$Ag_2(Se,S)$
Berzelianite—Cu_2Se
Eucairite—$Cu_2Se \cdot Ag_2Se$
Galena (selenium)—Pb(S,Se)
Clausthalite—PbSe
Tiemannite—HgSe
Klockmannite—CuSe
Ferrosilite—$FeSe_2$
Kerstenite—$PbSeO_4$
Chalcomenite—$Cu[SeO_3] \cdot 2H_2O$

LEAD

Galena—PbS
Altaite—PbTe
Clausthalite—PbSe
Sartorite—$PbAs_2S_4$
Baumhauerite—$Pb_4As_6S_{13}$
Dufrenoysite—$Pb_2As_2S_5$
Jordanite—$Pb_{14}As_7S_{24}$
Gratonite—$Pb_9As_4S_{15}$
Zinckenite—$PbSb_2S_4$
Plagionite—$Pb_5Sb_8S_{17}$
Semseyite—$Pb_9Sb_8S_{21}$
Boulangerite—$PbSb_4S_{11}$
Jamesonite—$Pb_4FeSb_6S_{14}$
Meneghinite—$Pb_{13}Sb_7S_{23}$
Galenobismuthite—$PbBi_2S_4$
Platynite—$PbBi(Se,S)_3$
Wittite—$Pb_5Bi_6S_{14}$?
Cosalite—$Pb_2Bi_2S_5$
Lillianite—$Pb_3Bi_2S_6$
Hoongarrite—$Pb_4Bi_2S_7$
Beegerite—$Pb_6Bi_2S_9$
Cotunnite—$PbCl_2$
Mendipite—$PbCl_2 \cdot PbO$
Penfieldite—$3PbCl_2 \cdot Pb[OH]_2$
Massicot—PbO
Minium—Pb_3O_4
Plumboferrite—$PbFe_4O_7$
Quenselite—$Pb_2Mn_2O_5 \cdot H_2O$
Cerussite—$PbCO_3$
Hydrocerussite—$Pb_3[CO_3]_2[OH]_2$
Phosgenite—$Pb_2[CO_3]Cl_2$
Ledhillite—$Pb_4[CO_3]_2[SO_4][OH]_2$
Anglesite—$PbSO_4$
Kerstenite—$PbSeO_4$
Crocoite—$PbCrO_4$
Wulfenite—$PbMoO_4$
Chillagite—$Pb(Mo,W)O_4$
Stolzite—$PbWO_4$
Pyromorphite—$Pb_5[PO_4]_3Cl$
Mimetesite—$Pb_5[AsO_4]_3Cl$
Vanadinite—$Pb_5[VO_4]_3Cl$
Descloisite—$Pb(Zn,Cu)[VO_4][OH]$
Corkite—$PbFe_3[PO_4][SO_4][OH]_6$
Beudantite—$PbFe_3[AsO_4][SO_4][OH]_6$
Larsenite—$PbZnSiO_4$
Barysilite—$Pb_3Si_2O_7$
Alamosite—$PbSiO_3$
Kentrolite—$Pb_3Mn_4Si_2O_{15}$
Melanotekite—$Pb_3Fe_4Si_3O_{15}$

SILVER

Native silver—Ag
Silver amalgam—Hg_3Ag_2
Dyscrasite—Ag_3Sb
Argentite (acanthite)—Ag_2S
Stromeyerite—$Cu_2S \cdot Ag_2S$
Jalpaite—$3Ag_2S \cdot Cu_2S$
Aguilarite—$Ag_2(Se,S)$
Naumannite—Ag_2Se
Sternbergite—$AgFe_2S_3$
Hessite—Ag_2Te
Petzite—$(Ag,Au)_2Te$
Polybasite—$(Ag,Cu)_{16}Sb_2S_{11}$
Pearceite—$(Ag,Cu)_{16}As_2S_{11}$
Polyargyrite—$Ag_{24}Sb_2S_{15}$
Stephanite—Ag_5SbS_4
Pyrargyrite—Ag_3SbS_3

Proustite—Ag_3AsS_3
Pyrostilpnite—Ag_3SbS_3
Miargyrite—$AgSbS_2$
Smithite—$AgAsS_2$
Trechmanite—$AgAsS_2$
Argyrodite—Ag_8GeS_6
Canfieldite—Ag_8SnS_6
Matildite—$AgBiS_2$
Schirmerite—$Ag_4PbBi_4S_9$
Alaskaite—$(Ag,Cu)_2PbBi_4S_8$?
Cerargyrite—AgCl
Embolite—Ag(Cl,Br)
Bromyrite—AgBr
Iodobromite—Ag(Cl,Br,I)
Miersite—4AgI·CuI
Iodyrite—AgI
Argentojarosite—$AgFe_3[SO_4]_2[OH]_6$

