

# Mineralogy



A.V. Milovsky and O.V. Kononov

Mir Publishers Moscow

The first part of the book contains a traditional crystallochemical classification of minerals, the description of their composition, structure, and morphology. The characterization of their physical properties is presented together with the analysis of their nature, methods of research, and the practical importance of geological exploration. Part two is devoted to the principles of classification and systematic description of minerals. In the third part there is a general outline of the genesis of minerals and natural mineral associations.

The textbook has been specially prepared for university students doing mineralogy or other geological sciences.




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# Mineralogy

А. В. Миловский,  
О. В. Кононов

## Минералогия

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# Mineralogy

A. V. Milovsky and O. V. Kononov

Translated from the Russian by G. G. Egorov



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# Preface

The present textbook has been prepared in compliance with the course in mineralogy set by the university curriculum. The first part contains a traditional crystallochemical characterization of minerals. Information on the types of crystalline structure and structural motifs of minerals has been supplemented by a discussion of polymorphic modifications and polytypes. A special section dealing with structural imperfections (defects) has also been introduced. Phenomena pertaining to isomorphism, resolution of solid solutions have received due prominence together with the role of water in the composition of minerals. The graphical representation of the chemical composition of minerals and the calculation of crystallochemical formulae have been illustrated. The description of physical properties is discussed in terms of their nature, the methods of their analysis and the importance for diagnostic purposes, in prospecting, the enrichment of ores, technology, etc.

Information on the origin of minerals, which is usually given in the introduction where general items are discussed, has been included into the third part of the textbook, and is treated together with natural associations of minerals. The authors have found such resetting of the material relevant in order that reiterations could possibly be avoided. It has also been taken into account that university students when doing their course in physical geology become familiar with the concepts of the origin of minerals and geological processes essential to a systematic study of minerals. Additional material

can always be found in the third part of the textbook.

The second part comprises a systematic description of minerals, which is preceded, as is usual, by an interpretation of principles of classification and the order in which the material is presented when classes, subclasses, and separate minerals are characterized. The classes of minerals are discussed in conjunction with their chemical composition, bonds, structure and physical properties, their origin, practical use, and interclass systematization. The authors have found it useful to supplement the general description of classes by an increased list of minerals which includes their formulae and systems. The number of minerals entering into the list exceeds that which is actually described in the book. However, they are mentioned in the third part where mineral associations are given a special treatment. As compared with the curriculum, the list of minerals given in the textbook has been extended and includes some of those that are either genetically interesting or have a practical value. The description of minerals includes information concerning their chemical composition, structure, system, morphology, external, including diagnostic, physical features and properties. Varieties and origin have also been characterized, together with deposits and the practical application of minerals.

The third part of the book includes general information on the genesis of minerals, natural mineral associations, generations and mineral typomorphism. A classification of geological processes of mineral formation is

presented here, in accordance with which various types of processes and natural mineral associations are discussed. When compiling the manual, the authors made every possible effort to bring it into conformity with the courses in 'General Chemistry', 'Physics', 'Physical Geology', and 'Crystallography', which, as far as university syllabus is concerned, precede the course in 'Mineralogy'. This has enabled the authors to avoid the reiteration of the already familiar material, particularly when crystallochemical, morphological characteristic features, physical properties, and the origin of minerals were described.

The work on the textbook has called for a substantial generalization of various scientific, academic, and bibliographic materials on mineralogy and the subjects adjacent to it. The said materials were made use of either in their original or edited form. The textbook contains, in particular, certain tables, representations of crystals, crystalline

structures of minerals and some other materials that have been borrowed from the works of N.V. Belov (1947, 1976), A.G. Betekhtin (1951), W.H. Bragg and G.F. Clarinbull (1967), A.A. Godovikov (1972, 1975), D.P. Grigoriev (1961), I. Kostov (1965, 1971), E.K. Lazarenko (1971), A.S. Marfunin (1974), A.V. Milovsky (1979), A.S. Povarennykh (1966), I.I. Shafranovsky (1978), et al.

The introduction and the first (general) part of the textbook have been mainly prepared by O.V. Kononov, the text of the second (descriptive) part is compiled by both A.V. Milovsky and O.V. Kononov. The author of the third part is A.V. Milovsky himself.

The authors wish to express their acknowledgements to Prof. G.A. Krutov for his help and criticism, and to Prof. G.P. Barsanov, who made most valuable suggestions when the manuscript was in preparation.

*A. Milovsky  
O. Kononov*

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## Introduction

# Concepts of Minerals and Their Development

## The History of Mineralogy

The first concepts of minerals were formed in ancient times. Having emerged with the advent of man, these concepts have had a long history and formed the basis of mineralogy—the scientific study of minerals.

The knowledge of the mineral world began with the use of stones that were picked up from the ground and directly employed as the most primitive tools of labour and arms. As early as those remote times Man was able to differentiate stones and select those that were more appropriate in form, mass and strength. Later, with the transition to more improved forms of processing, stones acquired even greater importance since their implementation for practical purposes had undergone substantial changes. Different properties of stones were made better use of, and the knowledge of how to discover and extract them had been gained. Articles made of silicon, obsidian, chalcedony, as well as nephrite were of particularly high quality. Besides axes and hammers, people learned to use stone to produce the more refined tips for their spears, darts, arrows, knives, scrapers and other labour tools. For the manufacture of pottery clay had to be extracted. Since ancient times stones, bright in colour and design, had been used extensively as ornaments and amulets. Mineral paints were used for rock and cave drawings, and ritual and everyday cosmetics. Some stones were used in food and for medicinal purposes. According to the data provided by the archeological finds, by the end of the prehistoric period people made practical use of approximately fifty types of rock and minerals such as: sandstone, quartzite, basalt, obsidian, silicon, chalcedony, quartz, nephrite, clay and sand, mineral pigments (iron ochre, colour clay) and rock salt.

With the emergence of ancient cities and states the malleability of metals, the mining and the processing of the ores of gold, silver, copper, tin, lead, mercury, iron, as well as precious stones become highly significant. Copper, and later, bronze (the alloy of copper and lead), and iron were used for the manufacture of arms, labour and domestic tools. Silver, gold and precious stones were employed as symbols of power, for ornamental purposes and were widely used in the trade. Since ancient times stones and clay have served as the most important building materials and when edifices were erected, it was

customary to use stone that could be easily handled, such as: limestone and sandstone; while for columns and for exterior and interior decorations, for sculptors, stones of higher ornamental quality were used. They include marble, granite, porphyry, basalt, quartzite among others. Baked clay and lead were used for the manufacture of water pipes.

For centuries and millennia a substantial knowledge of how stone and metals could be used for practical purposes, as well as the understanding of the mineral world as such, has been accumulated. This is brought to light by the remains of ancient cultures, ancient mines, the fragments of ancient Egyptian papyri and other written sources. In the Chinese chronicles (20-5 centuries B.C.), and the Indian epos (11-10 centuries B.C.), as well as in the works of the ancient writers that have reached us, we have the first generalizations concerning this kind of knowledge and copious information on stones, reflecting the state of the art that had been attained by that time, together with their concepts and systematization of minerals, as well as the properties, structure, origin and use of stones.

The ancient Greek philosopher Aristotle (384-322 B.C.) explained the formation of metals by their being sublimated in a gaseous state from the earth's interior, while his pupil Theophrastus gave the first description of approximately fifty minerals. In the books of the Roman natural scientist Pliny the Elder (23-79 A.D.) there are more detailed descriptions of stones, which he brought into his system in accordance with their practical uses.

In the early part of the Middle ages mining had acquired a particularly prominent stage in its development in the countries of the East, as well as in Central America, Western and Eastern Europe, where traces of ancient mining works, smelters and forging shops have remained up to the present day. It was the time when on the territory of Central Asia there was intensive mining of copper, mercury, lead, silver, tin, iron, precious stones, ceramic clay and mineral paints. The knowledge of minerals, accumulated empirically, was generalized in the works of the outstanding scientists of the Arabic East and medieval Central Asia. Minerals were regarded by them as natural substances characterized not only by physical but by chemical properties as well. And though the term 'minerals' had not yet come into general use, the concept of minerals becomes more and more concrete.

The outstanding scientist of the Middle Ages Ibn Sina (Avicenna) (980-1057) gives the following classification of minerals: (1) stones and soils, (2) metals (melting substances), (3) sulphuric (combustible) fossils, and (4) salts (soluble substances).

In the period of the early feudalism in Europe the development of mining gains considerable ground. As early as in the sixth-eighth centuries the mining of copper, lead and silver ores takes place in the regions that are in modern Czechoslovakia and Moravia. Mining becomes widely spread throughout the whole of Europe. Gold is mined in Hungary, copper and silver in Saxony, salt in Poland, and mercury on what is now known as the territory of Jugoslavia. In Russia, at that time, iron ores were prospected in the regions of Tula and Serpukhov, mica was mined in Karelia, and salt in Solvychegodsk.

The development of natural sciences in Europe, including the scientific study of minerals, began in the Renaissance period. By the



Mikhail Vasilievich  
Lomonosov

fifteenth-sixteenth centuries, in connection with urbanization, the growth of trade, industry, and the invention of firearms, the need in mineral raw materials becomes more pressing. There is a marked increase in the scale on which prospecting and mining of the ores of various metals, salts, mica, coal, building materials and other mineral resources takes place. By that time large industrial mining centres had been formed in Europe, such, for instance, as the Kutná Gora lead-and-silver mine in Czechoslovakia, where underground mine workings reached several hundred metres in depth. Together with the mines of the neighbouring Saxony they provided the whole of Europe with silver and lead. The famous thalers (in Russia they were called 'efimkas') were coined in the Saxonian mining centre—Sankt Joachimsthal. It is with this particular period in the rapid growth of mining in Europe that the emergence of mineralogy\*, as a science of natural resources, may well be associated. To the latter, together with various ores and crystals, we may also refer rocks, fossils, amber, coal, etc.

A considerable impact on the development of mining and geological and mineralogical studies in Europe was made by the activity of the German scientist Georg Bauer, known as Georgius Agricola (1494-1555). In his works he had brought together the experience and the knowledge accumulated during the exploration, extraction and processing of the silver, lead, and tin ores in Saxony, Bohemia and other places. He put forward a well-balanced classification of minerals based on their physical properties and morphology (colour, lustre, transparency, density, hardness, brittleness, odour, taste, external form, outer aspect, cleavage, fusibility, texture, porosity, compactness, dryness). In the given classification all natural substances are divided into gases, liquids and fossils. The latter, in their turn, were subdivided into the simple and the complex groups.

Within the former group soils, salts, stones, and metals were distinguished. Fine (compact) and coarse (porous) mixtures constituted the complex group. Agricola, however, does not make any distinctions among rocks, ores, fossils, and minerals proper. With minor variations the principles of this systematization have been retained up to the middle of the nineteenth century in the works of numerous scientists, and A.G. Werner's (1750-1817) classification, and had covered over three hundred names of minerals.

The flourishing of mineralogy in Europe is associated with the activity of the Freiberg Mining Academy, the founder of which in the end of the eighteenth century was A.G. Werner. Since that time the

\* The term 'mineralogy' (from the Latin *minera*—ore) was introduced by the Italian scientist Bernard Cesi.

scientific study of the mineral world had entered into the stage of differentiation. A.G. Werner suggested that from mineralogy there should be singled out such sciences as geology, which was then called geognosy, and paleontology as a science dealing with fossils (petromatognosy), while the science studying minerals and ores, up to the middle of the nineteenth century, was referred to as oryctognosy (from the Greek '*oryktos*' meaning mineral).

The flourishing of mineralogy in Russia was connected with the rapid growth of mining, which was initiated under Peter I, who in 1700 founded a special governing body for the management of prospecting and mining of mineral resources. It was the time when the mining of copper was carried out in the Ural region, iron ores in the north of Russia, mica in Karelia and Eastern Siberia, sulphur—along the Volga river, silver and lead ores in the Altai and the Transbaikal. Later, the mining and the processing of iron ore and copper were developed in the Urals. The mining of valuable industrial, ornamental and building stone was initiated.

The growth of mining in Russia, the investigation and the development of the country's natural resources were promoted by the organization of the Academy of Sciences founded in 1725, and the activity of the outstanding scientist Mikhail Vasilyevich Lomonosov (1711–1765). In his multilateral scientific and educational activity a prominent place was allotted to the organization of the geological and mineralogical research and the prospecting of ores on the vast territory of Russia. He began his work 'The Mineralogy of Russia' by preparing a project of the mineralogical study of the country, with an instruction containing a detailed account of all possible recommendations concerning the gathering of stones and ores. In his works 'On the Origination of Metals as a Result of Earthquakes', 'Primary Fundamentals of Metallurgy or Mining', 'On the Layers of the Earth' together with an elaborate characteristic of the ores of various metals, he points out the mineralogical features of mineralization and gives an account of the physical properties of minerals; he explains the morphology of minerals by their corpuscular structure, and associates the formation of minerals and seams with 'the thickening of the sap in the earth', and their origin with earthquakes. M.V. Lomonosov put forward a classification of minerals based not only on their physical properties, but on their chemical properties as well. He singled out 8 classes: (1) metals, (2) semi-metals, (3) fertile (combustible) minerals, (4) salts, (5) stones and soils, (6) ores, (7) precious stones, (8) medicinal stones.

Of considerable interest to the development of geological and mineralogical studies in Russia was the organization of the Petersburg Higher Mining School, which later was transformed into the Mining Institute, and where mineralogy—the main subject of specialization—was taught with the aim of meeting the practical needs of the rapidly developing mining industry.

In that period the mineralogical science in Russia, though still under the influence of the Freiberg Mining Academy, acquires its own specific features. To a great extent the state of the art owes much to the works of Academician V.M. Severgin (1765–1826), the follower of M.V. Lomonosov and the founder of the Mineralogical Society. In V.M. Severgin's works the chemical composition of minerals is given due



Vasilii Mikhailovich  
Severgin



prominence together with an accurate description of the external and physical properties. The description of minerals is supplemented by an inventory of deposits and mineral associations. His works were not only of scientific importance, but had a clear-cut practical trend directed at the development of the mineral wealth in Russia.

By the beginning of the nineteenth century mineralogy had already acquired the status of an independent science, and owing to the development of crystallographical and chemical investigations, as well as to the improved methods of studying the physical properties

of minerals, enters into its new stage of development accompanied by further differentiation.

*The crystallographical trend* in mineralogy was founded as far back as in the Renaissance period. After the description of snowflakes by J. Kepler (1571-1630) in 1611, when their forms were explained by the regularity in the arrangement of the smallest spheroidal particles, there follows the discovery made by the Danish scientist N. Stenson (Steno) (1638-1686) in 1669. By examining the crystals of quartz and hematite, he established the law of constancy of interfacial angles. A century later, in 1763, the law was confirmed by M. V. Lomonosov, and then in 1772 by Rome de l'Isle (1736-1790) who by using the contact goniometer on minerals described approximately 500 crystallographic forms. In collaboration with R. J. Haüy (1743-1821) who had elaborated the theory of crystal structure and determined the law governing the rational relationship of the parameters. Rome de l'Isle propounded the crystallographical trend in mineralogy, the development of which led to its disintegration into an independent science—crystallography.

In 1809 the English mineralogist W. H. Wollaston invented the one-circle goniometer, and since then a systematic evaluation of the crystals of minerals had been initiated. A considerable contribution to the study of the crystals of minerals was made by Academician N. I. Koksharov (1818-1892), the author of the monumental eleven-volume work 'The Materials for the Mineralogy of Russia', and the German crystallographer V. Goldschmidt (1853-1930), the author of the voluminous 'Atlas of the Crystal Forms'. In later years these works served as the basis for the scientific study of crystals—crystallochemistry, which was propounded by both P. Groth (1843-1927) and E. S. Fedorov (1853-1919).

*The physical trend* in mineralogy undergoes substantial changes in the beginning of the nineteenth century. There is a transition from the qualitative description of minerals to the evaluation of their physical properties. F. Mohs' 10-point hardness scale of minerals introduced in 1822 was widely used. Thermal, elastic, electrical and magnetic properties of minerals are being studied. Since the middle of the



Nikolai Ivanovich  
Koksharov

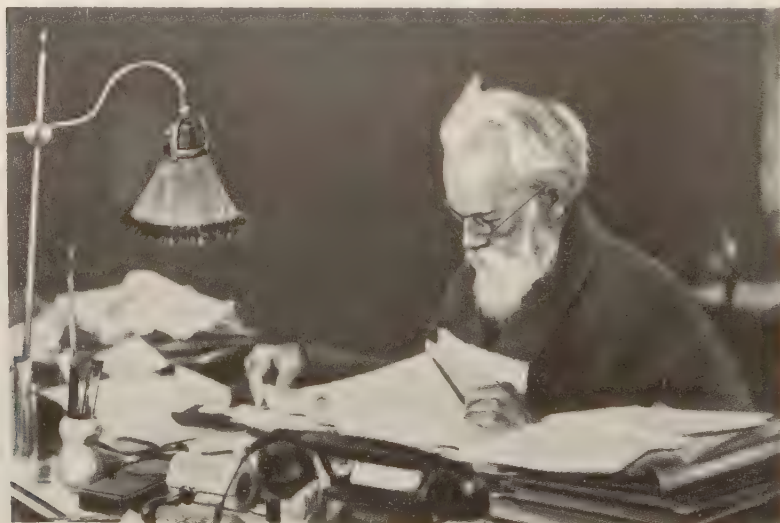
nineteenth century the study of optical properties had been initiated. It was carried out with the help of the polarized microscope invented by the English scientist H. Sorby in 1858, and was followed by a specialized microscopic study of rocks, which, being conducted on a wide scale, led to the singling out from mineralogy of an independent branch of science—petrology. By the end of the nineteenth century the study of the luminescence, and later the radioactivity of minerals gained its own growth.

*The chemical trend in mineralogy, deeply rooted in the medieval alchemy, was developed under the influence of the rapid growth of chemistry at the end of the eighteenth and the beginning of the nineteenth centuries. It was in that particular period of time that the chemical composition of a large number of minerals was established. The latter were discovered to contain such previously unknown chemical elements as: cobalt and nickel, chromium and manganese, molybdenum and tungsten, etc. At first it is*

assumed that minerals are characterized by a particular constant chemical composition. Later, however, it was discovered that the character of the chemical composition of a large number of minerals was extremely changed.

The attempts to elaborate the classification of minerals on a chemical basis in the beginning of the nineteenth century were confronted with the authoritative school of the Freiberg Mining Academy. The physical classification of minerals proposed by A. G. Werner was superseded by the chemical classification only after J. Berzelius (1826) singled out among minerals the group of oxides,

Vladimir Ivanovich  
Vernadsky





Alexander Evgen'evich  
Fersman

silicates, sulphates, halides, carbonates and other salts. Later, this principle of systematization with various additions and specifications has retained its leading role in all the classifications of minerals up to the present.

It was on the chemical basis that the initial concepts pertaining to the origin, or genesis, of minerals were developed in mineralogy. These concepts were grounded on detailed investigations of the pseudomorphic transformations of minerals and on the experiments aimed at obtaining their synthetic analogues. The achievements in colloidal and physical chemistry had exercised a considerable impact on the development of genetic ideas in mineralogy.

In later years, by the beginning of the twentieth century, they gave rise to the formation of the new *chemicogenetic trend* in mineralogy, the founder of which is by right considered to be the outstanding Russian scientist Academician V.I. Vernadsky (1863-1945). He regarded mineralogy as 'the chemistry of the Earth's crust' and referred mine-

erals to the products of natural reactions. His works on isomorphism, structural silicates, paragenesis, radioactive elements, the distribution of chemical elements of the Earth's crust, the chemical composition of water and the living matter, have constituted the fundamentals of contemporary mineralogy, as well as geochemistry, hydrochemistry and biogeochemistry.

V.I. Vernadsky's ideas were further elaborated in the works of his pupil Academician A. Ye. Fersman (1883-1945), whose prolific activity as a scientist and organizer had a tremendous influence on the development of modern mineralogy and geochemistry in the USSR. His name is associated with the scientific study of the crystallomorphology of diamonds, zeolites, layered silicates, pegmatites, the theoretical working out of fundamentals of geochemistry, the discovery and the development of the mineral wealth of the Kola peninsular, Central Asia and other regions of the USSR.

The development of mineralogy in the Soviet State is connected with a wide-scale geological research which led to numerous mineralogical investigations of the deposits of various mineral resources and separate regions. These *geologogenetic and topomineralogical trends* in the scientific study found their place in the well-known works of A. Ye. Fersman, A. K. Boldyrev, A. G. Betekhtin, I. I. Ginzburg, S. S. Smirnov, N. A. Smolyaninov, P. P. Pilipenko, A. A. Tvalchrelidze, A. S. Uklonsky, N. M. Fedorovsky and their pupils.

The contemporary stage in the development of mineralogy is characterized by the research propounded in various theoretical and applied directions. To a profound study of the mineralogy of various genetic types of deposits are devoted the works of: K. A. Vlasov, V. I. Gerasimovsky, E. K. Lazarenko, V. F. Barabanov, G. P. Barsanov, A. I. Ginzburg, G. A. Krutov, A. A. Kukharenko, N. V. Petrovskaya,

Nikolai Vasilievich  
Belov



F. V. Chukhrov, T. N. Shadlun and others. A tangible contribution to mineralogy was also made by S. T. Badalov, A. A. Godovikov, S. V. Malinko, A. S. Marfunin, V. G. Melkov, D. A. Mineev, E. I. Semyonov, D. P. Serdyuchenko, G. A. Sidorenko, N. A. Solodov, A. S. Povarennykh, L. K. Yakhontova and others. They have studied various minerals in detail, discovered a great number of new ones, including those that are of value to industry, compiled surveys covering the minerals of particular elements and the minerals of

various types of the deposits of mineral resources.

*The physicochemical trend* in mineralogy is developing on the basis of the scientific study of natural mineral associations and the theoretical analysis of mineral equilibrium worked out by D. S. Korzhinsky, V. S. Sobolev, V. A. Zharikov, A. A. Marakushev, L. L. Perchuk and others. Experimental modelling of endogenous and exogenous processes in the formation of minerals, their synthesis and the study of the composition and the state of aggregation of inclusions, and the establishing of the thermodynamic constants of minerals have been developed on a wide scale (V. S. Balitsky, A. A. Beus, A. A. Godovikov, N. P. Ermakov, D. S. Kalinin, I. Ya. Nekrasov, L. N. Ovchinnikov, V. F. Syromyatnikov, N. I. Khitarov and others).

*The morphogenetic trend* in mineralogy, thanks to the works of D. P. Grigoryev and I. I. Shafranovsky, became a well-balanced scientific study of the development of minerals and mineral aggregates—the ontogeny of minerals. In this field of research, the works of particular interest are those of G. N. Vertushkov, Yu. M. Dymkov, N. Z. Evzikova, A. G. Zhabin, D. V. Rundkvist, N. P. Yushkin and others.

*The crystallochemical trend*, owing to the works of N. V. Belov (1891-1982) and his pupils, was formed into structural mineralogy. The interpretation of the crystal structures of minerals became the basis of the modern systematization of minerals (G. B. Bokii, A. S. Povarennykh, V. A. Frank-Kamenetsky, B. B. Zvyagin, E. A. Pobedinskaya, Yu. A. Pyatenko, V. V. Bakakin, M. A. Simonov et al).

*The physical trend* in mineralogy is based on the theoretical and methodological achievements of physical sciences, particularly of solid-state physics, optical and resonant spectroscopy and electronic microscopy. Research in this field has substantially increased our knowledge of the inner structure of minerals and made it possible to interpret the nature of the physical properties of minerals. The development of these investigations led to the formation of a scientific trend—the physics of minerals. It was initiated in this country in the post-war period by S. A. Grum-Grzhimailo, N. I. Melankholin, G. P. Barsanov, A. S. Povarennykh, G. F. Komovsky, V. M. Vinokurov, G. S. Gritsaenko, A. S. Marfunin, A. N. Platonov, A. D. Rakcheev, M. I. Samoilovich, G. A. Sidorenko, et al.

In the post-war period special prominence is given to the applied

mineralogical studies, *prospecting and technological mineralogy*. On the basis of the scientific study of the typomorphism of minerals the mineralogical methods of exploration and the criteria of mineralization are being worked out. The mineralogical and technical investigations are carried out with the aim of attaining a complete and complex use of mineral raw materials and environment protection (F. V. Chukhrov, A. I. Ginzburg, N. V. Petrovskaya, V. I. Kuzmin, D. A. Mineev, N. F. Chelishchev and others).

The works of the Soviet mineralogical school are closely connected with the practical needs of national economy and together with other geological studies help to discover and explore various mineral resources, and thus play an important role in the creation and the development of the mineral raw-material basis in this country.

## Modern Concepts of Minerals

*Minerals, at present, are called physical and chemical homogeneous crystal bodies formed as a result of natural physical and chemical processes.*

*From the physical and chemical point of view* each mineral represents a solid phase. The stability of minerals depends on temperature, pressure, and the chemical composition of the environment. Thus, when pressure is increased, the crystal structure of the mineral can change, while when heated the mineral is either melted or dissolved in water. Conversely, the cooling of the melt, the condensation of gases or the saturation of the solution may lead to the extraction of the solid phase. Hence, natural liquids and gases are not minerals, but constitute the environment in which minerals are either formed or changed.

*From the physical point of view* each mineral is a dimensionally ultimate crystal body which is called a *mineral individual*. Each individual is characterized by a particular surface in the form of faces of crystals or arbitrary intergranular boundaries.

Mineral individuals are usually intergrown with other individuals, and thus form different types of rock, ores and other aggregates, the components of various geological bodies: intrusions, veins and deposits of mineral resources. They may also be found in a finely dispersed state, glassy and colloidal formations, as well as in the form of suspensions in the Earth's natural waters or in space.

*In terms of their crystallochemical properties* minerals are characterized by a crystal structure, i.e. by particular constituent features, such as the type of structure and the idealized chemical composition. All the mineral individuals occurring in nature are crystallochemically identical and represent a particular *mineral species*. Each mineral species has its own name, while its chemical composition is expressed by means of an idealized formula.

According to their definition minerals of the same composition with different structures pertain to different mineral species. The chemical boundaries of mineral species with variable composition and uniform structure are less determined, especially in those cases when the content of separate components undergoes considerable variation or becomes interchangeable. Minerals of the intermediate composition

with stoichiometric, or multiple prime numbers, relationship of the components, differing from other minerals of the variable composition in the structural degree of order, represent independent mineral species. Thus, when the general term 'mineral' is used, it is necessary to have in mind that it has a binary designation as a synonym for the concepts of 'mineral species' and 'individual'. Minerals may be represented by their varieties, each possessing some specific features of the chemical composition and structure, as well as morphology and physical properties.

*The chemical varieties* are characterized by the presence of additional elements within certain natural boundaries. Sometimes they have their own names, for instance, ferrous sphalerite is called marmatite.

*The structural varieties* of minerals are distinguished by some specific features of the crystal structure, usually with the chemical composition remaining constant. The right-handed and the left-handed structural forms of quartz, minerals with regular and irregular location of interchangeable atoms of the elements in their structure, i.e. with various degree of order (feldspars - orthoclase and sanidine), layered minerals with various order of alternation of atomic layers in the structure, etc. can serve as an example.

*The morphological varieties* of minerals possess innately their own shape of individuals or mineral aggregates. A large number of them have their own names too. For instance, chalcedony—a collomorph cryptocrystalline varieties of quartz, selenite—a parallel fibrous variety of gypsum and others.

*The physical varieties* of minerals are characterized by specific physical properties, mainly optical ones, such as: transparency and colour. Some varieties are precious minerals or used in industry. They include the bright green beryl, or emerald, the blue aquamarine, the yellow heliodor, the transparent variety of quartz, or rock crystal, the violet amethyst, the black morion etc.

It is necessary to point out that minerals are spread not only in the earth's crust. They enter into the mantle and the deeper interior of our planet, and are scattered in the hydrosphere and the atmosphere. Minerals also constitute the Moon, numerous planets, their satellites, the asteroids, and are found in the meteorites and the smallest particles of the cosmic dust that fall on the surface of the earth.

'*Artificial minerals*' have synthetic analogues of minerals that are often produced in the form of large crystals. Some of them have been cultivated on an industrial scale to substitute the deficient natural raw materials: the optical quartz, diamond, corundum, emerald and others. *Technogenic minerals* also refer to the domain of mineralogical research. Their formation in natural environment is stimulated by the productive activity of man, for instance on the walls of mine workings, external spoil heaps, in the pipes of the boreholes etc.

The crystalline products of the vital functions of various organisms are also referred to minerals. Thus, for instance, the formation of native sulphur and calcium carbonate at the expense of gypsum, is accounted for by the sulphate-reducing bacteria. Entering into the tissues of animals and plants, minerals form *organomineral aggregates*, as is the case with apatite in the bones, fluorite in the teeth, celestine and tridymite in the skeletons of radiolarians etc. On the extinction of organisms some of their minerals form accumulations of

valuable mineral raw material, for instance, phosphorite, tripoli etc.

At present more than 3 000 mineral species and almost the same number of varieties have been established. Every year several new minerals are discovered. The earth's crust is mainly composed of feldspar and quartz and accounts for their nearly 55% and 10% presence respectively. Pyroxenes, amphiboles, chlorites, micas, clay minerals, carbonates and others are widely spread too. A number of other mineral species are found rather often; others are of rare occurrence. Some minerals are represented by huge masses of almost monomineral rock or industrial accumulations, the deposits of mineral resources. Magnetite, magnesite, calcite, gypsum, halite and others can serve as an example. Meanwhile, there are minerals whose number is found to be inadequate for their diagnosis.

The spreading and the number of mineral species in the Earth's crust are basically determined by the spreading and the chemical properties of the atoms of the mineral-forming elements. Their ability to concentrate or to disperse in the process of the formation of minerals, i.e. their chemical activity, depends on the physical and chemical conditions of the environment. The spreading of chemical elements in the earth's crust determines the mass of predominant mineral species in terms of their number (or quantity). The multilateral character of species and varieties could be determined by the number of the possible combinations of chemical elements. The limited number of mineral species is conditioned by the fact that not all even the most spread chemical elements can interact with the formation of the stable combinations in the natural environment. The most widespread species-forming elements in minerals are: O, Si, Al, Fe, Ca, Na, Mg, K, Ti. Among those that are moderately spread are: S, Cl, C, Mn, H; while the number of those that are either rare or not spread at all includes B, Be, Pb, Sb, As, Bi, Se, U, Ag, Te and others. Some elements do not form independent species of minerals at all, and are in a dispersed state, as is the case with rubidium, and inert gases.

## The Importance and the Main Tasks of Mineralogy

Knowledge of the mineral world, the inception and the development of mineralogical studies have always been closely connected with the practical activity of people. The growth of production forces at all the stages in the development of human society has been linked with the direct implementation of minerals or their valuable components, such as precious, non-ferrous, ferrous, and rare metals and non-metals, trace elements, and various chemical compounds. With the further increase in the demand for mineral raw materials the role of mineralogical studies in meeting the needs of industry in this respect is becoming greater. All in all approximately 10% of all mineral species are used at present for industrial purposes, their number being on a steady increase conditioned by mineralogical research. (The average increase in every ten years is estimated at 10–15 mineral species.) Only within the past 15–20 years such rare minerals as phenacite  $\text{Be}_2[\text{SiO}_4]$ , bertrandite  $\text{Be}_4[\text{Si}_2\text{O}_7](\text{OH})_4$ , baddeleyite  $\text{ZrO}_2$ , and even the newly discovered minerals, for example, corderoite  $\text{Hg}_3\text{S}_2\text{Cl}_2$ , and gagarinite  $\text{NaTRCaF}_6$  and others, have acquired industrial significance.

The most important task in mineral research at present consists in developing the mineral raw-material basis and the discovery of new mineral raw materials. This can be achieved by (1) prospecting the industrial concentrations of rare minerals, (2) the study of the physical and the physicochemical properties of minerals, (3) the establishing of high concentrations of mineral impurities in the known and widely-spread minerals, and (4) the discovery of new ore minerals.

It is necessary to lay particular stress on the importance of mineralogical research when the prospecting and the assessment of the quality of ores takes place. The proficiency to determine minerals accurately and without loss of time, to know their prospecting and industrial values is the most important ingredient of high qualification for both the mineralogists and the geologists. An effective implementation of mineralogical studies at all the stages of geological research (the geological survey, geological exploration, the inspection of ore manifestations and anomalies established by geochemical and geophysical methods) has a tremendous practical significance, serves to evaluate the overall depth of perspective mineralization, as well as the possibilities of using the mineral raw materials on a complex scale. The further goals of mineralogy in this direction consist in elaborating reliable mineralogical features of industrial mineralization and the criteria of the technological quality of ores on the basis of theoretical and methodological achievements of the physics of minerals.

The impact of mineralogy on the development of other natural sciences can hardly be overestimated. Chemistry has developed on the basis of the study of the chemical composition and the properties of various minerals and ores. It was while studying minerals and their chemical properties that the methods of analytical chemistry have been elaborated and most of the chemical elements have been discovered. A large number of physical properties and phenomena were initially brought to light in the process of studying natural crystals. The latter, in their turn, served as the starting point for the development of our concepts concerning the crystalline structure of matter. As has already been stated, it was at the very inception of mineralogical studies that the research in crystallography, petrology, geochemistry, the study of mineral resources and other branches of science, was initiated and further developed.

Modern mineralogy is closely connected with such fundamental natural sciences as physics, and chemistry. By making an extensive use of the theoretical and methodological achievements of these sciences, mineralogy serves to promote the scientific and technical progress in the related to it geological and applied sciences connected with the study of the mineral composition of rocks and ores, the exploration, survey and processing of the mineral raw materials. Mineralogical methods are widely used in petrology, lithology, geochemistry, in the study of soils and grounds, in geocryology, in the composition of fossils and caustobiooliths, in medicine, archeology and other sciences. For scientific and applied purposes an elaborate study of the composition, structure and properties of minerals is called for. In its turn, this leads to a further development of highly sensitive, local methods expressed in physics and chemistry, the theoretical working out and the manufacturing (production) of modern equipment for scientific research.



## Part I

# Minerals. A General Outline

## The Crystallochemistry of Minerals

**The binding energy, interatomic distances and the electronic structure of atoms in minerals**

### The Interatomic Bond and the Coordination of Atoms in Minerals

Minerals are defined as crystalline matter, and the atoms of chemical elements entering into their composition are found to be in regular distribution in the points of lattices and maintained in the state of equilibrium by the forces of mutual attraction and repulsion. The nature and value of these forces are determined by the properties of the interacting atoms of chemical elements. These properties are conditioned by the charge of the nucleus, the electronic structure of the atoms and are unique for different chemical elements.

The formation of any chemical compound including minerals may be imagined as a convergence of free atoms till a certain distance between them is reached, at which point the forces of attraction and repulsion are brought into a state of equilibrium. The latter corresponds to the minimum of energy since in a chemical compound the potential energy of atoms is smaller than that of free, disconnected atoms. In general, the difference between the value of the energy of free atoms and the minimal potential energy of atoms in a bound state is determined as the energy-producing measure of the chemical bond. In crystals it is called the energy of the crystalline lattice. This value signifies that when crystals are formed a certain amount of free energy is discharged. For the destruction of the crystal, however, it is necessary to employ the amount of energy that will correspond to its value, e.g. when minerals are moderately heated the average interatomic distances become greater due to an increase in the amplitudes fluctuating movements of atoms and their displacement from their state of equilibrium. The latter takes place when there is a marked increase in temperature, as a result of which minerals are disintegrated. Conversely, an increase in pressure leads to the convergence of atoms and can be accompanied by structural transformations.

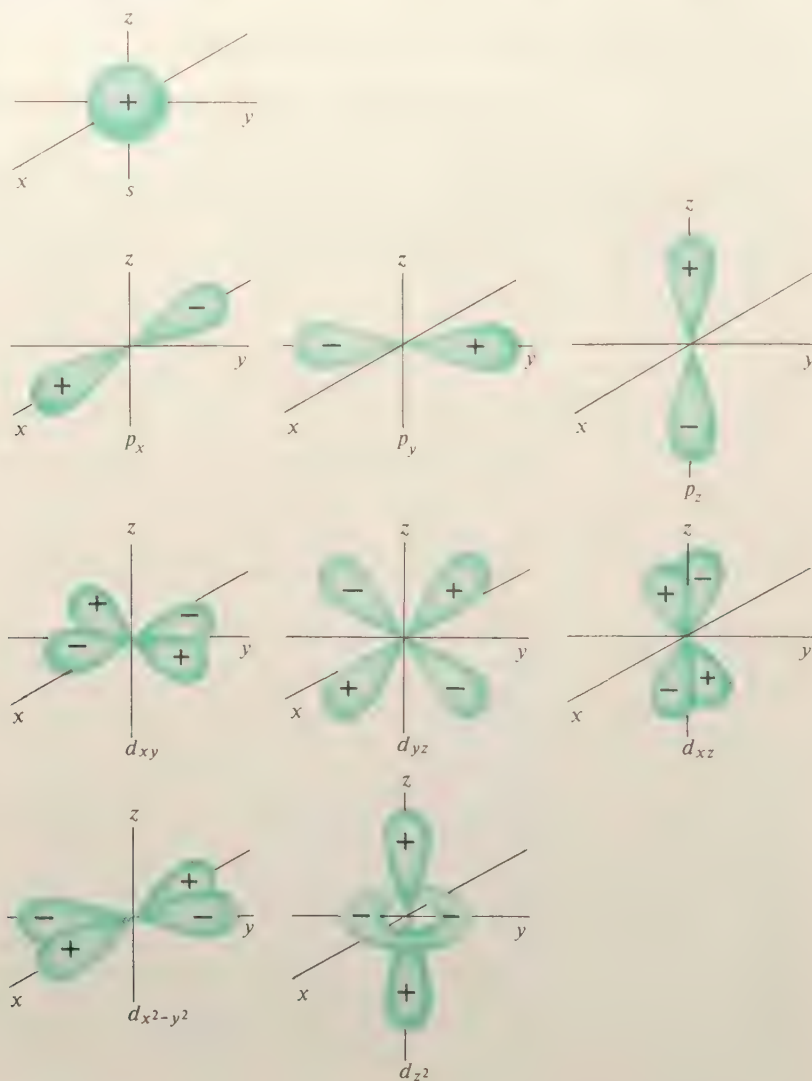
Hence, at a particular temperature and pressure the value of interatomic distances is fairly characteristic of each crystalline matter including minerals. It depends on the size of atoms and ions in crystals, and is determined, first and foremost, by the electronic struc-

ture of corresponding elements. The atoms of elements with different electronic structure differ not only in their dimensions, but also in configuration, which is described by orbitals. As is known, the  $s$ -orbitals have a spherical configuration, the three  $p$ -orbitals are located along the coordinate axes  $p_x$ ,  $p_y$ ,  $p_z$ , the five  $d$ -orbitals are characterized by the coordinate ( $d_{x^2-y^2}$ ,  $d_{z^2}$ ) and intercoordinate  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$  orientations (Fig. 1). The orientation of  $f$ -orbitals is more complex.

**The coordinate numbers and the coordinate polyhedrons**

The dimensions and the electronic structure of the atoms determine their coordination, i.e. the character of their spacial distribution in the crystalline structure of the minerals in respect to one another. *The coordinate number (C.N.)* indicates the number of atoms and ions of the opposite sign located at the closest distance from the given ion.

Fig. 1. Configuration of  $s$ -  $p$ - and  $d$ -orbitals (explained in the text; see Verhoogen, J. et al., p. 316)



The spacial location of coordinating atoms (ions) varies with minerals. It is described by means of geometrical figures, the apexes of which represent the centres of coordinating atoms. The three-dimensional coordinating figures are called *coordinate polyhedrons*. The coordination number and the type of coordinate polyhedron depend on the character of the spacial location of atoms in minerals. The coordinate polyhedrons with C.N. = 12 correspond to the simplest type of the closest packing of spheroidal atoms of the same size. Thus, for instance, the coordinate polyhedron of each atom of native copper represents a 12-apex cubooctahedron. The atoms and ions located in the voids of the closest packing of other atoms have octahedral or tetrahedral coordination. In halite NaCl, for example, the large anions of chlorine form the closest cubic packing, while the cations of sodium are located in all the octahedral voids. In this structure each cation is surrounded by 6 anions (C.N. = 6). In corundum  $\text{Al}_2\text{O}_3$  the ions of aluminium occupy only 2/3 of the octahedral voids of the closest hexagonal packing of oxygen ions. The closest packing undergoes distortion if the dimensions of the coordinate atoms are found to be greater than the corresponding octahedral and tetrahedral voids.

### The coordination of atoms and the types of chemical bonds

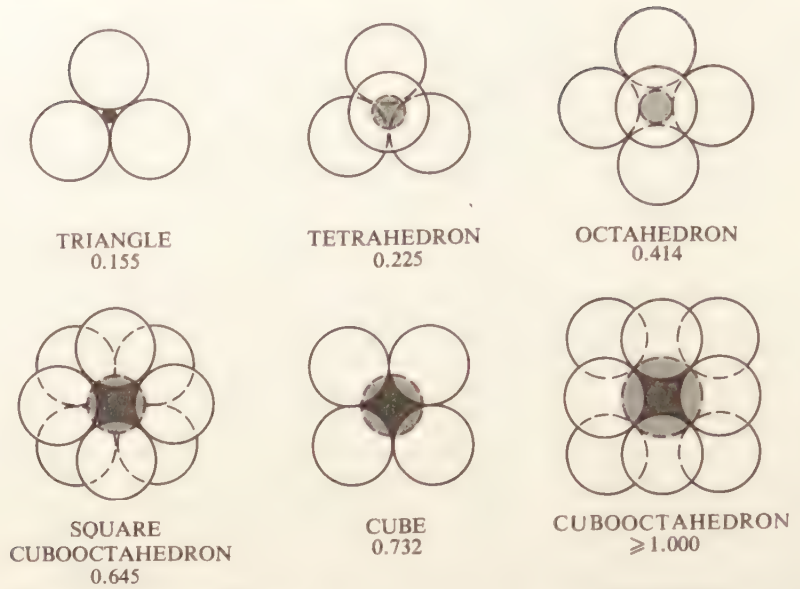
The coordination of atoms in the structure of minerals is also determined by the type of chemical bond between them, the electronic and energetic condition, which in its turn, depends on the electronic structure of the interacting atoms, and the distance between them. Ionic and covalent bonds are typical of most of the minerals. A comparatively small number of minerals is characterized by a metallic bond. Besides, residual, or van der Waals and hydrogen bonds are widely spread. Two or three types of chemical bond are usually manifested in minerals. The intermediate ionic and covalent and covalent and metallic bonds are particularly widespread in minerals. The structures of minerals with a single type of chemical bond of atoms are called homodesmic. In these cases when several types of interatomic bonds are found in minerals the structures are called aniso- or heterodesmic.

In case of an *ionic bond*, which is characterized by the electrostatic attraction of the oppositely charged ions, the coordination of atoms in the crystalline structure is mainly determined by the dimensional relationship of cations and anions (Table 1, Fig. 2). However, crystalline structures, in which the coordination numbers of atoms and

TABLE 1 *Coordination Numbers and Configurations in Minerals with Various Relationships of Cation and Anion Radii*

Ratio of cation and anion radii $r_c/r_a$	C. N.	Examples of coordination configurations in minerals
0.155-0.225	3	trigonal $\text{CO}_3$ in calcite
0.225-0.414	4	tetrahedral $\text{SiO}_4$ in olivine
0.414-0.732	6	octahedral $\text{SnO}_6$ in cassiterite
0.732-1	8	cubic $\text{CaF}_8$ in fluorite
$\geq 1$	12	cubooctahedral $\text{FeFe}_{12}$ in native iron

Fig. 2. The relationship of cation and anion radii (illustrated by black and white circles respectively) in various coordination polyhedrons characteristic of minerals with the ionic type of chemical bond



the coordinate figures are conditioned by the electronic structure of atoms and the type of the chemical bonds, are typical of a large number of other minerals (Fig. 3).

The covalent bond occurs when the overlapping of the orbitals with unpaired electrons of the interacting atoms is such that a pair of electrons with opposite spins occupies a separate, or the so-called molecular orbitals. In the native sulphur the covalent bond between 8 atoms of sulphur and its  $1s^2 2s^2 2p^6 3s^2 3p^4$  configuration (one orbital with two paired electrons and two orbitals with one nonpaired electron each corresponds to  $3p^4$  level) results from the overlapping of each of two orbitals with nonpaired electrons and analogous  $3p$ -orbitals of the neighbouring atoms of sulphur. As a result of pairing the electrons on each of the  $3p$ -orbital, molecular-bound orbitals with power gain are formed.