STRONTIUM

Strontianite—$SrCO_3$
Ambatoarinite—$Sr(Ce,La...)_2[CO_3]O$
Ancylite—
—$Sr_3(Ce,La...)_4[CO_3]_7[OH]_4\,3H_2$
Celestite—$SrSO_4$
Strontioapatite—$(Ca,Sr)_5[PO_4]_3[F,OH]$
Goyazite—$SrAl_3[PO_4][HPO_4][OH]_6$
Svanbergite—$SrAl_6[PO_4][SO_4][OH]_6$
Lamprophyllite—$Na_2Sr,FeTi_2[SiO_4]_3F$?
Brewsterite—$(Sr,Ba,Ca)[AlSi_3O_8]_2\cdot 5H_2O$

ANTIMONY

Native antimony—Sb
Allemontite—AsSb
Antimonite—Sb_2S_3
Ullmannite—NiSbS
Gudmundite—FeSbS
Tetrahedrite—Cu_3SbS_3
Famatinite—Cu_3SbS_4
Boulangerite—$Pb_5Sb_4S_{11}$
Other sulphoantimonites
Kermesite—Sb_2S_2O
Senarmontite—Sb_2O_3
Valentinite—Sb_2O_3
Servantite—Sb_2O_4 ?
Stibiconite—$Sb_3O_6[OH]$
Schneebergite—
$(Ca,Na,Fe)_2Sb_2O_6[F, OH, O]$
Stibiocolumbite—$SbNbO_4$
Stibiotantalite—$SbTaO_4$

THALLIUM

Vrbaite—$Tl(As,Sb)_3S_5$
Lorandite—$TlAsS_2$
Hutchinsonite—
$(Cu,Ag,Tl)_2S\cdot PbS\cdot 2As_2S_3$?
Marcasite—FeS_2

TANTALUM

(cf. Niobium)

TELLURIUM

Native tellurium—Te
Selen-tellurium—(Te,Se)
Tellurobismuthite—Bi_2Te_3
Tetradymite—$BiTe_2S$
Hessite—Ag_2Te
Petzite—$(Ag,Au)_2Te$
Altaite—PbTe
Coloradoite—HgTe
Krennerite—$AuTe_2$
Calaverite—$AuTe_2$
Sylvanite—$(Ag,Au)Te_2$
Melonite—$NiTe_2$
Niggliite—$PtTe_2$?
Montanite—$Bi_2TeO_4[OH]_4$
Teineite—$Cu[(Te,S)O_4]\cdot 2H_2O$
Durdenite (emmonsite)—
$Fe_2[TeO_3]_3 4H_2O$

TITANIUM

Ilmenite—$FeTiO_3$
Geikielite—$MgTiO_3$
Pyrophanite—$MnTiO_3$
Rutile—TiO_2
Brookite—TiO_2
Anatase—TiO_2
Perovskite—$CaTiO_3$
Ti-containing minerals of perovskite, pyrochlore, and fergusonite-euxenite-samarskite
Schorlomite—
$Ca_3(Al,Fe,Ti)_2[(Si,Ti)O_4]_3$
Sphene—$CaTiSiO_5$
Murmanite—$NaTi_2[SiO_4]_2[OH]\cdot H_2O$?
Fersmanite—
$(Ca,Na)_2(Ti,Nb)[SiO_4][OH,F]_3$?
Benitoite—$BaTiSi_3O_9$
Ramsayite—$Na_2Ti_2Si_2O_9$
Vinogradovite—
$Na_5Ti_4AlSi_6O_{24}\cdot 3H_2O$

THORIUM

Thorianite—ThO_2
Monazite (thorium-bearing)—
$(Ce,La,Th)[PO_4,SiO_4]$

Thorite—$ThSiO_4$
Ferrithorite—$(Th,Fe)SiO_4$
Yttrialite—$(Y,Th)_2Si_2O_7$
Thorium may also be isomorphously admixed to such multiple oxides (titano-tantalo-niobates) of the perovskite, pyrochlore, fergusonite-samarskite-euxenite groups