When different orbitals are overlapped, the redistribution of their respective nonpaired electrons is such that the latter are found to be equal in value and form a set of 'hybridized' orbitals. The diamond serves as a good example of the covalent bond with the hybridization of orbitals in minerals. In its basic state the electronic configuration of carbon  $1s^2 2s^2 2p^2$  has two  $2p$ -orbitals filled with nonpaired electrons. The formation of diamond is preceded by the transition of the atom of carbon into the excited state of  $1s^2 2s^1 2p^3$  which takes place when one  $2s$ -electron is transferred to one of the free (unoccupied)  $2p$ -orbitals. The orbitals with nonpaired electrons, overlapping with analogous orbitals of the neighbouring atoms of carbon, lead to the formation of hybrid binding  $sp^3$ -orbitals, which are identical as far as their geometrical and power quotients are concerned. In cases of reciprocal repulsion the orbitals of carbon atoms produce a multidirectional covalent bond and the maximum angle of  $109^\circ 28'$  which corresponds to the tetrahedral environment of each carbon atom by four others characteristic of the diamond (Fig. 4).

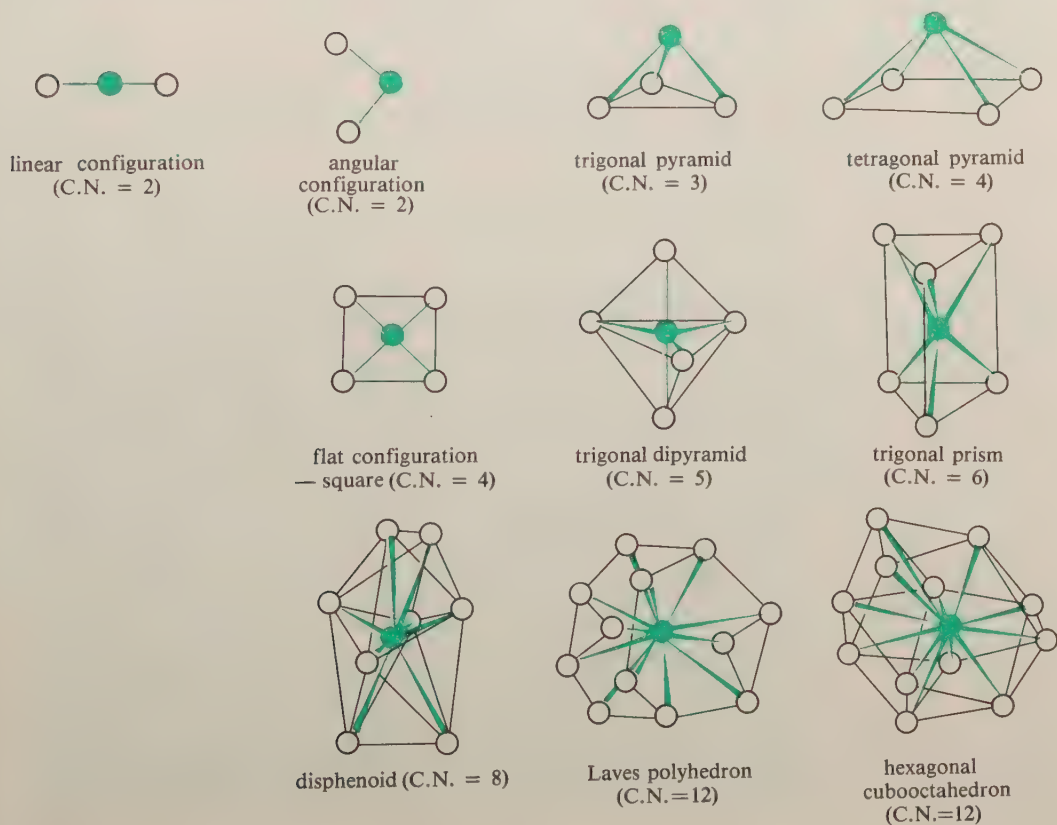
The distance between the atoms in minerals with the covalent

chemical bond and the covalent radius of atoms respectively are smaller than in the cases of the ionic bond. The covalent radius depends on the electronic configuration of the interacting atoms. Thus, the covalent radius for carbon can have different values depending on the type of binding hybridized orbitals: 0.0722 nm ( $sp^3$ ) in diamond and 0.0665 nm ( $sp^2$ ) in graphite (Fig. 5).

Hence, the coordination number and the coordinating polyhedrons in the structure of minerals with covalent atomic bonds are determined by the number of the binding orbitals and their direction. The characteristic coordinate figures for elements with different types of hybridization of covalent bonds are given in Table 2. The closest packing of atoms with the formation of the three types of crystalline structures is typical of minerals with the *metallic* type of chemical bond, which occurs when a complete collectivization of the electrons in the bond takes place. In the face-centered cell of the structure of native iron each atom finds itself in the cubooctahedral environment with C.N. = 12. In the body-centered cell of the structure of native gold the coordinate polyhedron represents a cube with C.N. = 8. In the hexagonal closest packing of native osmium the atoms form a hexagonal cubooctahedron with C.N. = 12.

The intermediate *covalent and metallic* interatomic bonds with a wide span of hybridization of *s*-, *p*- and *d*-orbitals and a partial collectivization of electrons are typical of minerals in which the

Fig. 3. Coordination polyhedrons in minerals with covalent bond



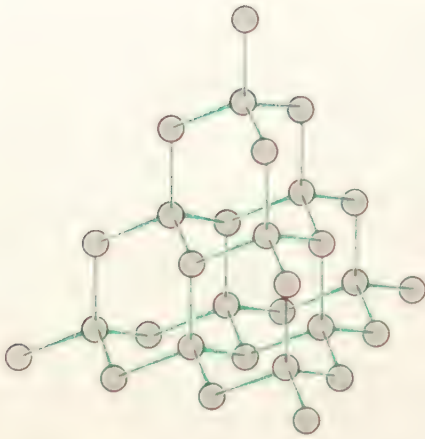
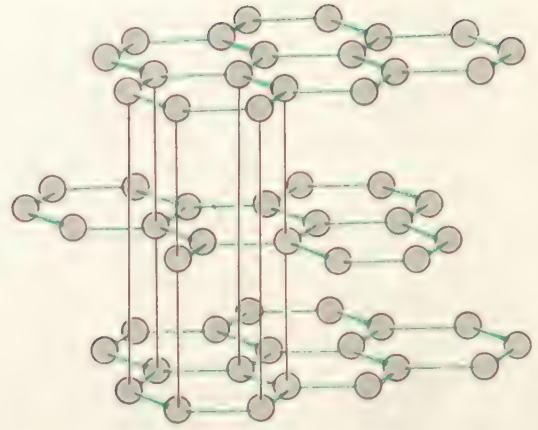


Fig. 4. The structure of diamond—fragment of tetrahedral  $sp^3$  bond of carbon atoms

Fig. 5. The structure of graphite with van der Waals bond between the hexagonal planes of the nets of carbon atoms with trigonal  $sp^2$  bond



number of ions of the transitional metals is predominant. They are particularly typical of oxides and sulphides. The atoms in these minerals are characterized by a variety of coordinate polyhedrons which is determined by the number and the trend of the binding orbitals (see Fig. 3, Table 2).

The *van der Waals* bond is characteristic of the heterodesmic structures of minerals that are not equidistant in different directions. For instance, in graphite the distance between the carbon atoms in the hexagonal plane net is 0.0665 nm, while between the nets it is 0.337 nm (see Fig. 5).

The *hydrogen bond* results from the collective use of the proton by the neighbouring oxygen atoms and has a substantial impact on the interatomic distances and the atom coordination in the structure of minerals. In its full form it is realized in the structure of ice  $H_2O$ ,

TABLE 2 *Coordination Numbers and Polyhedrons of Atoms with Various Types of Hybridization of Covalent Bonds in Minerals*

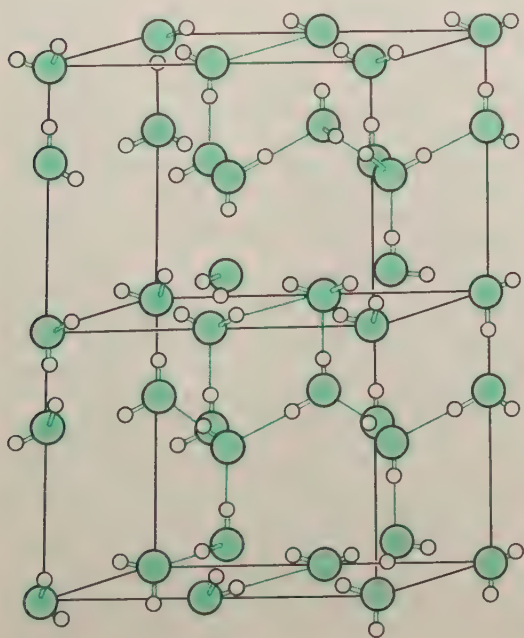
C. N.	Coordination configuration	Type of hybridization of covalent bonds	Examples of coordination of minerals
2	line angle	$sp$ , $dp$ $p^2$ , $ds$	Hg in cinnabar S in native sulphur
3	triangle trigonal pyramid	$sp^2$ , $dsp$ $p^3$ , $d^2p$	C in graphite Pb in galenite
4	square tetrahedron	$dsp^2$ , $d^2p^2$ $sp^3$ , $d^3s$	Cu in azurite Zn in sphalerite
5	tetragonal pyramid trigonal dipyramid	$d^2sp^2$ , $d^4s$ $d^3sp$	Cu in malachite V in vanadinite
6	trigonal prism octahedron	$d^4sp$ , $d^5p$ $d^2sp$ , $sp^3d^2$	Mo in molybdenite Sn in cassiterite

where the oxygen atoms find themselves in a tetrahedral coordination of the four other oxygen atoms, while the hydrogen atoms are located between the two neighbouring oxygen atoms (Fig. 6). As a result of the interaction with four hydrogen atoms, oxygen acquires four  $sp^3$ -orbitals, two of which take part in the covalent bond with the two closely located hydrogen atoms, the other two remaining intact. In the crystalline structure of ice such dipole  $H_2O$  molecule is connected with other forces of weak electrostatic interaction which are discussed in terms of the hydrogen bond. The latter also manifests itself in those cases when the water molecules enter into the structure of minerals, participating in the coordination of cations, as, for instance, in sulphates, epsomite  $Mg[SO_4] \cdot 7H_2O$  and chalcantite  $Cu[SO_4] \cdot 5H_2O$  or in the form of the more loosely bound molecules in layered silicates, and zeolites.

### Interatomic distances and ionic coordination of the transitory groups of elements

The interatomic distances and the configuration of coordinate polyhedrons in minerals containing the ions of transitory metals, are characterized by their electronic structure and the type of interaction with the coordinating anions (ligands). This interaction is studied by *the theory of the crystalline field of anions* which is based on the assumption of the electrostatic interatomic interaction corresponding to a purely ionic type of chemical bond. In accordance with this theory five  $d$ -orbitals of the free ion, having identical power potential, are degenerated. In the crystalline field the degeneration is removed, as a result of which five identical levels are being split. The character and the degree of splitting depend on the coordination of ligands and the distribution of electrons along the orbitals. Thus, for instance, in the octahedral field two coordinate  $d$ -orbitals— $d_{x^2-y^2}$  and  $d_{z^2}$ —oriented along the coordinate axes, are directed towards the ligand, situated

Fig. 6. The structure of ice—hydrogen bond between  $H_2O$  molecules



in the apexes of the octahedron, while the other three intercoordinate  $d$ -orbitals— $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ —occupy an intermediate position. The coordinating  $d$ -orbitals, undergoing the repulsion of anions, are found at a higher power level while that of the intercoordinate orbitals is comparatively low in accordance with the law of conservation of energy. The value of the split  $\Delta$  in the octahedral field is greater than that in the tetrahedral field (Fig. 7). The electronic configuration, or the distribution of electrons along the orbitals of different power quotients, depends on the value of the split  $\Delta$ . When the  $\Delta$  value is insignificant the electrons are found to be in regular distribution along the orbitals of all the levels which leads to the formation of the high-spin configuration (Fig. 8a). If the number of electrons is greater than that of the orbitals, then the pairs of electrons with different spins are located on the orbitals with a smaller degree of energy. If, however, the value  $\Delta$  is greater than the energy of the electron-electronic repulsion, the

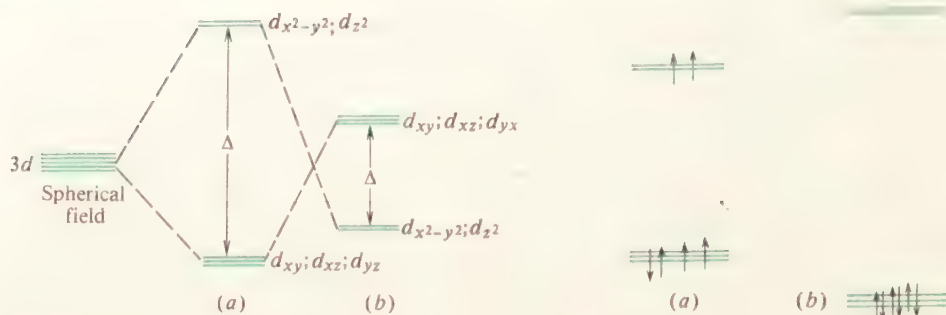


Fig. 7. The splitting of  $d$ -electron levels in the octahedral (a) and tetrahedral (b) fields

Fig. 8. Distribution of  $d$ -electrons in high-spinned (a) and low-spinned (b) electronic configuration

electrons are located only on the orbitals of the low degree of energy, thus forming pairs with compensated spin—low-spin configuration (Fig. 8b). The value of  $\Delta$  and the character of orbitals filling at different levels condition the presence of certain properties, such as optical, magnetic and those which will be discussed further, as well as interatomic distances and the symmetry of the immediate environment.

If, in case of high-spin configuration, the  $d$ -electrons are located on the orbital coordinates, they screen the positive charge of metal from ligand. This results in the weakening of the bond and an increase in the interatomic distance. It may well be considered that the ions in a high-spin configuration are of larger size, while in a low-spin configuration their size is smaller. Hence, when the pressures are high, the formation of minerals with ions in the low-spin configuration is more preferable as is assumed. It is in this particular configuration that numerous ions of the transitory elements in minerals in the depth of the Earth exist.

## The Structure of Minerals

### Basic structural types of minerals

The whole variety of crystalline structures of minerals can be reduced to five types, each of them having its own location of atoms.

1. *The coordinate structures* are characterized by identical distances between atoms. It is immanent for the structures of this type in minerals with metallic and ionic chemical bond to have a closest packing of metals (native gold), anions, for example, oxygen in hematite, or cations, as calcium in fluorite.

2. *The island structures* are characterized by a variety of interatomic distances. In these structures the complex anion radicals or closed molecules represent what may loosely be called 'island bodies'. The interatomic distances within the limits of the latter are smaller than in the remaining part of the structure, though the strength of the chemical bond is substantially greater. Examples of the latter include numerous silicates with isolated tetrahedral anion radical  $[\text{SiO}_4]^{4-}$ : olivine  $(\text{Mg, Fe})_2[\text{SiO}_4]$ , topaz  $\text{Al}_2[\text{SiO}_4](\text{OH, F})_2$  and others; carbonates with isolated trigonal radical  $[\text{CO}_3]^{2-}$ : calcite  $\text{Ca}[\text{CO}_3]$ , dolomite  $\text{CaMg}[\text{CO}_3]_2$  and others. In other minerals the 'island bodies' have a more complex structure; double radicals  $[\text{Si}_2\text{O}_7]^{6-}$ , for example in calamine  $\text{Zn}_4[\text{Si}_2\text{O}_7](\text{OH})_2\text{H}_2\text{O}$ , triple, quadruple, six-fold and more complex rings, for example,  $[\text{Si}_6\text{O}_{18}]^{12-}$  in beryl.



Realgar  $[As_4S_4]$  and native sulphur  $[S_8]$  serve as examples of the molecular insular structures.

3. *The chain* structures are formed by infinite one-dimensional radicals, which consist of linearly connected coordinate polyhedrons. The distance between the atoms within the chains is smaller and the stability of the chemical bond is greater than between them. In the structures of certain minerals the chains are single, as for instance, in sillimanite  $Al[SiAlO_5]$ . In the structures of other minerals the chains are paired, these are the banded structures, an example of which is anthophyllite  $Mg_7[Si_4O_{11}]_2(OH)_2$ .

4. The distinguishing feature of *the layered* (foliated) structures consists in that the interplanary distances within the limits of the plane (layer) are smaller than between the planes (layers), and consequently the atoms are more firmly bound with the neighbouring atoms of the plane than with the atoms of another plane. Graphite, talc  $Mg_3[Si_4O_{10}](OH)_2$  and brucite  $Mg(OH)_2$  may serve to exemplify this structure.

5. *The frame* structures are characterized by a lace-patterned space connection of coordinate polyhedrons by all the common apexes or edges. In the large voids of the frame there can be situated large-sized atoms. Structures with frame motive are typical of quartz  $SiO_2$  and feldspar, for instance, albite  $Na[Si_3AlO_8]$ .

Within the framework of certain structural types it is possible to single out structural motives that are situated in the structures of minerals of atoms or their groupings. Thus, the sulphates characterized by an island type of structure comprise gypsum  $Ca[SO_4] \cdot 2H_2O$ , in which the layered motive of the  $H_2O$  molecules location and packings, formed by  $Ca^{2+}$  and  $[SO_4]^{2-}$  ions becomes apparent.

### Polymorphism and polymorphic transformations

The phenomenon of crystallization of matter with one and the same composition in the form of crystals of different systems was established in the last century and called *polymorphism*, and the transitions from one crystalline form into another—*polymorphic transformations* or *transitions*. Polymorphism of minerals implies a diversity of their crystalline structure with one and the same chemical composition. Minerals with identical composition but with different crystalline structure are called *polymorphic modifications*. The latter can be distinguished by their coordinate number. For instance, for the polymorphic modifications of the composition  $Al_2SiO_5$  for ions  $Al^{3+}$  the C.N. = 6 (disthene), 6 and 5 (andalusite), 6 and 4 (sillimanite). When the C.N. is the same, the polymorphic modifications are sometimes distinguished by the type of closest packing. Thus, the structure of sphalerite is based on the closest cubic packing of sulphuric ions and the structure of wurtzite of the same composition is hexagonal.

Polymorphic modifications are also widely spread among minerals. Their only distinguishing feature consists in that the identical coordinate groupings of atoms with one and the same motive are located in respect to one another at different angles. The structure of polymorphic modifications of this type is characterized by a frame motive. Polymorphic modifications of the composition  $SiO_2$ :  $\alpha$ - and  $\beta$ -quartz,  $\beta$ -cristobalite, tridymite and others. From the physical and

chemical points of view polymorphic modifications of minerals are phases characterized by stability within certain limits of temperature and pressure, which can be determined either experimentally or by means of calculations. Polymorphic transformations can be reversible (enantiotropic) and irreversible (monotropic). For instance, when heated up to 340° aragonite is monotropically transformed into calcite, when cooled, however, the reversible transformation does not take place. Enantiotropic transformation can be exemplified by the transmission of  $\alpha$ -quartz into  $\beta$ -quartz at the temperature of 573°. Polymorphic modifications of minerals are used as geothermometers and geobarometers.

Not infrequently polymorphic transformations take place with the outer form remaining unchanged. These formations are called *paramorphs*. The following types are often found:  $\beta$ -quartz by  $\alpha$ -quartz, calcite by aragonite, pyrite by marcasite.

### Polytypes of minerals

A large number of minerals with closest packing or layered structure, having identical interatomic distances and coordinate polyhedrons, differ from each other in an insignificant displacement of some of the layers and packings in respect to others. These displacements may be referred to as a dislocation or a shift at a certain angle. This results in a change in the periodicity of the alternating layers or packings with their inner structure remaining intact. These polymorphic modifications are called *polytypes* and phenomenon itself – *polytypism*. It has been established that graphite possesses two polytypes: the hexagonal graphite 2H and the rhombohedral graphite 3R, the figure 2 designates a sequence of alternating layers AB/AB/AB..., the figure 3 – ABC/ABC/ABC.... The literal symbol stands for the first letter of the cell's name: H – hexagonal, R – rhombohedral, M – monoclinic, O – orthorhombic etc. The formation of polytypes is accounted for by the peculiarities of the layer growth, various degrees of structural regularity and so on.

## Structural Imperfections of Minerals

Minerals are not ideal, but real systems of interacting atoms characterized by break-downs in the periodicity of crystalline structure.

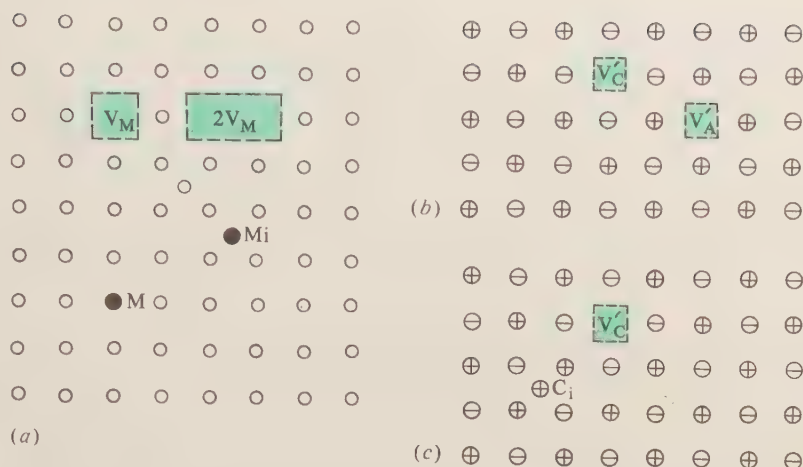
### Point defects

Elementary imperfections in the structure of minerals are called point defects or vacancies and interstitial atoms. The concentration of these defects is mainly connected with thermal conditions of formation, i.e. they are in a state of equilibrium with temperature. Hence, point defects are called *thermal* or *equilibrium*.

The vacancies of  $V$  atoms represent free, unoccupied positions of atoms in an ideal crystalline structure (Fig. 9a). For instance, vacancies of copper  $V_{Cu}$  atoms in the crystals of native copper, can be referred to them. For minerals of a more complex composition, for example, in the ionic crystals there may be cation  $V_C$  and the anion  $V_A$  vacancies. *Interstitial atoms*  $M_i$  may be described as atoms displaced from their positions into neighbouring interstitials. (Fig. 9b). The coordination number of the implanted atom may differ from the C.N. in its usual position; thus, for instance in halite NaCl the interstitial atoms  $Na_i$  fill the free tetrahedral voids with C.N. = 4.

Fig. 9. Types of point defects:

$a$ —in metal:  $M$ —admixing atom of replacement,  $V_M$ —vacancy  
 $M_i$ —interlattice atom,  
 $A_i$ —admixing interlattice atom (penetration),  
 $2V_M$ —divacancy;  $b$ —a pair: cation  $V_C$  and anion  $V_A$  vacancies in an ionic crystal (Schottky defect);  
 $c$ —a pair of cation vacancy  $V_C$  and interstitial cation  $C_i$  in an ionic crystal (Frenkel defect)



Point defects of minerals (excluding native ones) are characterized by *excess* or *effective charges*. For instance, anion vacancy has a redundant positive charge marked by dots:  $V_A^{\cdot}$ , while the cation vacancy has a negative charge and is indicated by a stroke:  $V_C^{\prime}$ . The interstitial ions have a redundant charge and a sign corresponding to their valency. Thus, in fluorite  $\text{CaF}_2$  the interstitial fluorine ion has a redundant negative charge:  $F_i^{\prime}$ .

Various types of point defects that have redundant charges different in value and sign, are, as a rule, synchronically present in minerals. A complete volumetric or local compensation of redundant charges of different sign results from the necessity to observe an electrostatic neutrality. In the case of local compensation of their own point defects paired and more complex associative defects are formed. The pair comprising an interstitial atom and the atom vacancy [ $M_i V_M$ ] is called *Frenkel defect*. Twinned anion and cation vacancies [ $V_C^{\prime} V_A^{\cdot}$ ]<sup>x</sup> represent the *Schottky defect* with the neutral charge (marked by a slanted cross).

*Nonequilibrium* point defects usually comprise radiational defects which result from the dislocation of atoms along the trajectory of particles with high energy connected with the disintegration of radioactive elements and the formation of tracks. The concentration of tracks exposed by the etching of mineral surface is proportional to the dose of radiation treatment and is thus used to determine the absolute age of minerals. In the case of high concentration of radiational defects the crystalline structure of a number of minerals containing radioactive elements may be disintegrated and be transmitted into a *metamict* state which (in its turn) closely resembles glassy and amorphous states (pyrochlore, zircon, samarskite and others). When these minerals are heated the conserved energy of their metamict disintegration is most actively released. As a result of this metamict minerals are brought to red heat, and when cooled their decrystallization takes place.

*The linear defects.* The law-governed deviations from the ideal location of atoms along certain directions (lines) in the crystalline structure of minerals are called *dislocations* and may be brought under two types (Fig. 10): edge and screw dislocations. The edge dislocation

Fig. 10. Edge (a) and screw (b) dislocations

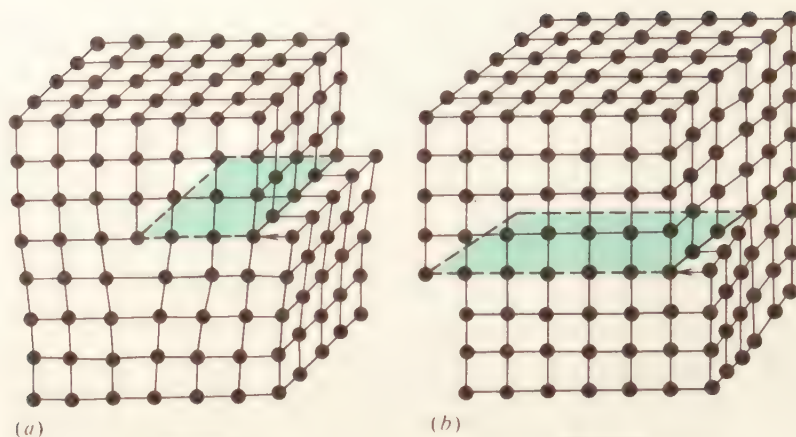
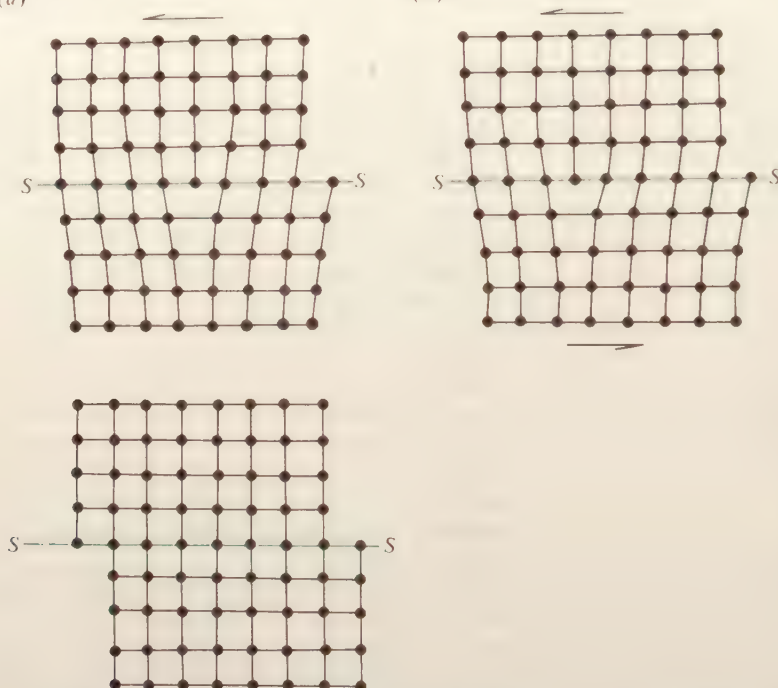


Fig. 11. The formation and the gliding of edge dislocation under mechanical deformation of minerals



corresponds to a half-plane or the presence of an additional incomplete atom net in the structure of mineral. The half-plane of 'implantation' is delimited by a line or edge of dislocation. Screw dislocations represent lines, along which atom planes are dislocated with the result that screw steps are formed. Along the dislocation lines tense conditions in the structure are developed. They are the states of compression and extension. The atoms here are in unusual coordinations with unsaturated bonds, as a result of which dislocation acquires redundant charges. The edge dislocation often results from mechanical deformations or shifts of the crystalline structure of minerals accompanied by a change of the form of crystalline grains (Fig. 11). On the other hand, the process of growth is typical of the screw dislocations.

Admixtures of various elements usually coincide with the dislocation lines in minerals. Changes in the mechanical properties and the morphology of minerals are also connected with dislocation. The latter usually becomes apparent when the method of etching is applied, and the etching marks can be observed under the microscope.

### The surface and boundaries of grains

represent dimetric defects characterized by the irregular location of atoms and the redundant surface energy. They are distinguished by a higher chemical activity, composition and coordination of atoms. The surface has a growth and deformation nature.

### Volume defects

are not connected with the crystalline structure of minerals. They may be regarded as the imperfections of mineral individuals.

## The Finely Dispersed State of Minerals

Minerals in a finely dispersed state differ from the holocrystalline minerals by the absence of remote order in their atomic structure.

This state is characteristic of solidified supercooled glasseous fluids. For instance, obsidian glass resulting from the rapid cooling of the erupted magma, as well as glasseous impactites formed as a result of meteoritic explosions. Certain minerals are also found in an amorphous state in surface conditions. Special mention should be made of opal  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ , composed of the smallest (up to  $1 \mu$ ) globules of amorphous silica with regular closest packing, with the noble varieties of this mineral having greater order.

The *colloidal state* is characteristic of such natural heterogeneous systems in which the finely dispersed particles are in a dispersed environment which is either water solution, gas, or a solid body. The finely dispersed particles whose dimensions are usually within the range covering fractions of micrometres to several dozens, can have a crystalline structure and even the form of microcrystals. However, they differ from large particles and crystals in that their surface has certain properties connected with the fact that matter in a finely dispersed state has a high specific surface. Suffice it to say that  $1 \text{ cm}^3$  of finely dispersed matter with the average dimensions of the particle approximately  $1 \mu$  has a surface of several hundred or even thousand square metres. These particles have a high degree of adsorption. The adsorption of ions or molecules on the surface of the particles leads to the formation of *mycelle* with an equal surface charge.

In the water solution the mycelle is maintained in a suspended state by the forces of electrostatic repulsion. The colloidal systems—*sols*—are widely spread in nature. The fine suspension of silica or clay minerals in water can serve as an example of *hydrosols*. *Hydrogels* in a colloidal and dispersed state are formed as a result of coagulation and sedimentation of hydrosols. An example of *aerosols* is the mineral dust in air. The tiniest particles of gold scattered in pyrite can be regarded as *crystalloqels*. In the case of hydromica and clay particles coagulation the formation of finely dispersed mixed-layered aggregates with a practically identical orientation of agglutinated scale characterized by a fairly distinct remote order, is possible.

The colloidal and dispersed systems and phases usually occur in surface conditions under mechanical or chemical disintegration of

minerals. In endogenic conditions the formation of colloidal and dispersed phases may be conditioned by the saturation of mineral forming water solutions resulting, for instance, from fluctuations in pressure. Presumably this is precisely how coliformous aggregates of cassiterite (wood tin), pitchblende, sphalerite (brookite) and others are formed. The colloidal and dispersed phases usually have cryptocrystalline structure and form earthy porous or dense masses of irregular or sintered form.

## The Chemical Composition of Minerals

### The Characteristic Features

The chemical nature of minerals is determined by the main or *species forming* elements the content of which usually amounts to units and tens of per cent by mass. In minerals they are found to be in a particularly quantitative relationship multiple to the prime numbers. Numerous minerals have a constant chemical composition, for example, quartz  $\text{SiO}_2$ , diamond C, antimonite  $\text{Sb}_2\text{S}_3$ . However, minerals of variable composition, with various content of separate or all species forming minerals as well as foreign admixtures are much more widely spread. For instance, in native gold the presence of several per cent of silver and copper the content of which in samples from different deposits is different, is usual. In minerals of more complex composition the content of only a part of the elements, but not all of them is often variable. Thus, in olivine each cell of the structure contains a constant number of oxygen and silicon atoms, and only the content of magnesium and iron is variable, though their sum remains unchanged.

Variability in the content of admixtures in minerals is very great even for one and the same mineral species. The form of their entering in minerals is varied. A part of them is connected with the mechanical inclusions of minerals of another composition. The chemical impurities mainly occupy the positions of species forming elements, functioning as their quasi-substitutes, or are located in the interstices of the crystalline structure. Besides, the chemical impurities often correspond to the dislocations or are concentrated on the boundaries of individuals in the crystallogrammed mineral aggregates, and are also adsorbed in dispersed minerals. Certain deviations from the ideal chemical composition of minerals may be connected with *unstoichiometry*. Minerals of the latter type, as a rule, are distinguished by a high concentration of anion or cation vacancies and unusual charges of ions. The unstoichiometry of minerals is often conditioned by the entering of the interstitial ions, the redundant charges of which are compensated by an increase in the ionic charges of the opposite sign.

### Isomorphism

The development of concepts pertaining to the nature and variability of the chemical composition of minerals is connected with the study of isomorphism which was initiated by E. Mitscherlich (1819). For a more detailed study of the concept of 'isomorphism' and

the broadening of its content we are indebted to the works of D. I. Mendeleev, V. I. Vernadsky, V. M. Goldschmidt, A. Ye. Fersman, N. V. Belov, V. I. Lebedev, V. S. Urusov and others.

The concept of *isomorphic elements*, or *components*, forming *isomorphic mixtures* or *solid solutions* are at present widely used in mineralogy. The extreme terms of the isomorphic mixtures are called *isomorphic minerals* and form *isomorphic series*. In accordance with the degree of miscibility in isomorphic series the following types of isomorphism are distinguished: *unlimited* (perfected) and *limited* (imperfect). Examples of the former are the isomorphic series of wolframite (hübnerite  $MnWO_4$ –ferberite  $FeWO_4$ ) and the series of olivine (forsterite  $Mg_2[SiO_4]$ –fayalite  $Fe_2[SiO_4]$ ). The imperfect isomorphism has been established between orthoclase  $K[Si_3AlO_8]$  and anorthite  $Ca[Si_2Al_2O_8]$ , between Zn and Fe in sphalerite etc.

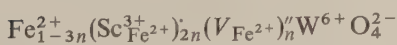
A considerable flexibility of the chemical composition of minerals causes a regular change of their structural parameters, density, hardness, refractive indices. The influence of smaller isomorphic impurities on the physical properties is insignificant, but sometimes a sharp change of the electrical properties, the emergence of colour and luminescence is connected with such impurities. The impact exercised by them on the surface properties of minerals is also significant.

Isomorphic components are atoms of elements, simple ions, their groupings, radicals or molecules. In the simplest case isomorphic components—simple and complex ions—have a similar charge, which corresponds to *isovalent isomorphism*, as for instance, in the isomorphic series of wolframite and olivine.

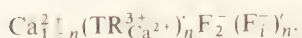
In nature *heterovalent isomorphism* accompanied by the interchangeability of ions of different valency is more widely spread. Heterovalent isomorphism always goes hand in hand with the conditions set by the valency balance, i.e. the compensation of redundant charges of ions that have greater or smaller valency as compared with that of the replacing ions.

Heterovalent isomorphism with the retention of the general number of atoms can be manifested in various ways: (1) conjugate replacement of the pairs: cation-anion; for example, in fluorite there is a replacement of the  $Ca^{2+}$  ions by the  $TR^{3+}$  ions and of the  $F^-$  ions by the  $O^{2-}$  ions according to the pattern:  $Ca_{1-n}(TR_{Ca^{2+}}^{3+})_n F_{2-n}(O_{F^-}^{2-})_n$ ; (2) the replacement of two similar atoms by two atoms of different elements of different valency with the retention of the summary charge of the type  $2R^{4+} \rightleftharpoons R^{2+} + R^{4+}$ , for example, in cassiterite, according to the pattern:  $Sn_{1-2n}^{4+}(Fe_{Sn^{4+}}^{2+})_n \times (W_{Sn^{4+}}^{6+})_n O_{2n}^{2-}$ ; (3) the replacement of two pairs of atoms of different elements with the retention of the summary charge of the type  $R^+ + R^{4+} \rightleftharpoons R^{2+} + R^{3+}$ , for example in plagioclases according to the pattern:  $Na_{1-n}^+(Ca_{Na^+}^{2+})_n [Si_{3-n}^{4+}Al^{3+}(Al_{Si^{4+}}^{3+})_n O_8^{2-}]$ .

Under heterovalent isomorphic replacements accompanied by a change in the number of atoms in the structure of minerals, the compensation of the redundant charges that takes place in some cases is marked off by the formation of the vacancies of atoms of the type  $R_3^{2+} \rightarrow R_2^{3+}(V_R)$ , as is the case in fluorite:  $Ca_{1-3n}^{2+}(TR_{Ca^{2+}}^{3+})_{2n}(V_{Ca^{2+}})_n F_2$ — or ferberite:



In other cases the isomorphic replacements take place with the filling of the interstitial positions, for example in fluorite by replacing the  $\text{Ca}^{2+}$  ions by the  $\text{TR}^{3+}$  ions with a synchronous entering of the  $\text{F}_i^-$  ion into the interstitial position according to the pattern:



One of the main conditions of isomorphism is *the proximity of dimensional parameters of isomorphic components* or the volume of the elementary cell of the isomorphic minerals and the atomic radii of isomorphic elements and ions. According to V. M. Goldschmidt's rule in ionic crystals of simple composition and analogous structure the relationship of the difference of ionic radii of isomorphic ions to the radius of the smaller ions ( $\Delta r/r$ ) should not exceed 15%. However in minerals of more complex composition and structure this value reaches 40%.

Another important condition of isomorphism is the similarity of electronic structure of isomorphic elements, *the proximity of their chemical properties* and, consequently, *the character of the chemical bond* in isomorphic minerals. The univalent ions  $\text{Na}^+$  and  $\text{Cu}^+$ , closely related in size and having different electronic structure, are never interchangeable in minerals. Minerals with an ionic type of chemical bond are non-isomorphic with minerals characterized by a covalent chemical bond, even if their crystalline structure is uniform. These *isostructural* minerals can be exemplified by sylvite  $\text{KCl}$  and galenite  $\text{PbS}$ .

One more condition of isomorphism is determined by *the rule of polarity*, in accordance with which the entering of the ion with smaller radius or greater charge into the general crystalline structure is more preferable as compared with the ion of greater radius and smaller charge. The examples of polar isomorphism are: heterovalent series  $\text{Li}^+$  (0.069)– $\text{Mg}^{2+}$  (0.075)– $\text{Sc}^{3+}$  (0.081)– $\text{Zr}^{4+}$  (0.082) in magnesian micas and  $\text{Na}^+$  (0.098)– $\text{Ca}^{2+}$  (0.105)– $\text{Y}^{3+}$  (0.106) in pyrochlore and other rare-earth minerals, where the value of ionic radii in nanometres is given in brackets.

The significance of external *physicochemical factors* of isomorphism was brought out by V. I. Vernadsky who was the first to show that isomorphic elements in minerals form natural associations, or isomorphic series.

As compared with low temperature conditions the limits of isomorphic miscibility of a large number of minerals of variable composition are widened at high temperature. This often leads to the formation of perfect solid solutions with unlimited miscibility. The composition of feldspars of various origin can serve as an example of the influence exercised by the temperature conditions of formation on the miscibility of a solid solution. Figure 12 exemplifies triple diagram of the three-component solid composition of orthoclase  $\text{K}[\text{Si}_3\text{AlO}_8]$ –albite  $\text{Na}[\text{Si}_3\text{AlO}_8]$ –anorthite  $\text{Ca}[\text{Si}_2\text{Al}_2\text{O}_8]$ . These diagrams clearly show the widening of the miscibility field with the growth of temperature formation.

The temperature range of continuous solid solution and its disintegration are given in the diagram of composition and temperature (Fig. 13). Above the disintegration curve of the two-component solid solution *A-B* we have the area of the solid



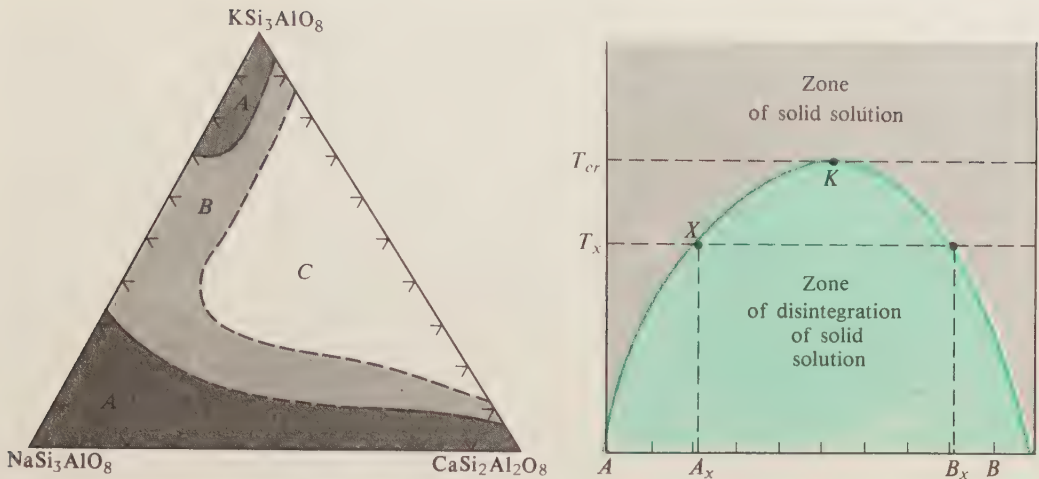


Fig. 12. Fields of isomorphic miscibility in the system of orthoclase-albite-anorthite:  
 A—field of stability of the solid solution at all temperatures; B—only when the temperature is higher than  $1000^\circ\text{C}$ ;  
 C—field of nonmiscibility

Fig. 13. The diagram shows the disintegration of the solid solution A-B:  
 AkB—curve of disintegration;  $T_{cr}$ —critical temperature of disintegration;  
 $T_x$ —temperature of disintegration of the solid solution of the composition X;  $A_x$  and  $B_x$ —chemical composition of the products of the disintegration of the solid solution

solution of unlimited miscibility. Below the critical temperature  $T_{cr}$  the solid solution is unstable. At the temperature  $T_x$  as a result of the disintegration of the solid solution of the composition X two phases of the composition  $A_x$  and  $B_x$  are formed. The quantitative relationship between them is determined by the composition of the solid solution.

The disintegration products in the form of plate, needle and rounded extraction of minerals usually have a regular crystallographical orientation. The disintegration of a solid solution begins with diffusion (or dislocation) of atoms in crystals with their ordering or segregation at dislocations. The disintegration of solid solutions does not take place if the diffusion velocity is small, and the velocity of cooling the crystals is high. Thus, for instance, when volcanic eruptions of liparite magmas take place the sanidine crystals (K, Na)  $[\text{Si}_3\text{AlO}_8]$  are cooled at a greater speed as a result of which they remain homogeneous. In contrast to them the soda-potash feldspars of granites or pegmatites whose cooling is considerably slower always have regularly oriented inclusions of perthitic intergrowths of albite. Insignificant isomorphic impurities of iron replacing the positions of aluminium in high-temperature feldspar can be extracted in the form of the smallest plate inclusions of hematite when cooled and then cause pink colouring.

Structures revealing the disintegration of solid solutions are comparatively widely spread in minerals. They are not accessible to the naked eye. Exceptions include disintegrating structures in feldspars. Similarly oriented perthites of white albite in green miclocline (amazonite) are particularly visible. Since the temperature of disintegration of solid solution corresponds to the minimal temperature of crystallization, the minerals with disintegrating structure can be used as geothermometers.

In a large number of minerals the disintegrating structures are unstable. The oriented inclusions are often segregated into larger extractions with the formation of grained intergrowths of two minerals. The recrystallization of disintegrating structures has been discovered in, for example, marmatite and titanomagnetite.