URANIUM

Uraninite—UO_2
Bröggerite—$(U,Th)O_2$
Janthinite—$2UO_2 \cdot 7H_2O$
Clarkeite—$UO_3 \cdot nH_2O$
Becquerelite(Schoepite)—$2UO_3 \cdot 3H_2O$?
Schoepite—$4UO_3 \cdot 9H_2O$
Fourmarierite—$PbO \cdot 4UO_3 \cdot 5H_2O$
Curite—$2PbO \cdot 5UO_3 \cdot 4H_2O$
Uranosphcrite—$Bi_2O_3 \cdot 2UO_3 \cdot 3H_2O$
Vandenbrandeite—$CuO \cdot UO_3 \cdot 2H_2O$?
Rutherfordine—$[UO_2]CO_3$
Sharpite—$[UO_2]_3[CO_3]_5[OH]_2 \cdot 7H_2O$
Uranothallite—$Ca_2[UO_2][CO_3]_3 \cdot 10H_2O$
Voglite—$Ca_2Cu[UO_2][CO_3]_4 \cdot 6H_2O$
Schroeckingerite—$NaCa_3[UO_2][CO_3]_3[SO_4] \cdot [OH] \cdot 9H_2O$
Zippeite$[UO_2]_2[SO_4][OH]_2 \cdot 3\text{-}5H_2O$
Uranopilite—$[UO_2]_6[SO_4][OH]_{10} \cdot 12H_2O$
Johannite—$Cu[UO_2]_2[SO_4]_2[OH]_2 \cdot 6H_2O$
Trögerite—$[UO_2]_3[AsO_4]_2 \cdot 12H_2O$
Torbernite—$Cu[UO_2]_2[PO_4]_2 \cdot 12H_2O$
Zeunerite—$Cu[UO_2]_2[AsO_4]_2 \cdot 12H_2O$
Uranospathite—$Ca[UO_2]_2[PO_4]_2 \cdot 12H_2O$
Metatorbernite—$Cu[UO_2]_2[PO_4]_2 \cdot 8H_2O$
Metazeunerite—$Cu[UO_2]_2[AsO_4]_2 \cdot 8H_2O$
α-Uranospinite $Ca[UO_2]_2[AsO_4]_2 \cdot 8H_2O$
β-Uranospinite $Ca[UO_2]_2[AsO_4]_2 \cdot 8H_2O$
Fritzscheite—$Mn[UO_2]_2[PO_4,VO_4]_2 \cdot 8H_2O$
Bassetite—$Fe[UO_2]_2[PO_4]_2 \cdot 8H_2O$
Autunite—$Ca[UO_2]_2[PO_4]_2 \cdot 8H_2O$
Saleite—$Mg[UO_2]_2[PO_4]_2 \cdot 8H_2O$
Uranocircite—$Ba[UO_2]_2[PO_4]_2 \cdot 8H_2O$
Tuyamunite—$Ca[UO_2]_2[VO_4]_2 \cdot 8H_2O$
Phosphuranylite—$[UO_2]_3[PO_4]_2 \cdot 6H_2O$
Ferganite—$[UO_2]_3[VO_4]_2 \cdot 6H_2O$
Carnotite—$K_2[UO_2]_2[VO_4]_2 \cdot 3H_2O$
Sengierite—$Cu_2[UO_2]_2[VO_4]_2[OH]_2 \cdot 9H_2O$
Renardite—$Pb[UO_2]_4[PO_4]_2O_2 \cdot 9H_2O$
Dewindtite—$Pb_3[UO_2]_5[PO_4]_4O_2 \cdot 12H_2O$
Dumontite—$Pb_2[UO_2]_3[PO_4]_2O_2 \cdot 5H_2O$
Parsonsite—$Pb_2[UO_2][PO_4]_2 \cdot H_2O$
Rauvite—$CaO \cdot 2UO_3 \cdot 6V_2O_5 \cdot 20H_2O$
Uvanite—$2UO_3 \cdot 3V_2O_5 \cdot 15H_2O$
Walpurgite—$Bi_{10}[UO_2]_3[AsO_4]_4O_{10} \cdot 10H_2O$
Uranothorite—$(Th,U)SiO_4$
Sklodowskite—$MgU_2[SiO_4]_2[OH]_6 \cdot 4H_2C$
Uranotil—$CaU_2[SiO_4]_2[OH]_6 \cdot 3H_2O$?
Cuprosklodowskite—$CuU_2[SiO_4]_2[OH]_6 \cdot 3H_2O$
Kasolite—$Pb[UO_2][SiO_4] \cdot H_2O$
Soddyite—$[UO_2]_2[SiO_4] \cdot 2H_2O$?
Urhyte—$UO_3 \cdot nH_2O$
Coffinite—$U[SiO_4]_{1-x}[OH]_{4x}$
Umohoite—$UO_2[MoO_4] \cdot 4H_2O$
Moluranite—$UO_2 \cdot 2UO_3 \cdot 5MoO_3 \cdot 12H_2O$?
Iriginite—$UO_3 \cdot 2MoO_3 \cdot 4H_2O$
Brannerite—$(U,Ca,Fe,Y,Th)_3Ti_5O_{16}$?
Nenadkevite—$(U,Y,Ce,Th)U(Ca,Mg,Pb)SiO_4[OH]_4$?