The influence of pressure on the perfection of solid solutions and their disintegration of minerals has not yet been adequately studied.

According to experimental data its increase in a large number of cases decreases the reciprocal solubility of the components.

In a large number of cases the restriction of isomorphic miscibility is connected not so much with the crystallochemical factors, pressure and temperature, as with the concentration of impurities. The microisomorphism of minerals can be explained by a concentrational factor. For instance, the low content of Cd in sphalerite, Ni in olivine, Cr in beryl is usually and primarily conditioned by a low concentration of these impurities in the mineral-forming environment. In some cases the isomorphic miscibility depends on the relationship of ionic concentration of one and the same element of different valency connected with the reduction-oxidation conditions of mineral formation. Thus, the content of molybdenum in molybdooscheelite  $\text{Ca}[(\text{W}, \text{Mo})\text{O}_4]$  depends, in a large number of cases, not only on temperature, but also on whether its form in the mineral-forming solutions is oxidized or reduced.

## The Role of Water and Other Oxyhydrogen Groupings in Minerals

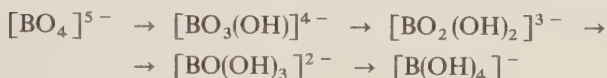
Among the species-forming elements hydrogen holds the leading place. It enters into the composition of over 2 000 mineral species. In minerals hydrogen almost invariably forms oxyhydrogen groupings of various types.\* The heating of minerals containing hydrogen results in the extraction of water. The separation of water takes place within one or several intervals of temperature which shows various degrees of strength, and consequently, various types of bond sustaining water molecules. The following forms of water in minerals have been established.

*The constitutional water* entering into the composition of minerals in the form of hydroxyl anion groups  $(\text{OH})^-$  forms stronger bonds with crystalline structure. The hydroxyl group enters into the composition of numerous minerals of silicates, oxygenous salts and oxides. In the silicate structures it is usually isomorphic with the fluorine ions  $\text{F}^-$  as in topaz  $\text{Al}_2[\text{SiO}_4](\text{OH}, \text{F})_2$ , phlogopite  $\text{K}(\text{Mg}, \text{Fe})_3[\text{Si}_3\text{AlO}_{10}](\text{OH}, \text{F})_2$ .

The heating of hydroxides, as for example brucite, is accompanied by the extraction of water and the formation of simple oxides, as in the case of periclase  $\text{MgO}$  according to the set:  $\text{Mg}(\text{OH})_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$ . There are fewer cases when hydrogen enters into the composition of oxygenous salts, as in oxygenous carbonate of the  $\text{Na}[\text{HCO}_3]$  type, at the heating of which anhydrous salt is formed and the separation of water and carbonic acid takes place according to the set:  $2\text{Na}[\text{HCO}_3] \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ . Besides, water can be found in certain minerals in the form of oxonium ion  $(\text{H}_3\text{O})^+$ , which usually replaces large cations  $\text{K}^+$ , in particular, in layered silicate structures.

\* Various hydrocarbons that sometimes enter into the composition of minerals can be regarded as an exception. This may also refer to ammonium ions  $(\text{NH}_4)^+$ ; besides it is assumed that there are hydrides of metals in the depths of the earth.

The crystallization water forms looser bonds in minerals. Two of its types are clearly distinguished: the *crystallohydrate* and the *zeolite water*; when heated, the crystallohydrate water is usually separated by degrees within a wide range of temperature. There are two varieties of crystallohydrate water: the *cation* and the *anion water*. The colour of minerals is often connected with the hydrated ions of the transition group of elements. Thus, for instance, the bright-blue colour of chalcantite  $\text{Cu}[\text{SO}_4] \cdot 5\text{H}_2\text{O}$  is accounted for by the absorption of light on the hydrated complexes  $\text{Cu}(\text{H}_2\text{O})_4$ . The mineral loses its colour when it is either heated or dehydrated. Saturation leads to the restoration of colour. Anion crystallohydrate water is typical of a vast majority of borates. Hydroxyl groups coordinate the boron ions instead of oxygenous in tetrahedral radicals of the following simplest series of the types:



A large number of sulphates of bivalent metals serve as an example of minerals containing both varieties of crystallohydrated water. In the said chalcantite the fifth molecule of water functions as a sort of buffer by encircling both the cation and anion.

The zeolite water enters into the composition of minerals with a stronger (more stable) crystalline structure, occupying in it large cavities and channels. Typical representatives of these minerals are aluminosilicates with framework structure, zeolites and several others, as for instance alkaline beryl and diopside; when heated up to  $500^\circ\text{C}$  zeolites gradually dehydrated without drops while the structure of their aluminosilicate framework remains unchanged. When dehydrated zeolites are saturated the quantity of  $\text{H}_2\text{O}$  molecules is restored.

*Adsorbed water* with the lowest degree of stability as far as its bond is concerned is separated when minerals are heated up to  $110^\circ\text{C}$ . The most widely-spread variety of this type of water—the *hygroscopic water*—is retained at the surface of mineral grains and fills in the intergranular space, thus forming continuous and interrupted lamination. Hence, the content of the hygroscopic water in minerals is proportional to their density area. Large and perfect crystals, for example, rock crystals, hardly contains any hygroscopic water at all. It is the opposite with the cryptocrystalline (fibrous spherulite) chalcedony or the fine-dispersed opal which contain a greater amount of water—up to 5.5 and 20 weight respectively. In clay and other layered minerals the molecules of adsorbed water may be located between the layers (packages); with the growth of saturation of *interlayer* water the distance between the packages increases. For example, the specific volume of the preliminarily dried montmorillonite during the water saturation becomes 2.5 times greater.

A certain portion of water contained in minerals enters into the composition of gaseous-liquid inclusions. The content of such water does not usually exceed 1 weight.

The investigation of the content and forms of the water entering into minerals is conducted by the methods of the thermal analysis, infrared spectroscopy and nuclear (proton) magnetic resonance. The isotopic composition of hydrogen in minerals is studied by applying the methods of mass-spectroscopy.

## Crystallochemical Formulae of Minerals

There are several ways of expressing the chemical composition of minerals in a concise form. It is usual for the results of the chemical analyses to be recalculated for molecular and atomic ratios, and then presented in the form of empirical, crystallochemical formulae or on diagrams of the composition.

A recalculation for the chemical formula presupposes the following succession of steps. Mass percentage of each component (in the form of oxides or elements) is to be divided by a corresponding molecular or atomic mass, and the figures thus received—molecular or atomic quantities—should be brought to prime numbers, which show in what proportions (quantitative relationships) the components entering into the composition of minerals are present. An example of the simplest calculation of the chemical analysis of chalcopyrite for the chemical formula is given below:

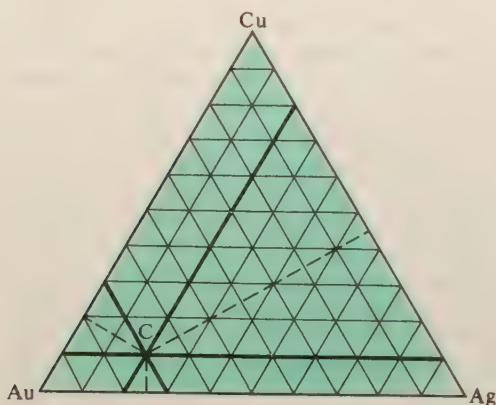
Components (atoms)	Content weight, %	Atomic mass	Atomic quantities ( $\times 1000$ )	Atomic ratios
Fe	30.47	55.80	544	1
Cu	34.40	63.50	541	1
S	35.87	32.07	1120	2
Total	100.74			

The atomic ratios thus obtained enable us to express the chemical composition of chalcopyrite in the form of the empirical formula  $\text{CuFeS}_2$ , where alongside with the chemical symbol of sulphur we have the index 2, which shows that the content of the sulphur atoms is twice as greater as the atoms of copper or iron whose symbols are not provided with any index in print.

It is also possible to proceed from the permanent context of a certain element or their sum. Thus, for instance, if we assume that in pyroxene the content of oxygen atoms corresponds to the theoretical composition, i.e. equals 6, then the calculation of the chemical analysis of this mineral can be conducted according to the pattern given below. In order that the coefficients for each atom could be received, it is found necessary to divide the atomic quantities of each element by a common divisor which is calculated by dividing the sum of the atomic quantities of oxygen by 6.

The following is a chemical analysis of pyroxene for the crystallochemical formula of oxygen:

Fig. 14. A graphic illustration of the composition in the tricomponent Au-Ag-Cu system



Components	Content (weight)	Molecular mass	Molecular quantities ( $\times 10\,000$ )	Atomic quantities of		
				cations	oxygen	Coefficients of atomic ratios
SiO <sub>2</sub>	52.25	60.09	8696	8696	17392	1.920
TiO <sub>2</sub>	0.72	79.90	90	90	180	0.019
Al <sub>2</sub> O <sub>3</sub>	2.54	101.94	249	498	747	0.110
Fe <sub>2</sub> O <sub>3</sub>	1.81	159.70	114	228	342	0.050
FeO	1.95	71.85	271	271	271	0.059
MnO	0.64	70.94	90	90	90	0.019
MgO	14.97	40.32	3713	3713	3713	0.819
CaO	24.38	56.08	4348	4348	4348	0.960
Na <sub>2</sub> O	0.56	61.98	90	180	90	0.039
Total	99.93			Divider: 27 173 : 6 = 4529		



The composition of a mineral can also be expressed on a composition diagram. Thus, the chemical composition of a three-component mineral may be shown by a point on a triangular diagram (Fig. 14). Each of its apexes corresponds to 100% of the ion content of one of the components in the absence of the two other components. Each point on the sides of the triangle corresponds to 100% content of the sum of the two components in the absence of the third component. Any point within the triangle corresponds to 100% of the sum of the three components. To determine the composition at such a point it would suffice to measure the length of the perpendiculars dropped from it on all the three sides. The length of the perpendicular dropped on any of the sides expressed as a percentage, corresponds to the content of the component of the opposite apex. To mark the composition of the mineral containing 70 atomic percent Au, 20 atomic per cent Ag and 10 atomic percent Cu on a three-component diagram it is necessary and sufficient to lay off first a line with an equal content of one component (70% Au). It will be parallel to the side (Ag-Cu), opposite to the apex of this component. Similarly a second line is laid off with an equal content of another component (20% Ag). The point of intersection of lines will correspond to composition of mineral; plotting of third line is not required.

In order that the chemical and the structural nature of minerals, i.e. their constitution, may be expressed in formulae, the results of the chemical analyses are recalculated for the *crystallochemical formulae*. A calculation of this kind can be accomplished only if the crystalline structure is identified or the parameters of the elementary cell of the given species of mineral are measured, the physical properties and the types of isomorphic replacements are studied and the forms of water in the composition of minerals are determined. The calculation of formulae should be based on the general number of atoms corresponding to a single elementary cell. The formula, in its written form, should acquire a more simplified form with the number of elementary units of the formula reduced.

When recording formulae it is customary to record cations and anions separately with the former preceding the latter—the simple and the complex varieties. In crystallochemical formulae the atoms situated in identical structural positions, i.e. those that are isomorphic, are recorded as separate groups; the symbols of isomorphic elements in theoretical formulae are placed within round brackets separated by commas, with those that are predominantly species-forming coming first, followed by secondary and admixing elements. Anion radicals are usually inserted into the square brackets, while round brackets serve to enclose additional anions.

Structural distinguishing features of minerals can also be reflected in crystallochemical formulae. Partial information on the structure is contained in the form of radical recording. For instance,  $[\text{SiO}_4]^{4-}$  and  $[\text{Si}_2\text{O}_7]^{6-}$  correspond to single and doubled island radicals, and  $[\text{Si}_6\text{O}_{18}]^{12-}$  belongs to the ring radical. The structure of cyclosilicates, inosilicates, nesosilicates, sorosilicates and tectosilicates is determined in the same way.

## The Morphology of Minerals

### Outer Appearance of Minerals

Minerals are practically always in the form of monomineral or polymineral *intergrowths* or *aggregates*. Mineral individuals entering into the composition of aggregates are distinguished by their outer appearance, i.e. size and morphology.

#### The size of minerals

Mineral individuals can be of various size—from the tiniest particles distinguished only under a microscope with ten- or even hundred-fold increase of their dimensions to gigantic crystals whose volume equals tens of cubic metres. Depending on their size the following types are distinguished: finely dispersed ( $10^{-6}$  m and less) and cryptocrystalline ( $10^{-6}$ - $10^{-5}$  cm) individuals, not identifiable without a microscope, fine-grained ( $10^{-5}$ - $10^{-4}$  m), close-grained ( $10^{-4}$ - $10^{-3}$  m), medium-grained ( $10^{-3}$ - $10^{-2}$  m), coarse-grained ( $10^{-2}$ - $10^{-1}$  m) and gigantic ( $> 10^{-1}$  m) individuals that are respectively clearly identifiable under a microscope, a magnifying glass or the naked eye. Some minerals never form large crystals. Thus, for instance, the size of the clay mineral particles is always smaller the hundredths or even the thousandths of a millimetre. Minerals are more often represented by smaller crystalline grains whose size does not exceed several millimetres. A large number of them, particularly quartz, feldspar, mica and others can be found in the form of the tiniest grains and very large crystals. For instance, the cryptocrystalline variety of quartz—chalcedony—consists of the finest crystalline fibres whose width equals hundredths of a millimetre and even less. However, there are crystals of quartz weighing several tons. The record is with the gigantic crystals of feldspar weighing more than 100 tons. They are often found in the ceramic pegmatites in Karelia.

**The degree of idiomorphism**

serves as an important morphological feature of minerals. Faced mineral individuals of regular form are called *idiomorphic*. As a rule, the crystals of the following minerals are idiomorphic: diamond, quartz and sanidine in effusive rocks, magnetite in metamorphic rocks, zircon in alkaline pegmatites. It has also been ascertained by magnifying that the smallest particles of kaolinite clay are idiomorphic too. The degree of relative idiomorphism in a large number of cases reflects the consecutive character of crystallization of mineral individuals and is consequently used when studying the age relationships of minerals.

The morphology of minerals characterized by the degree of isometricity, is expressed in various relationship of their length, width and thickness. In conjunction with what has been said here morphological types, and varieties of minerals are singled out. Isometric crystals or grains have identical dimensions in all three directions. For instance, the crystals of diamond, magnetite, garnet, sphalerite and pyrite are isometric.

Minerals of the non-isometric shape are not equal in size in different directions. With minerals of the elongated type the length is considerably greater than thickness. Among them we distinguish the rod-like, the acicular, the fibrous, or the thread-like varieties. Tourmaline, beryl, natrolite, scapolite, jamesonite, chrysolite-asbestos and others serve as examples of the elongated minerals. Flattened

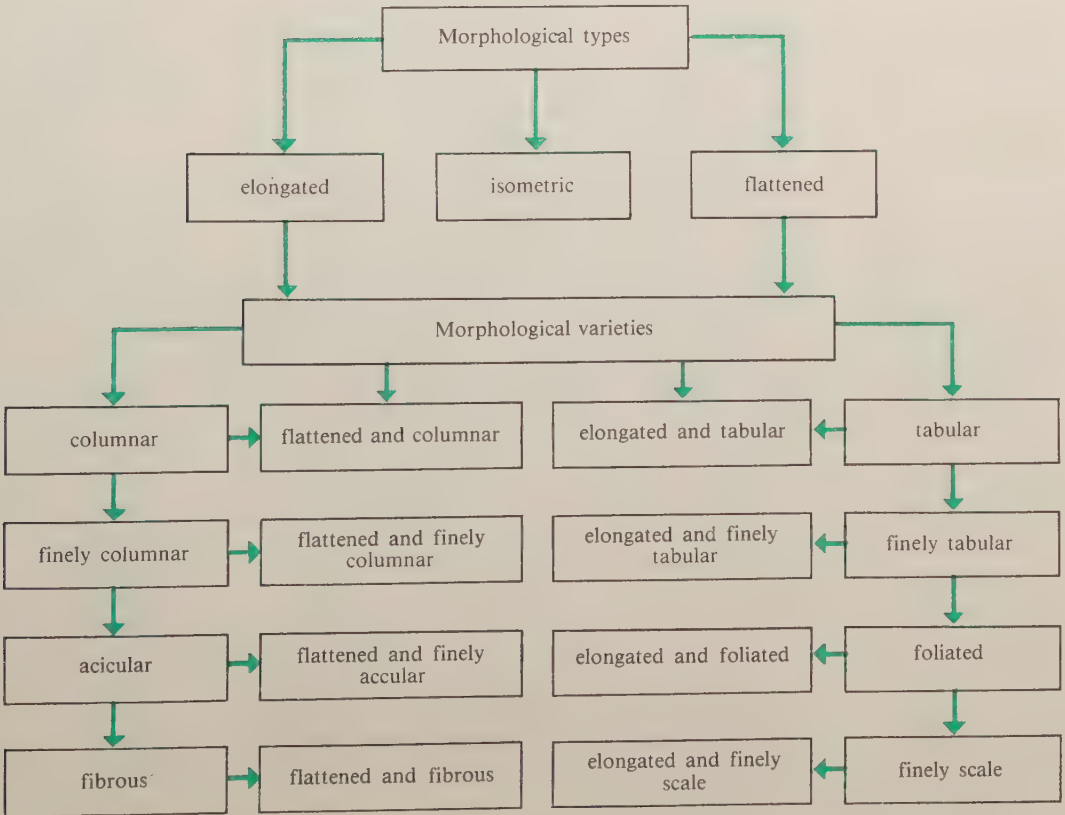
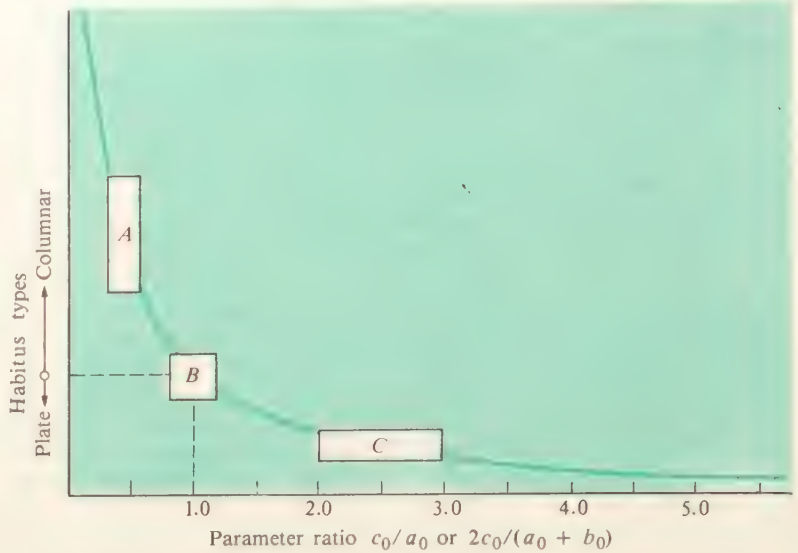


Fig. 15. The dependence of main morphological types of mineral crystals on the parameter ratio of the elementary cell (according to I. Kostov):

A – elongated;  
B – isometric; C – flattened (tabular) individuals

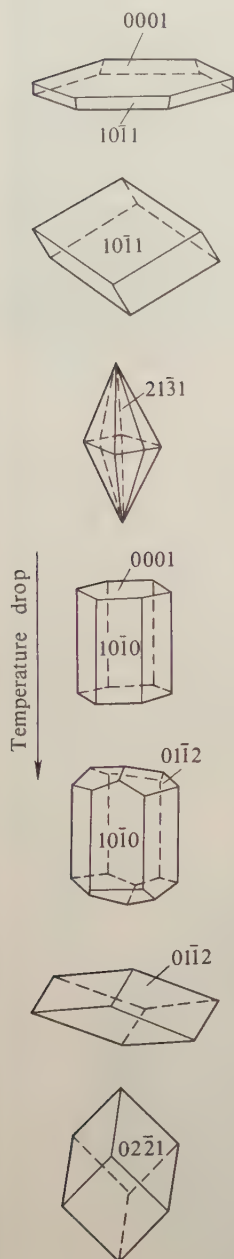


minerals are distinguished by their thickness which is smaller than width. They are represented by tabular, foliated and imbricate varieties. As a rule the flattened shape is characteristic of ilmenite, hematite, biotite, chlorite, tornbernite and others. The flattened-and-elongated and the elongated-and-flattened morphological subtypes are intermediate and are typical of a large number of minerals. Wollastonite, spodumene, cyanite, antimonite and others can exemplify the former. Columbite, gypsum and barite are usually found to represent the latter subtype.

The morphology of minerals is largely predetermined by the characteristic features of their crystalline structure. For instance, minerals with inosilicate and inosilicate structural motive are found more often in the form of elongated individuals, while those with layered motive have the form of flattened individuals. Minerals with the closest cubic packing of atoms are usually isometric. They are flattened or elongated if the packing is hexagonal. The outer form of faced mineral individuals, or their *habit*, is determined by the predominance of faces of various simple forms. Minerals are most frequently found in the form of crystals whose faces are characterized by a dense distribution of atoms, i.e. by maximum reticular density. Hence, minerals of the cubic system with a primitive cell usually occur as cubes, since this face possesses maximum reticular density. In the body-centered cell the flatness, corresponding to the faces of the rhombododehedron have greater density. In the face-centered cell they correspond to the faces of the octahedron. The mineral habit of medium and lowest category of symmetry also depends on the parameters of elementary cell. If the ratio of the parameters  $c_0/a_0$  and  $2c_0/a_0 + b_0$  approaches 1, the minerals are more often found in the form of isometric crystals. Most of the minerals of the elongated morphological type are different from them in that the ratio of the same parameters is smaller and that of the flattened type is greater than one (Fig. 15).



Fig. 16. The morpho-genetic series of calcite (according to I. Kostov)



The habit of minerals pertaining to one and the same system is determined by their affinity to this or that class of symmetry and by the degree of the development of corresponding simple form faces. Thus, for instance, the pyrite crystals are often found in the form of cubes, pentagondodecahedrons, octahedrons or their combinations, but are never covered by the tetrahedron or rhombododecahedron faces.

The habit of minerals also depends on the conditions of formation. Thus, a gradual change in the habit of calcite from its pinacoidal to pointed rhombohedron nature corresponds to the change from the high-temperature conditions of crystallization to the low-temperature conditions (Fig. 16). The short-prismatic or the bipyramidal habit of zircon is characteristic of alkali rocks and pegmatites, while the elongated-prismatic habit is characteristic of granites and granite pegmatites.

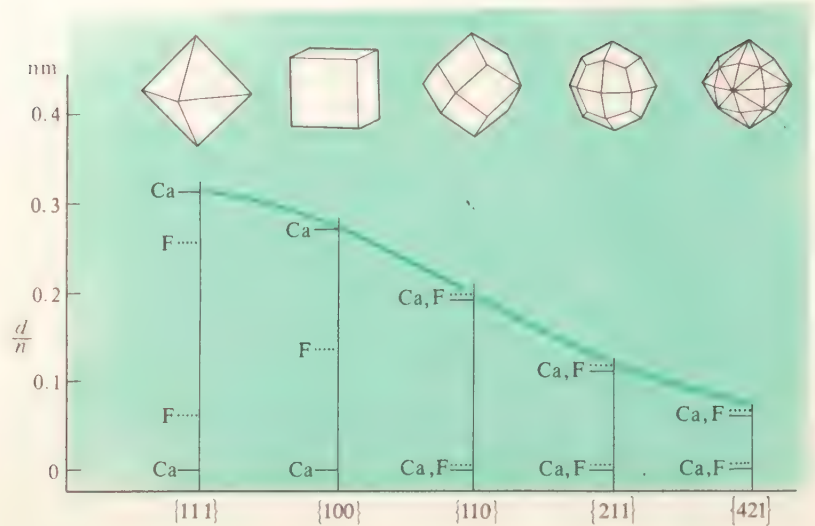
The change of mineral habit in the process of growth is traced on the crystals of rhythmic-and-zonal or zonal-and-sectorial structure. The contours of the inner growth zone are usually parallel to the faces of the mineral. Owing to a difference in colour, inclusions or prisypki\* on the inner growth zones it is possible to see the crystal contours as if they were inserted into one another. Hence, the terms *phantoms*, or *crystal-spectres* have emerged.

In the zonal-and-sectorial crystals one may often trace a change in the habit form. For instance, the octahedral habit is often changed to rhombododecahedron or cubic habit in fluorite; in calcite the rhombododecahedron habit is changed to scalenohedral and the latter to prismatic. A consistent change of the mineral habits is congruous with a decrease in the reticular density of various simple form faces (Fig. 17) and is accounted for by a difference in the rate of their growth, connected with the chemical activity of the species-forming and impurity elements in the mineral-forming solutions—which depends on the degree of their saturation, temperature, pressure and other factors.

The formation of *combinational faces* is conditioned by the change in the rate of growth along particular directions—pyramids or growth sectors (combinational faces). They have a step-like structure, conditioned by a decrease in the area of the subsequent layers of growth. Combinational faces are characterized by a *striation due to oscillatory combinations* whose orientation, together with the habit functions as an important diagnostic feature. The crystals of pyrite (Fig. 18), arsenopyrite, tourmaline, quartz and other minerals are often covered with a striation due to oscillatory combinations; with some minerals their habit is characteristic to such an extent that it is reflected in the names of the minerals. For instance, tetrahedrite, which is found in the form of tetrahedral crystals, sphene—in the form of wedge-shaped crystals (from the Greek ‘*ophnis*’—wedge); axinite (from the Greek—‘*acus*’—axe) etc. An unusual habit of minerals often serves as a basis for the extraction of morphological varieties of minerals, among which it is possible to mention, in particular, the plate epidote from the Akhmatovo mine in the South Urals—pushkinite; the pinacoidal-and-prismatic crystals of vesuvianite, found in the basin of the Vilyui River (Eastern Siberia)—viliuite.

\* *Editor's note.* Prisycki (pl. Russ.) means that crystal fragments or mineral crystals are accumulated on the crystal's upward face.

Fig. 17. Gradual variation of fluorite habit depending on the interplanary distances (according to N. Evzikova)



### Deformation of minerals

Faced minerals are seldom found in the form of regular crystals. As a rule, they are represented by deformed samples of unequal face dimensions of the same simple forms. They usually have a step-like structure or are deformed, often covered with striation, various figures of growth or dissolution.

The most widespread garbled or even false habit forms are conditioned by the irregular development of faces. The actual symmetry of faced minerals is lower than that of their analogous ideal crystals, if the outer (external) symmetry of the mineral-forming environment is lower than the symmetry of the mineral (the Curie principle of symmetry). For instance, the granite crystals, pertaining to the cubic system often acquire an elongated or tabular form in

Fig. 18. Striation due to oscillatory combination on the faces of pyrite crystals. One and a half times smaller

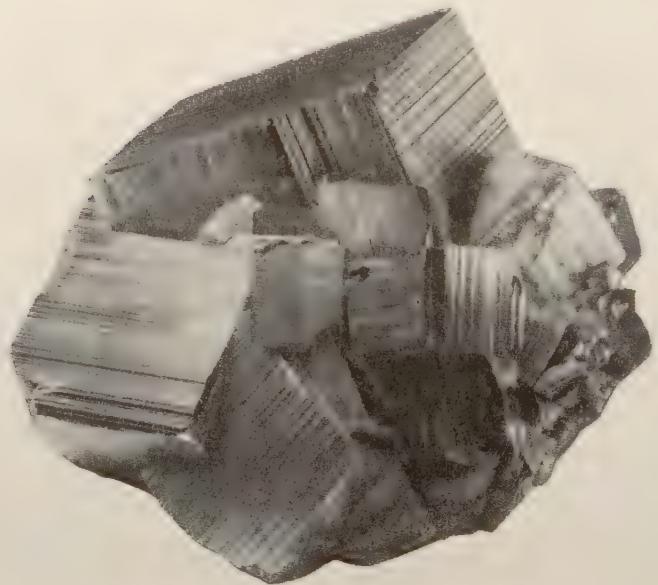
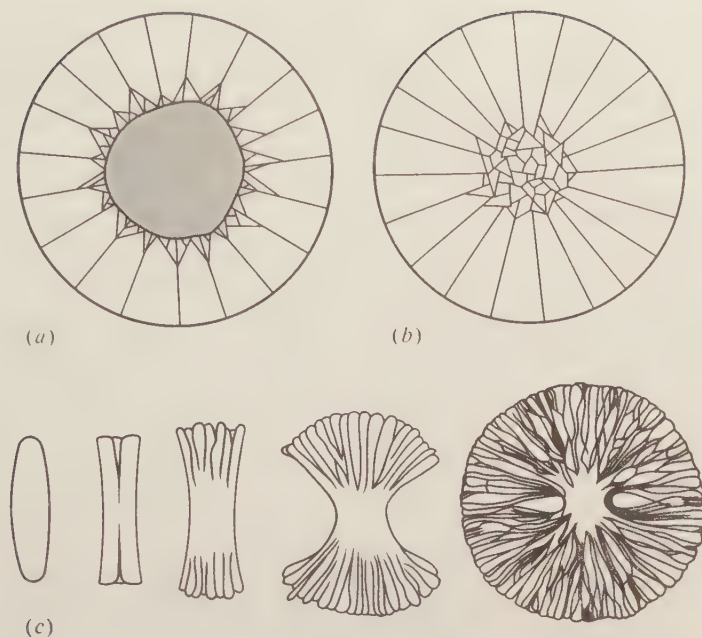


Fig. 19. The scheme showing the disintegration of a crystal and the formation of spherulites of various types: *a*—on the globular particle; *b*—out of a number of crystals; *c*—with the bifokiate (according to D. P. Grigoriev)



metamorphic rocks, which is conditioned by the prevalent growth along the schistosity. The formation of deformed flattened forms of pyrite, scheelite and other minerals related to the thread veinlets, is conditioned by the growth in restricted conditions. The lowering of symmetry of quartz crystals which is expressed in the irregular growth of the rhombohedral faces, can be accounted for by their dissimilar orientation in relation to the direction of the flow of the mineral-forming solutions, etc.

The characteristic feature of the face topography with a large number of minerals is their distortion which is often connected with mechanical deformations and dislocational shifts which have been determined, for instance, for antimonite, galenite, molybdenite and other minerals. On the face surface of these minerals one may often see a *gliding striation*. The convex faces of the combinational type is characterized by the crystals of globular habit, for example, diamond, which have acquired the names of octahedroids and dodecahedroids.

Distorted or step-like mosaic structure is also typical of the faces of *cleaved crystals* which compose the saddle-shaped, fan-shaped or twisted habit forms of dolomite, pyrite, quartz, heulandite, desmine and many other minerals. Mineral cleavage is connected with the intake (capture) of impurities and the formation of edged dislocations in the process of growth. As has been determined for manganous calcite, the degree of cleavage is proportional to the content of isomorphic impurities of manganese and is increased together with the size of crystals. In the process of growth the cleaved curvifaced crystals are often transmitted into radiate-fibrous aggregates or serve as *spherulite* embryos consisting of repeatedly cleaved fibres or needles (Fig. 19c). It should be pointed out that other types of spherulites can be formed on the surface of globular particles (Fig. 19a), or from the chaotically-oriented accumulations of numerous embryos (Fig. 19b).

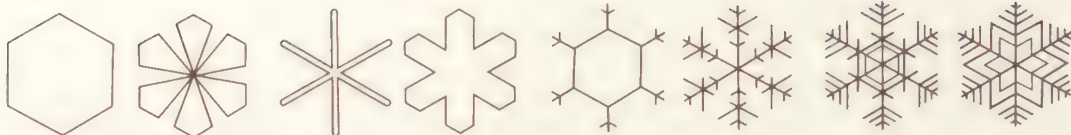
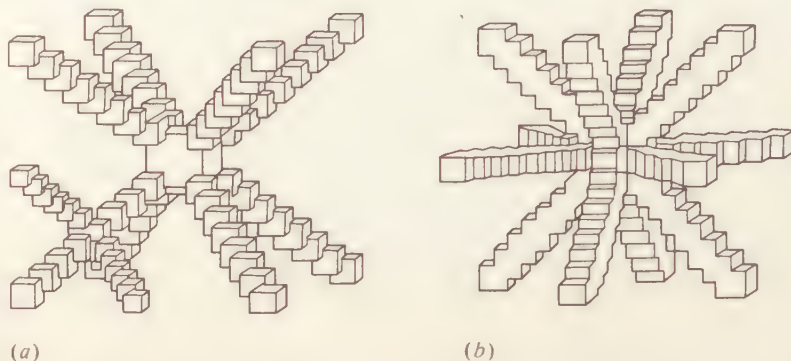


Fig. 20. Eight main types of snowflakes

Fig. 21. Skeletal crystals of native copper (a) and silver (b) in the form of edge bundles



Characteristic parts of the mineral face topography include various positive and negative forms of the growth and solubility of minerals. The orientation of these figures wholly corresponds to the class of crystal symmetry. The study of the growth and solubility enables us to identify the simple forms and the origin of minerals. In some cases, they are employed in the diagnosis of structural varieties of minerals. For example, the etching figures help to determine whether quartz belongs to the right or the left varieties.

### The skeleton crystals

Alongside with the common volume-convex faced individuals a large number of minerals are found in the form of 'skeleton' crystals of various habit, which are described in terms of one-dimensional (linear), two-dimensional (plane) and three-dimensional (volume) edges, apicals and polyhedrons with re-entering angles (faced bundles). The one-dimensional skeleton crystals include thread-like crystals (Vickers or, 'tendrils-crystals'), for example, jamesonite in the form of thin fibres, helicoids (twisted along the elongation or spring-like) and even the encircled hair-like little crystals of rutile or actinolite.

Snowflakes serve as a typical example of two-dimensional skeleton crystals. Among snowflakes together with the varieties of tabular faced forms  $\{0001\}$  or without them edged and apical varieties, hexagonal bundles (rays), frames, plane rays, apical hexagons and dihaxagons, hexagonal stars etc. are developed (Fig. 20). Branched dendrite tabular skeleton crystals are often called *dendrites*. Native copper is often found in the form of crystallographic regular two-dimensional dendrites. Dendrites also include film extractions of manganese oxides related to the thin fissures in various rocks.

The three-dimensional skeleton crystals are also characterized by the formation of various faced, apical and edged forms. For instance, the skeleton crystals of copper and silver are respectively described as octahedral and rhombododecahedral edged forms (bundles), composed of small cubes (Fig. 21). Skeleton crystals also include full, sheath-like crystals of apatite, tourmaline, garnet and others.

## Regular Intergrowths of Minerals

### Parallel intergrowths

of two or more individuals are characterized by a similar crystallographic orientation. As a rule they are found in monomineral parallel intergrowths. Some of them represent syngenetic intergrowths, while others are epigenetic and are formed during the accretion of the late mineral generation on a preceding stage. They are usually represented by independent varieties differing in morphology, the composition and the content of chemical impurities, structural features or physical properties. They include, for instance, the sceptre-like quartz with a garland of oriented little crystals, forming the edged and apical forms (Fig. 22). Sceptre-like growths are known to be typical for other minerals as well, particularly of quartz. There are cases when the position of the numerous similarly oriented individuals of one simple form is parallel to the faces of another simple form, thus forming larger combined crystals, incrustated from the surface. The oriented parallel intergrowths of tabular calcite microcrystals with faces of obtuse rhombohedron  $\{01\bar{1}2\}$  are particularly characteristic. This kind of construction has the form of a regular scalenohedron (Fig. 23a) or a hexagonal prism (Fig. 23b); the rhombohedral microcrystals of calcite often form parallel intergrowths in the form of imbricate plates parallel to the pinacoid faces  $\{0001\}$  (Fig. 23c).

### Epitaxy

is crystallographically-oriented intergrowths of individuals of various mineral species. Epitaxial intergrowths of minerals take place in cases when structural elements with similar cations or anions coincide completely or partially. In epitaxial growths the mineral individuals of a certain mineral species can grow on faces, edges or apices, sometimes forming polymineral skeleton intergrowths. Regular intergrowths of calcite and rhodochrosite, scheelite and fluorite, staurolite and cyanite, samerskite and columbite, sphalerite and grey ore etc. can serve as an example. Regularly oriented *endotaxic*

Fig. 22. Parallel-oriented intergrowths of quartz crystals (the sceptre-like quartz)

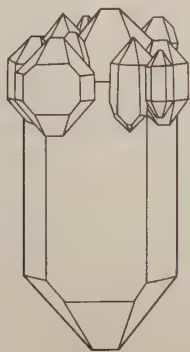
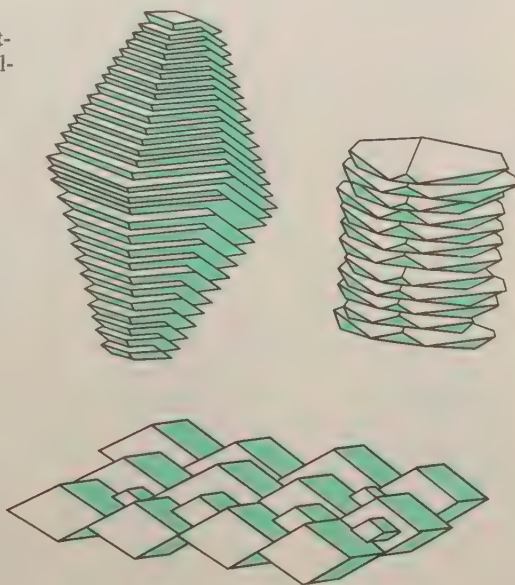


Fig. 23. Parallel-oriented intergrowths of calcite crystals. The Tyrnyauz deposit (Northern Caucasus)



intergrowths also corresponds to cases of disintegration of solid solutions with the formation of oriented inclusions of one type of minerals into others, as is the case with chalcopyrite in sphalerite, sphalerite in chalcopyrite, cubanite in chalcopyrite, spinel in magnetite. Secondary orientated intergrowths of minerals are also formed within their changes and substitutions. For instance, during the martitization of magnetite crystals hematite is found to be parallel to the faces of octahedron.

## Twins

Crystallographically-regular intergrowths are called *twins*, *trillings*, *foublings*, etc. if their component parts are connected with one another by slewing axes and the planes of mirror image. These elements of symmetry are consequently called *twinning axes* and *twinning planes*. The borderline of twins usually coincides with the twinning plane. As a rule on the surface of twinings one may see composition faces, in which certain mineral individuals are in contact with each other, thus forming *interpenetration twins*. The twins of noble spinels (Fig. 24a), sphalerite (Fig. 24b and c) and many other minerals can serve as an example. The other case can be exemplified by *interpenetration twins* with arbitrary borderlines, as for fluorite (Fig. 25b), pyrite (Fig. 25a) and other minerals. Parallel intergrowths with numerous twinings, resembling a harmonica, are called *polysynthetic*; they are particularly typical of plagioclase (Fig. 26), calcite and other minerals. They are easily recognized by the striation due to repeated twinning on the faces or spallings. Geniculated twins and their intergrowths into trillings, foublings etc., with the formation of cyclic twins, which are, for example, typical of cassiterite and rutile (Fig. 27a and b) correspond to the cases of repeated twinning.

Frequently recurring characteristic *types and laws of twinning*, which have received their own names, have been established for a large number of widespread minerals. Minerals of cubic system form twins in accordance with the *spinel law* (see Fig. 24a). Twins formed according to the law of *diamonds* are typical of diamond and sphalerite (see Fig. 24b). (For twins formed according to the *fluorite law* see Fig. 25b, and for those formed according to the *pyrite law* 'the iron cross' see Fig. 25a.) For quartz of the trigonal system *the Dauphine* and *the Brazilian penetration twins* are known to exist (Fig. 28a and b), as well as *the Japanese variety* (Fig. 28c). Geniculated penetration twins of cassiterite and rutile (see Fig. 27) serve as an example of mineral twinning of the tetragonal system. The cruciform twins are typical of minerals of the rhombic system, particularly of staurolite (Fig. 29). This is reflected in the name of the mineral (from the Greek '*stauros*'—cross). The twins formed according to *the aragonite law* (Fig. 30) are also widely spread among minerals of this system. Feldspars mainly form *Carlsbad twins* (Fig. 31a and b), twins formed according to *the albite law* (see Fig. 26) and the less characteristic types—*the Manebach* and *the Baveno* ones (Fig. 31c and d). For gypsum the most common type of twins is '*the swallow's tail*' (Fig. 32).

The laws of twinning are connected with the peculiarities of the crystalline structure. Twinning intergrowth planes are usually parallel to the faces or to the directions with maximum reticular density. The twinning axis can be normal to these faces and directions, coincide

Fig. 24. Interpenetration twins of two octahedral crystals of spinel according to the spinel law (a) and the tetrahedral crystals of sphalerite according to the diamond law: b-rotation twin; c-symmetrical twin of mirror reflection

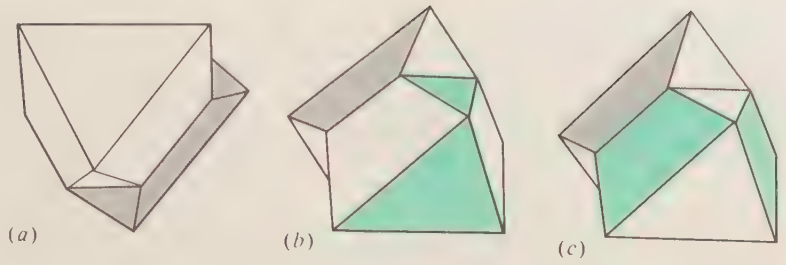


Fig. 25. Interpenetration twins: a-of pyrite ('the iron cross') according to the pyrite law; b-of fluorite according to the fluorite law

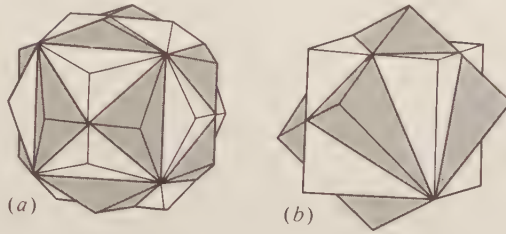


Fig. 26. Polysynthetic twins of albite (the albite law)

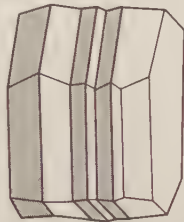


Fig. 27. Articulate (a) and cyclic (b) twins characteristic of cassiterite and rutile

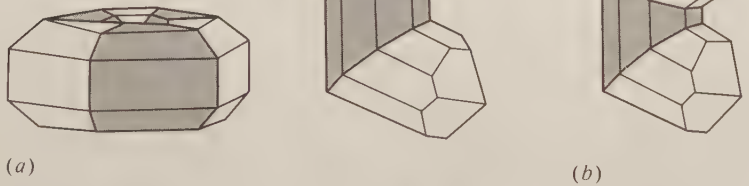
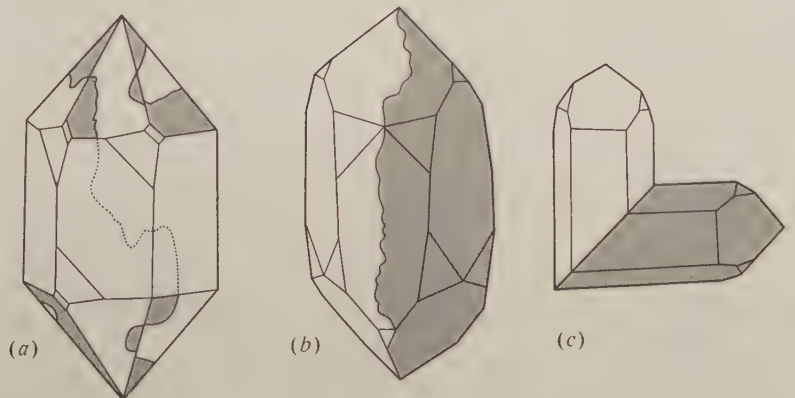


Fig. 28. Dauphine (a), Brazilian (b) and Japanese (c) twins of quartz



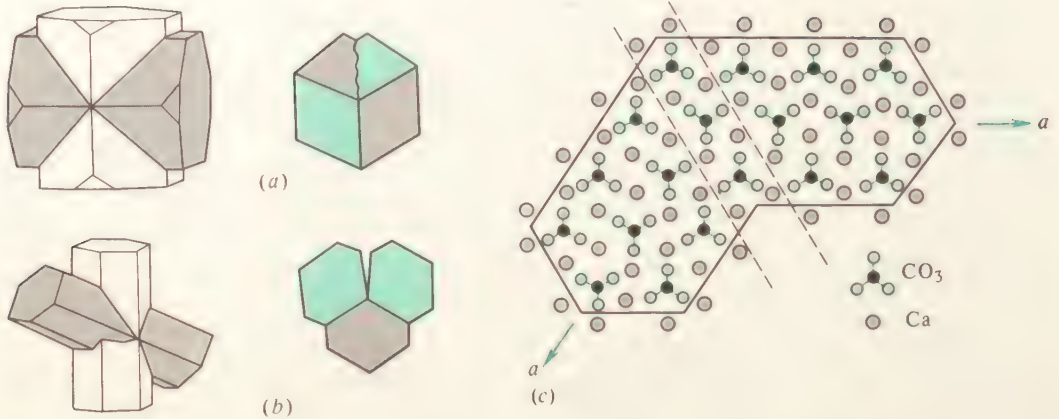


Fig. 29. An interpenetration twin of staurolite

Fig. 30. Interpenetration (a) and increment (b) twins of aragonite according to the aragonite law and the atom model of twinning (c)

with the direction of the edges at the intersection of the maximally denser atom lattices or be perpendicular to these edges, if it occurs in the twinning plane. In the cubic crystals of atoms with the face-centered cell the twinning plane is parallel to the octahedral face of maximum density, which is particularly typical of the spinel law of twinning. The regular orientation of individuals in geniculated twins of cassiterite and rutile (sagenite) are approximately accounted for by the structure of these minerals in which the coordination octahedra are connected with each other by common edges; in case of twinning the joining of octahedral chains at the angle of  $120^\circ$  takes place without any perceptible distortion of the crystalline structure at all. In aragonite twins a part of the structure along the twinning plane has a common orientation in neighbouring individuals (see Fig. 30c).