CHROMIUM

Chromespinellids—$(Mg,Fe)(Cr,Al,Fe)_2O_4$
Stichtite—$Mg_6Cr_2[OH]_{16}[CO_3] \cdot 4H_2O$
Crocoite—$PbCrO_4$
Phoenicochroite—$Pb_3[CrO_4]_2O$
Vauquelinite (Laxmanite)—$Pb_2Cu[CrO_4][PO_4]$
Uvarovite—$Ca_3Cr_2[SiO_4]_3$
Kaemmererite—$(Mg,Fe)_5(Al,Cr)[AlS_3O_{10}][OH]_8$
Kotschubeite—chromoniferous clinochlore
Volkonskoite—$(Cr,Fe,Al)_4[Si_4O_{10}][OH]_8 \cdot 2H_2O$

CESIUM

Rhodizite—$KNaLi_4Al_4Be_3B_{10}O_{27}$
Vorobyevite—$Cs(Be_2Li)Al_2[Si_6O_{18}]$
Pollucite—$Cs[AlSi_2O_6]$

ZINC

Sphalerite—ZnS
Wurtzite—ZnS
Stileite—ZnSe
Zincite—ZnO
Ghanite—$ZnAl_2O_4$
Franklinite—$(Zn,Mn)Fe_2O_4$
Heterolith—$ZnMn_2O_4$
Chalcophanite—$(Mn,Zn)Mn_2O_5 \cdot 2H_2O$
Smithsonite—$ZnCO_3$
Monheimite—$(Zn,Fe)CO_3$
Hydrozincite—$Zn_5[CO_3]_2[OH]_6$
Goslarite—$ZnSO_4 \cdot 7H_2O$

Zincchalcanthite—$(Zn,Cu)SO_4 \cdot 5H_2O$
Zincaluminite—
$Zn_3Al_2[SO_4][OH]_{13} \cdot H_2O$
Adamine—$Zn_2[AsO_4][OH]$
Tarbuttite—$Zn_2[PO_4][OH]$
Descloisite—$(Zn,Cu)Pb[VO_4][OH]$
Köttegite—$Zn_3[AsO_4]_2 \cdot 8H_2O$
Legrandite—$Zn_3[AsO_4]_2 \cdot 3H_2O$
Hopeite—$Zn_3[PO_4]_2 \cdot 4H_2O$
Parahopeite—$Zn_3[PO_4]_2 \cdot 4H_2O$
Willemite—Zn_2SiO_4
Hodkinsonite—$Zn_2Mn[SiO_4][OH]_2$
Calamine—$Zn_4Si_2O_7[OH]_2 \cdot H_2O$
Clinohedrite—$Zn_2Ca_2Si_2O_7[OH]_2 \cdot H_2O$
Hardystonite—$Ca_2ZnSi_2O_7$
Sauconite—$Zn_3[Si_4O_{10}][OH]_2 \cdot nH_2O$

ZIRCONIUM

Baddeleyite—ZrO_2
Zircon—$ZrSiO_4$
Zirkelite—$(Ca,Fe,Th)_2[Ti,Zr]_2O_5$
Guarinite—$Ca_2NaZr[SiO_4]_2F$
Eudialyte—$Na_4Ca_2ZrSi_6O_{17}(O,OH,Cl)$?
Elpidite—$Na_2ZrSi_6O_{12}[OH]_6$
Catapleite—$Na_2Zr[Si_3O_9] \cdot 2H_2O$
Zircon as an isomorphous admixture may enter into the composition of other complex silicates occurring in alkali-rich igneous rocks and also of multiple oxides of the pyrochlore and fergusonite-euxenite-samarskite groups.

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TO THE READER

Peace Publishers would be grateful for your comments on the content, translation and design of this book. We would also be pleased to receive any other suggestions you may wish to make. Our address is: 2, Pervy Rizhsky Pereulok, Moscow, U.SS.R.

Printed in the Union of Soviet Socialist Republics