Faced twins are usually characterized by the re-entering angles, as a result of which the habit of twinned individuals differs from the habit of the corresponding monocrystals. They are either elongated or flattened. For instance, the manebach and Baveno twins of orthoclase, 'the swallow's tail' of gypsum are distinguished by a marked elongation in one direction, while the Japanese twins of quartz and the twinned ones formed according to the albite law of the phenocrysts of plagioclase in the dikes of diabase or in the outbursts of the existing volcanoes are considerably flattened.

Twins are of different origin. The growing twins are formed as a result of 'errors' at the beginning and within the process of crystallization, as well as by the oriented intergrowth of microcrystals—the embryos of crystals. Deformed twins are usually

Fig. 31. Twins of feldspars: interpenetration twins of sanidine (Carlsbad twinning), shown here on the right (a) and on the left (b) and the interpenetration twins of orthoclase Baveno twinning (c), and Manebach twinning (d)

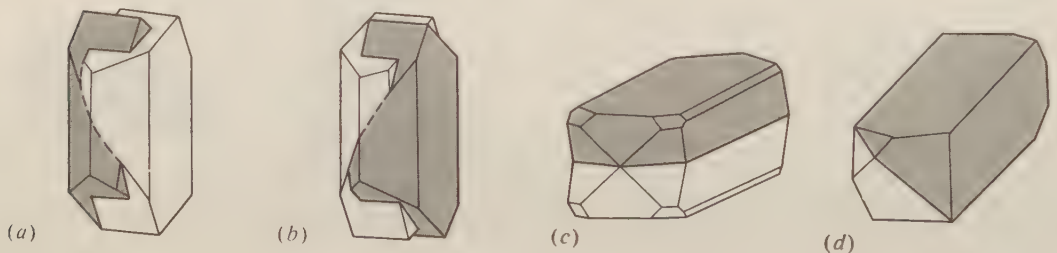




Fig. 32. The gaelic twin of gypsum ('swallow's tail')



formed during the polymorphic transformations and under the influence of oriented pressure. Deformed twins include, for example, polysynthetic twins of calcite in marble. In the process of their formation the inception and the gliding of edge dislocations take place. Twins are characteristic of certain minerals and, consequently, can function as a diagnostic feature.

## Mineral Aggregates

Minerals are usually found in the form of irregular growths, i.e. mineral aggregates composed of one or several minerals. Mineral aggregates are distinguished by their size, form and the character of spatial distribution of mineral individuals of which they consist. There are macro- medium- and microgranular, crystalline-granular, cryptocrystalline, equigranular and inequigranular aggregates with regular or irregular orientation of mineral grains. Mineral aggregates can be dense or massive, porous, earthy, viscous, loose, or friable. Most of the erupted, metamorphic, sedimentary rocks as well as various ores are composed of crystalline-granular aggregates of minerals. Porous and friable aggregates are typical of the products of volcanic eruptions, a large number of sedimentary rocks, soils etc.

## Secretions

Incrustate aggregates: druses, crystalline, sinter and spherulite crusts compose voids or secretions of different size and form. Large secretions (from several centimetres to several metres) are called *geodes*, *bags*, *pogrebs*,\* or *ventholes*. The smaller ones (under 1 cm) are called *miaroles* and *amygdules*. Secretions can be formed either completely or partially by the crystals or spherulites of one or several mineral species.

Mineral individuals composing incrustate aggregates in secretions can have haphazard, or rarely, regular, usually parallel orientation. Haphazardly oriented individuals are formed of numerous microcrystalline embryos with accidental fastening on the uneven walls of the voids. There are various reasons causing the orientation of crystals in secretions. The largest crystals are formed in compliance with the law of geometrical selection at the expense of the individuals whose maximum growth direction is normal to the walls in the cavity (Fig. 33). When these individuals are fastened on an even surface of the cavity walls, the parallel oriented rod-like aggregates are usually formed.

Oriented aggregates result from the crystallization on a porous wall with the formation of parallel-fibrous aggregates of fibrous crystals, as for instance, gypsum, chalcantite, and others. Besides, oriented effect on the individuals can be caused by the basis on which crystallization takes place. These can include the regularly oriented fissure net, the layering of enclosing rocks or a large crystal that can serve as the base during the epitaxial growth.

Various reniform, collomorphic and spherulite crusts and films as well as stalactites and stalagmites with concentrated-and-zonal structure, dendrite, branched aggregates—corallites and microcrystalline

\* *Editor's note.* From the Russian *pogreb* that means a cavity in the vein containing rock crystal, amethyst, etc.

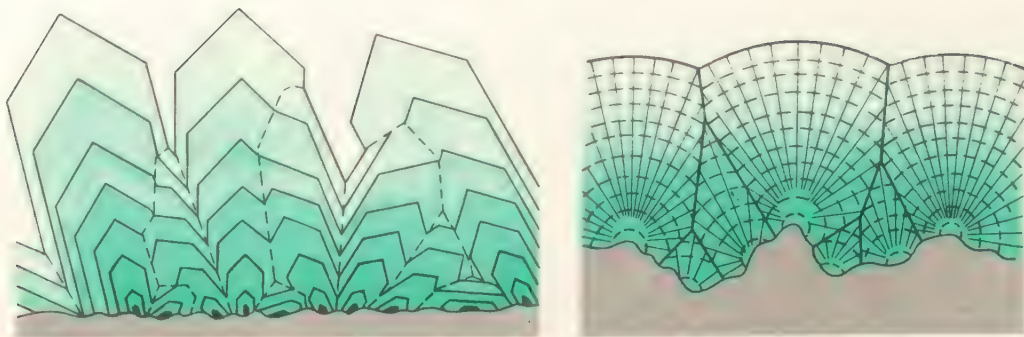


Fig. 33. The formation of the quartz crystal druse following the law of geometrical selection (according to D. P. Grigoriev)

Fig. 34. Group growth of spherulite on an uneven surface (according to D. P. Grigoriev)

### Concretions

structures of aragonite and calcite are characteristic of karst caves. Analogous aggregates of carbonates and hydroxides of iron of smaller dimensions are found in cellularly porous and geode formations of the surface changes in rocks and ores. The formation of spherulite aggregates, as is the case with druse aggregates, is submitted to the law of geometrical selection. In this case each spherulite functions as a mineral individual (Fig. 34). The formation of mineral aggregates with the growth of crystals and spherulites, as for instance, calcite and chalcedony is also submitted to the law of geometrical selection.

Spheroidal, nodular, oval, reniform and other mineral aggregates of the rounded form are called *concretions*, *septarian nodules* and *oölites* (Figs. 35 and 36). Concretions, in contrast to secretions, are formed in the process of crystallization from the centre to the periphery. They usually have radiate-fibrous or concentric-and-zonal structure. The formation of concretions is connected with collective crystallization in porous, usually sedimentary rocks at the expense of the matter dispersed in them. Oölites are of small size (up to 1 cm) and are formed in mineral wells, at the bottom of the lakes in caves, in weathering crusts, in the form of pearls in mollusk shells. They sometimes form secretions with crystals.

The outer surface of concretions can be smooth and even, as is the case with phosphorite nodules and aragonite oölites, or pectinal with a clearly-cut facing, particularly characteristic of marcasite. In some cases the central part of concretions can be hollow. It is assumed that hollow oölites are formed on gaseous bubbles. Voids can also appear as a result of dissolution or recrystallization of the central part of concretions which is sometimes succeeded by the filling of other minerals. Phosphorites containing the crystals of galenite, sphalerite, calcite and other minerals can serve as an example of transformations of concretions into secretions.

*Earthy, porous and friable aggregates, blooms and coatings* are characteristic of zones of surface rock change or sedimentary deposit of minerals.

### Inclusions and Other Heterogeneities in Minerals

Mineral individuals homogeneous in the chemical and physical sense, are extremely rare. They usually contain various inclusions of other phases, have mosaic structure and are characterized by chemical

Fig. 35. Phosphorite concretions. Khmelnit-skii region of the Ukrainian SSR

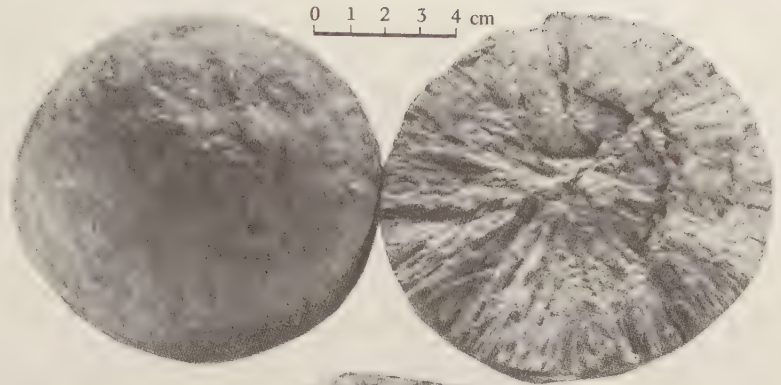
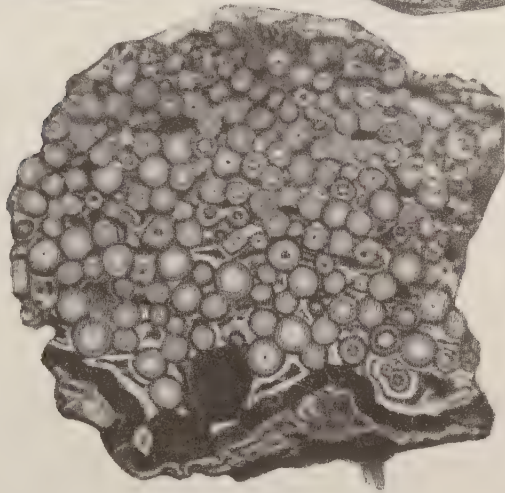


Fig. 36. Aragonite oörites, Karlovy Vary, Czechoslovakia



and physical heterogeneity, expressed in irregular or zonal-and-sectorial distribution of chemical or mechanical impurities, transparency or colour. In a large number of cases to establish heterogeneity microscopic investigations with the use of special methods are called for.

Heterogeneous structure of minerals depends on the conditions of their formation and their subsequent change. In this connection various types of heterogeneities are subdivided by N. V. Petrovskaya into protogenetic (inherited or relict), syngenetic and epigenetic.

*Protogenetic heterogeneities* are of various forms and nature. Mechanical inclusions of foreign minerals intercepted in the process of mineral growth are widely spread. They form poikilitic intergrowths (from the Greek *'poikilos'*-variegated), which usually represent monocrystals with inclusions of mineral grains of enclosing rock. 'Sandy' crystals of gypsum or calcite, crystals of aegirine with inclusions of the early formed nepheline can serve as an example. Protogenetic inclusions also include the relict inclusions which are retained as a result of an incomplete replacement in various magmatic, metamorphic or metasomatic rocks. Thus, zircon of the metamorphic rocks after undergoing granitization remains in the form of rounded inclusions in the regenerated crystals of the accessory zircon of the granites.

*Syngenetic heterogeneities* are characteristic, for example, of drusy aggregates, crystallized gels, disintegrated solid solutions, as well as for zonal-and-sectorial crystals.

*Epigenetic heterogeneities* in minerals are caused by processes involving a change in their composition, depositions of newly-formed minerals in fissures or by replacing them with new minerals.

Hardened, liquid and gaseous-and-liquid inclusions in minerals are also referred to the proto-, syn- and epigenetic types of heterogeneity.

## The Physical Properties of Minerals

Physical properties of minerals are found and can be measured only in the result of applying external forces and various by their nature of actions—mechanical, radiational, electromagnetic, thermal and others. The interaction with the minerals of various forms of energy is accompanied by its partial or complete absorption and dispersion, change and conversion into other forms which is expressed in the emergence of various physical effects and properties. The effect of mechanical forces on minerals is accompanied by their deformation or disintegration. The resistance of minerals to their breakdown by means of inserting a sharp object or scratching their surface is expressed through hardness.

The behaviour in the gravitational field is determined by the density of minerals. Depending on the energy of the electromagnetic field in the mineral excitation of electrons can take place accompanied by a selective absorption of light which serves as a direct cause of colour. The magnetic properties of minerals emerge in the magnetic field.

A large number of physical properties are connected with the structure and chemical composition of minerals and undergo changes with them. For other properties the presence of defects in minerals plays a significant role. In accordance with this all physical properties are subdivided into primary and secondary. The former comprise density, hardness, cleavage, optical properties, lustre, reflecting capacity and others. The primary properties have the main diagnostic value. Among the secondary ones it is necessary to bring out various semiconductive and thermoelectrical and luminescent properties, the admixing and radiational colouring, residual magnetization and others. The study of the secondary properties has the function of identifying the actual structure of minerals, the diagnosis of their genetic varieties and the information concerning the mineral-forming processes.

The importance of the physical properties of minerals is by no means confined to what has been said here. They are widely implemented in industry, science and everyday life. Thus, for the charging of the solution at drilling barite is used. Hard minerals are employed as abrasives, while the light minerals are used as concrete fillers. High transparency of quartz and fluorite in the ultraviolet, visible and infrared light determine the value of these minerals as optical raw-material; wonderful colouring in conjunction with strong lustre, transparency and a high degree of hardness distinguish numerous precious stones from other minerals.

## Density

The density of minerals measured in the units of mass per unit of volume (in  $\text{g/cm}^3$ ) fluctuates within the wide limits and reaches  $23.0 \text{ g/cm}^3$  (platiniridium). The more widespread minerals have density from  $2.5$  to  $3.5 \text{ g/cm}^3$ . A great number of the mineral species have density less than  $5 \text{ g/cm}^3$ . Among them silicates, oxygen salts and haloids are predominant. Sulphides and native metals have greater density.

Minerals can provisionally be divided into three groups: the light minerals (up to  $3.0 \text{ g/cm}^3$ ), the medium (from  $3.0$  to  $4.0 \text{ g/cm}^3$ ) and the heavy minerals (more than  $4.0 \text{ g/cm}^3$ ).

The density of minerals depends on the chemical composition and the type of the structure and hence, is the most important diagnostic feature. All the minerals composed of the elements pertaining to the upper part of the periodic table are light minerals. Minerals, containing heavy metals have, as a rule, greater density. Maximum density is typical of the native elements of gold, silver, and the minerals of the platinum group.

For minerals representing isomorphic series an increase (or decrease) of density is proportional to the change in the chemical composition. Thus, in the isomorphic series of olivines from forsterite  $\text{Mg}_2[\text{SiO}_4]$  to fayalite  $\text{Fe}_2[\text{SiO}_4]$  the density increases from  $3.20$  to  $4.35 \text{ g/cm}^3$ , in the series of albite  $\text{Na}[\text{Si}_3\text{AlO}_8]$ –anorthite  $\text{Ca}[\text{Si}_2\text{Al}_2\text{O}_8]$ —increases only from  $2.61$  to  $2.75 \text{ g/cm}^3$ . In the series of scheelite  $\text{Ca}[\text{WO}_4]$ —powellite  $\text{Ca}[\text{MoO}_4]$  it decreases from  $6.1$  to  $4.2 \text{ g/cm}^3$ , i.e. by  $1.9 \text{ g/cm}^3$ .

The dependence of density on the crystalline structure is particularly manifested in the polymorphic modifications of minerals and is determined by the character of the atom packing. Diamond and graphite with the density  $3.5$  and  $2.3 \text{ g/cm}^3$  respectively, calcite ( $2.6$ – $2.8 \text{ g/cm}^3$ ) and aragonite ( $2.9$ – $3.0 \text{ g/cm}^3$ ) mentioned above can serve as an example. It is exactly the same with quartz  $\text{SiO}_2$  with framework structure which is considerably lighter than stishovite of the same composition but having rutile-like chain structure ( $2.65$  and  $4.35 \text{ g/cm}^3$  respectively). In general, minerals with close packing have greater density as compared with that of minerals of chain, ribbon, layered and particularly framework structure.

Several methods of determining the density of minerals are known. The most accurate ones are the pycnometric and the hydrostatic methods. The pycnometric method is based on the measurement of the mass of the mineral by means of weighing it in a pycnometer, a vessel of a given volume. The hydrostatic method presupposes the weighing of the mineral in air and in liquid.

The more unsophisticated *volumetric methods* of determining the density of minerals include the weighing with the subsequent measurement of the liquid volume displaced by the minerals. This is done with the help of the volumetric flask or special vessels—volumeters. The microscope is used to measure the volume of the mineral microsamples in the thin vessels of a given section.

*The immersion methods* make it possible to determine the density of minerals by comparing it with the density of heavy liquid which is determined directly by applying the Westphal balance (the hydrostatic method) or indirectly, by measuring the value of refraction ratio. The

density of liquid can be regulated by heating or dilution (the thermogradient method). The method of light floats with grains attached to them is used to determine the density of heavy minerals in a liquid of lower density.

## Mechanical Properties

The mechanical properties of minerals become apparent when the mechanical action, exerted on them by the external forces during compression, stretching or shock, takes place. They are expressed in the changing of their form and integrity. The following types of deformation are distinguished: elastic, brittle and plastic.

### Cleavage

is the ability of crystals to break down into preferred crystallographic planes with the formation of lustrous surfaces. Cleavage can be manifested in one, two, three, four or six crystallographic lines. The mica crystals can be cleaved into minutest leaves. According to pinacoid its cleavage in one direction is {001}. The calcite rhombohedral crystal is easily split in free directions (along the rhombohedron), whereas in other directions cleaved planes are not formed.

The cleavage planes are parallel to the flat nets of the space lattice with a maximum interplanar distances, as for instance, in graphite (see Fig. 5). Since cleavage is connected with the crystalline structure, it functions as an important diagnostic feature of minerals.

To evaluate cleavage the following scale is used.

1. *Perfect cleavage*—when the crystal is split into very thin plates of specular surface (mica, gypsum).
2. *Good cleavage*—the crystal is split into certain directions, at any place, thus forming even, sometimes step-like surfaces; cases of irregular surfaces are extremely rare (calcite, halite, galenite).
3. *Distinct cleavage* is exemplified by the formations of both even and uneven surfaces resulting from a splitting (feldspar, hornblende).
4. *Imperfect cleavage*—even cleaved surfaces are rare. In most cases splitting results in the formation of irregular surfaces (beryl, apatite).
5. *None cleavage* occurs when the cleavage is absent and the crystals have uneven surfaces resulting from the split (quartz, cassiterite).

Along different lines crystal cleavage can be either identical or different depending on the degree of perfection.

*Fracture.* Minerals that have imperfect cleavage or no cleavage at all are split into uneven surfaces of the fracture. According to the character of these surfaces the fracture in minerals can be uneven (native sulphur, apatite, cassiterite), step-like (feldspars), splintery (actinolite, tremolite), shelly (quartz, chalcedony, opal), hackly (native elements—gold, brass, platinum) and other species.

### Jointing

implies the ability of minerals to break down and form even surfaces on the chippings along the directions coinciding with the twinning planes, the epitaxial intergrowths, the oriented inclusions of the disintegrating products of solid solutions, the heterogeneity, and the inclusions along the zones of growth etc. For instance, jointing

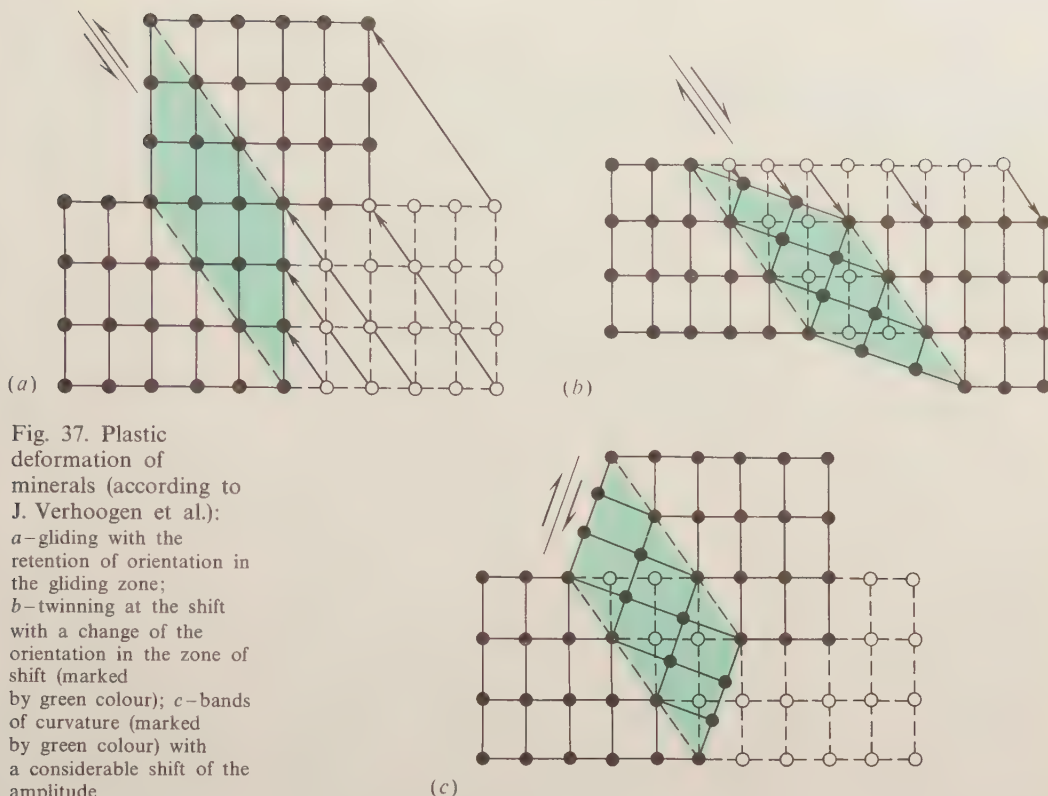


Fig. 37. Plastic deformation of minerals (according to J. Verhoogen et al.):  
*a*—gliding with the retention of orientation in the gliding zone;  
*b*—twinning at the shift with a change of the orientation in the zone of shift (marked by green colour);  
*c*—bands of curvature (marked by green colour) with a considerable shift of the amplitude

according to pinacoid  $\{0001\}$  is characteristic of corundum. It is connected with the minutest inclusions of muscovite.

### Elasticity

is a property shared by minerals the original size and form of which is restored after the external tension has been removed. A high degree of elasticity is characteristic of mica scale. The elasticity is connected with the strength and type of interatomic bonds. With the growth of temperature elasticity decreases. When the elastic deformation exceeds its limit, there appear brittle or plastic deformations.

### Brittleness

is a property which manifests itself in that minerals are easily crushed as a result of the application of external forces, for instance, when the surface of the mineral is either struck by a hammer, or a knife, a steel-needle are applied to it. When such a brittle mineral as grey ore is scratched, some powder remains at the edges. It can easily be blown off. As compared with the latter, on the surface of chalcosine there remains a shining cut with even edges. Most of the native metals share exactly the same property. They change their form when they are struck and are flattened, i.e. are characterized by *malleability*.

### Plastic deformation

emerges during the gliding of the neighbouring parts of the crystalline individuals in respect to each other and parallel to the atomic planes with a minimal stability of the bond between them by the appearance and gliding of the edge dislocations. The direction of the gliding coincides with the minimal interatomic distance. As a result of

mechanical gliding the inner homogeneousness of the crystal is retained, though its form changes (Fig. 37a). Plastic deformations are favourably effected by a high temperature. Impurities and mechanical inclusions, fixing dislocations, hinder plastic deformations. Those of the shift, as compared with the gliding deformations, are accompanied by the formation of mechanical twins. The shift along the plane of twinning leads to the regular orientation of certain parts of the crystals (Fig. 37b). Mechanical twinning is characteristic of minerals of metamorphic rocks, for instance marble calcite. Deformation results in that certain minerals can be crushed, acquire an irregular form without impairing their integrity and retain the form after the applied actions have been removed. Bending in a crystal conditions the emergence of fields of tensions with a high concentration of similarly oriented edge dislocations or a band of the bending which have a close resemblance to the bands of the polysynthetic mechanical twinning. The amplitude of the shift during the bending is greater than during the twinning (Fig. 37c). The bands of the bending are characteristic of disthene, spodumene, chlorite, muscovite, molybdenite, chrysotile-asbestos and others.

### Hardness

Mineral hardness is defined as its resistance to the mechanical disintegration which takes place under the action of a stronger body. Hardness is the most important diagnostic feature of minerals. It reflects the strength of the chemical bonds between atoms and depends on the type of chemical bonds. For minerals with an ionic type of chemical bond a low or moderate degree of hardness is characteristic, while minerals with a purely covalent bond are very hard. Halite and diamonds can be adduced as an example. Minerals with a mixed type of chemical bond usually have lowered hardness, whereas those with hydrogen and Van der Waals bonds have low hardness. In accordance with this a large number of layered, aqueous and molecular crystals are distinguished by low hardness. Minerals with a coordinate and frame types of structure are characterized by a moderately high degree of hardness. The comparison of structurally similar and chemically analogous minerals shows that with the increase of cation or anion charge, hardness increases. For instance, the hardness of calcium layered aluminosilicate—margarite  $\text{CaAl}_2[\text{Si}_2\text{Al}_2\text{O}_{10}](\text{OH})_2$ —is considerably higher than its potassic analogue—muscovite  $\text{KAl}_2[\text{Si}_3\text{AlO}_{10}](\text{OH})_2$ . In isomorphic series mineral hardness changes with the composition. Simultaneous changes in the degree of ionic-covalent chemical bond, the valency of ions and their dimensions, and consequently, the density of packing and coordination are particularly significant.

A perceptible impact on the microhardness of minerals is caused by various defects—vacancies, interstitial atoms and microimpurities, dislocations and the degree of perfection of the crystalline individuals. The theoretical stability of the crystals is known to be considerably greater than the actual stability. Only the undislocational filamentary crystals (Vickers) have a stability corresponding to the one that has been calculated.

There are several methods of determining hardness. In mineralogical practice *Mohs' scale* is employed. The following minerals listed according to the degree of hardness can serve as standards of Mohs'



scale of hardness:

1. Talc  $\text{Mg}_3[\text{Si}_4\text{O}_{10}](\text{OH})_2$
2. Gypsum  $\text{Ca}[\text{SO}_4] \cdot 2\text{H}_2\text{O}$
3. Calcite  $\text{Ca}[\text{CO}_3]$
4. Fluorite  $\text{CaF}_2$
5. Apatite  $\text{Ca}_5[\text{PO}_4]_3(\text{F}, \text{Cl})$
6. Feldspar (orthoclase)  $\text{K}[\text{Si}_3\text{AlO}_8]$
7. Quartz  $\text{SiO}_2$
8. Topaz  $\text{Al}_2[\text{SiO}_4](\text{F}, \text{OH})_2$
9. Corundum  $\text{Al}_2\text{O}_3$
10. Diamond C

Mineral hardness is usually determined by the scratching of one mineral against another. If, for instance, apatite (hardness 5) scratches the mineral under analysis, but fluorite (hardness 4) does not, hence, the hardness of the mineral under investigation is to be approximately 4.5.

Mohs' scale standards can serve as substitutes for the following: the blade of a steel knife—hardness approximately 5.5–6, a file—approximately 7, glass—5; minerals whose hardness is less than 2 are easily scratched by a finger nail.

It is necessary to point out the relative character of Mohs' scale. If the hardness of talc is 1, and of gypsum 2, it does not mean that gypsum is twice as hard as talc. The same may be said of other standard mineral.

Hardness can be determined with a great degree of precision by means of applying special instruments, viz. *sclerometers*. In the sclerometer devised by M. M. Khrushchev and E. S. Berkovich the hardness is determined on the even surface of a mineral by pressing into it a little diamond pyramid of a square section (under a certain pressure  $P$ —in kg). The dimensions of the imprints thus received are smaller for hard minerals than for the soft ones. The diameter of the imprints ( $d$ ) is measured (in mm) with the help of a micrometric ocular on the microscope. The microhardness of minerals ( $H$ ) is calculated according to the formula

$$H = 2 \sin \frac{\alpha}{2} \frac{P}{d^2}, \text{ or } H = 0.7 \frac{P}{d^2} \text{ kg/mm}^2$$

with the angle between the faces of the square diamond pyramid  $\alpha = 136^\circ$ . The values of microhardness for mineral specimens of the Mohs' scale show that the hardness of diamond is five times greater than that of corundum, and three times greater than the hardness of talc.

Talc	2.4	Feldspar	795
Gypsum	36	Quartz	1120
Calcite	109	Topaz	1427
Fluorite	189	Corundum	2060
Apatite	536	Diamond	10060

When hardness is estimated it is necessary to take into account the fact that mineral hardness tends to be anisotropic. This becomes particularly apparent with heterodesmic minerals which have either

chain or layered structure. Disthene  $\text{Al}_2[\text{SiO}_4]\text{O}$ , for example, is distinguished by various degree of hardness when its surface of perfect cleavage is scratched along its elongation (4.5) and across (6), which is reflected in the name of this mineral (from the Greek 'dis' meaning 'two', and 'sthenos' meaning 'resisting', i.e. 'double-hard'). As has been established, the hardness of graphite along the surface of the most perfect cleavage is 1, while across it is over 5. The hardness is not the same with different faces even of cubic crystals of one and the same mineral, which may well be accounted for by their different reticular density. The crystals of diamond, for instance, have maximum reticular density on the faces of the octahedron  $\{111\}$ . The faces of the rhombic dodecahedron are characterized by minimal reticular density  $\{110\}$ , while the least reticular density is typical of the faces of the cube  $\{100\}$ . From what has been said above it may be inferred that the hardness on the faces of the octahedron will be greater than that along the faces of the rhombic dodecahedron, and the faces of the cube will have the least degree of hardness.

The heterogeneous structure of minerals also influences their hardness. For example, the zonal crystals of molybdoscheelite, as has been shown by measurements, have, as a rule, a lower degree of hardness (up to  $180 \text{ kg/mm}^2$ ) in the central zones enriched by molybdenum than in the peripheral zones (up to  $600 \text{ kg/mm}^2$ ) which are composed of practically pure scheelite. A high degree of hardness is shared by the crystals of magnetite, containing the inclusions of spinel, which is the product of the disintegration of the solid solution.

It is also necessary to point out that the virtually measured hardness of minerals in porous, earthy, as well as fibrous aggregates is always underrated; what is actually disclosed is the stability of the coalescent particles.

## Optical Properties

Optical properties are submitted to the laws of geometrical optics. They are connected with the change in the velocity of light, travelling through the transparent minerals and are described on the basis of concepts pertaining to the electromagnetic nature of light. In accordance with these concepts light is characterized by the wavelength and the amplitude of harmonic fluctuations of electric and magnetic components of electromagnetic field in the directions perpendicular to each other and the ray of light (Fig. 38). In the ordinary light fluctuations are perpendicular to the ray of light in all radial directions, while in the plane-polarized light they occur only in one plane or polarization.

The refractive index of light  $n$  is called ratio of the velocity of light  $c$  in the vacuum (approximately in the air) to the velocity of light  $v$  in the mineral

$$n = \frac{c}{v}$$

The index of refraction is determined in the same way as the relationship between the sines of the dip angle  $i$  and the refraction of

Fig. 38. Electrical and magnetic fields—components of the plane-polarized electromagnetic radiation

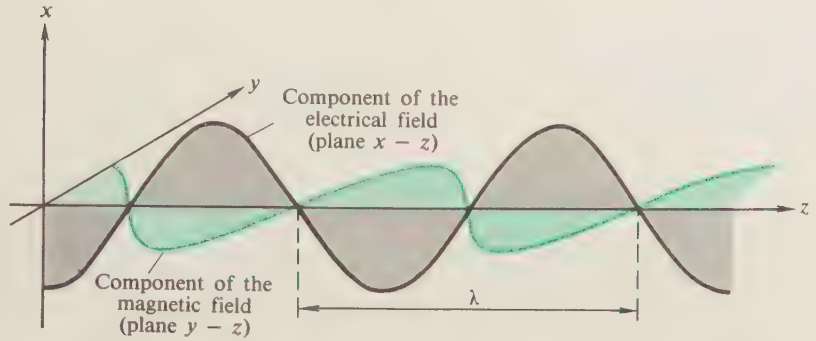
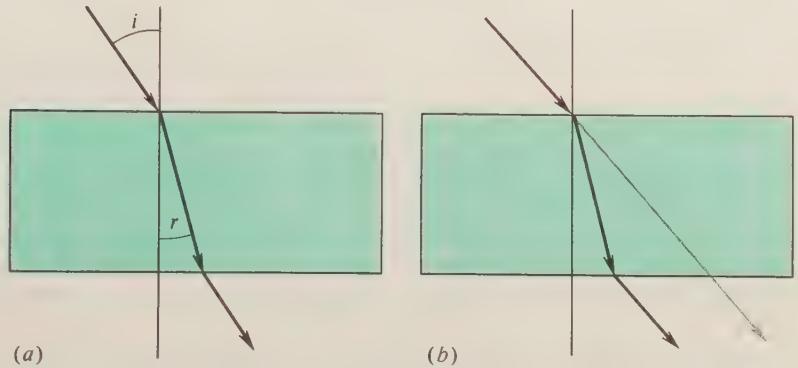


Fig. 39. Refraction of light in isotropic (a) and anisotropic (b) crystals



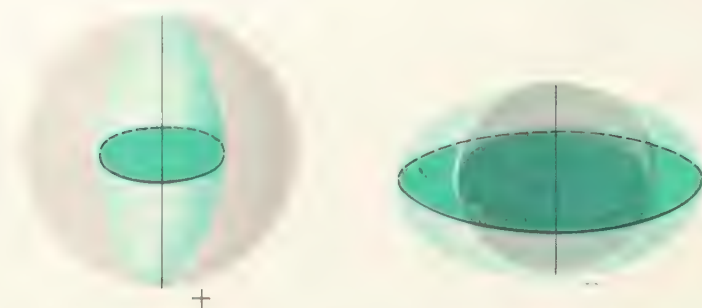
ray  $r$  on the border of two media (Fig. 39a):

$$n = \sin i / \sin r$$

In crystals of the cubic system or in noncrystalline bodies the light is propagated with equal speed in all directions. The index of refraction of such optically isotropic crystals does not depend on the direction of the ray of light that passes through them. From the point source the light in the optically isotropic crystals propagates by waves that have global surface. In the isotropic medium the direction of the wave propagation is determined by normal to the tangent on the global surface and coincides with the direction of the radius (the ray of light) to the point of contact. Hence, in optically isotropic minerals the ordinary light is not polarized. The polarization of light occurs only when the light passes through anisotropic media to which minerals of all the systems, excluding the cubic system, belong. Under these circumstances the natural (nonpolarized) light is penetrated into crystals and falls into two plane-polarized waves differing from each other in the velocity of light, and in that with one of them there are fluctuations of the electric component in the plane of polarization, whereas the plane that is perpendicular to it is characterized by the fluctuations of the magnetic component. The light wave with a constant velocity of propagation in different directions is called the *ordinary wave*. The constant, or ordinary, refractive index  $n_0$  corresponds to it.

The surface of its propagation is described as a sphere. For waves of variable velocity of propagation of light in different directions, called the *extraordinary wave*, (it is characterized by the inconsistency of

Fig. 40. Surfaces of light wave for crystals of the middle categories of symmetry



indices of refraction  $n_e$  (extraordinary index of refraction). The surface of its propagation in crystals of the middle category of symmetry represents a globe, inscribed into an ellipsoid, or, conversely, an ellipsoid inscribed into a globe (Fig. 40).

In the direction coinciding with the main axis of symmetry of crystals, the values of the ordinary and the extraordinary indices of refraction are alike. In crystals of the middle categories of symmetry only one direction is possible. It is called *the optical axis*, and the corresponding crystals are termed *uniaxial*. If the value  $n_e > n_o$ , then the crystal is *optically positive*, if, however,  $n_o > n_e$ , the crystal is *optically negative*. The difference in the maximum and the minimum values of refraction indices is called *birefringence*, or double refraction of light. This phenomenon discovered by E. Bartholin in 1669 and studied by Ch. Huygens on the cleaved specimens of Iceland spar, the transparent variety of calcite, is conditioned by the fact that two waves with mutually perpendicular planes of polarization have different indices of refraction and are different as far as their refraction is

Fig. 41. Birefringence in an Iceland spar crystal (double-refraction). Actual size

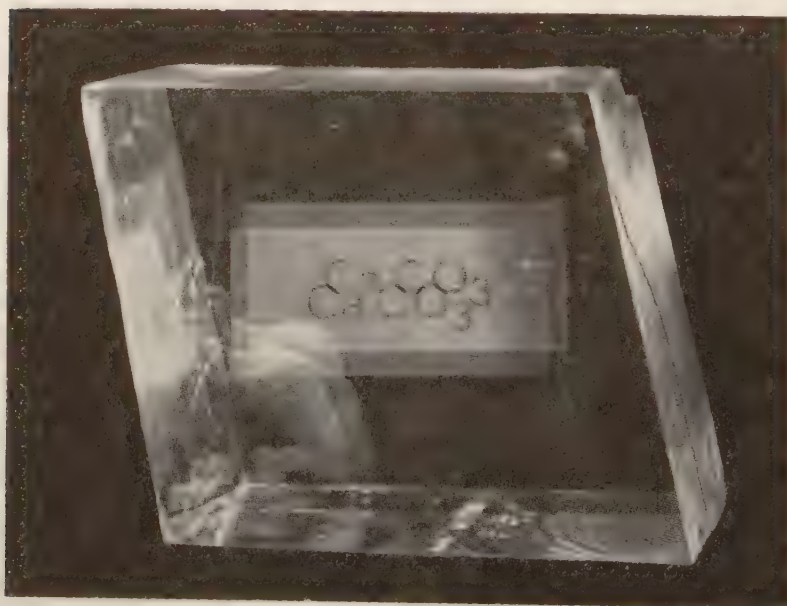
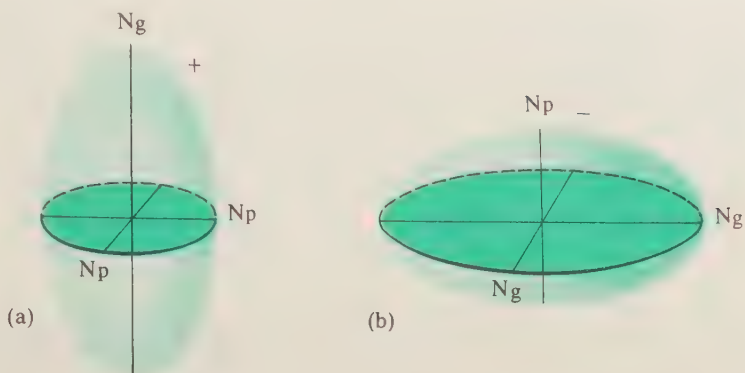


Fig. 42. Optical indicatrices of uniaxial positive (a) and negative (b) crystals



concerned when entering or leaving the crystal (see Fig. 39b). Two clear-cut images can be discerned in the transparent cleaved specimen of the Iceland spar (Fig. 41). The thickness of the cleaved plate is directly responsible for the discreteness of the image.

Crystals of the lowest categories of symmetry are characterized by three different values of refraction indices ( $n_g$ —the greatest;  $n_m$ —the intermediate;  $n_p$ —the least) in various crystallographical directions and two optical axes, in connection with which they are called *optically biaxial*. Biaxial positive crystals have  $n_g - n_m > n_m - n_p$ . The negative ones have  $n_m - n_p \geq n_g - n_m$ .

Changes in the indices of refraction and other optical properties of the anisotropic crystals can be represented visibly by means of a surface constructed on the values of indices of refraction set in the directions of the fluctuations of the light wave called *the optical indicatrix*.

For crystals of the cubic system the optical indicatrix has the form of a sphere. For crystals of the middle category of the symmetry the indicatrix has the form of the ellipsoid of rotation. If the crystal is optically positive, i.e. if the maximum index of refraction coincides with the direction of the ray of the extraordinary light, then the ellipsoid is elongated along the optical axis. The optically negative crystal is characterized by the direction of the mineral index of refraction coinciding with the direction of the ray of the extraordinary light, and its optical indicatrix represents a truncated ellipsoid of rotation (Fig. 42). The optical axis of the indicatrix of crystals of the middle systems always coincides with the main crystalline axis. The optical indicatrix of crystals of the lowest category of symmetry represents a triaxial ellipsoid with three unequal main axes  $N_g$ ,  $N_m$ , and  $N_p$ . Two circular sections of such an ellipsoid are located perpendicular to the two optical axes (Fig. 43). The optical axes  $A_1$  and  $A_2$  are situated in the plane of the optical axes  $N_g - N_p$ , perpendicular to the axis  $N_m$ .

The angle between the optical axes  $A_1$  and  $A_2$  is called *the angle of optical axes* ( $2V$ ). The biaxial crystal is said to be *positive*, if it is characterized by the axis  $N_g$  coinciding with *the acute bisectrix* which divides into halves the acute angle ( $+2V$ ). The biaxial crystal is *negative* when it coincides with *the obtuse bisectrix* which divides the obtuse angle ( $-2V$ ) into halves. The axes of rhombic crystal indicatrices coincide with the crystallographical axes  $X$ ,  $Y$  and  $Z$ , while

Fig. 43. Optical indicatrix of the crystal of the low category of symmetry

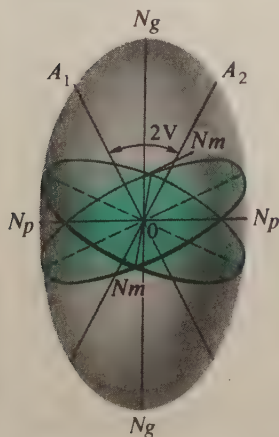
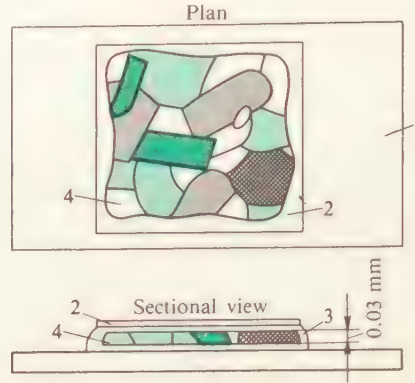


Fig. 44. Transparent section for microscopic investigation:  
 1—(microscopic) glass;  
 2—cover glass; 3—Canada balsam;  
 4—crystal-grained plate of the mineral aggregate



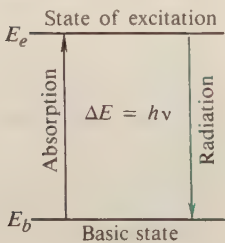
the monoclinic crystals have only one axis of indicatrix which coincides with the Y axis. Crystals of triclinic system are characterized by the absence of any cases when the crystallographic axes would coincide with the axes of the indicatrix.

Optical properties of minerals are widely used for the diagnosis of minerals and in determining their chemical composition with the help of a special *polarized microscope*. The methods of optical microscopy are based on the constant character of optical properties of minerals of invariable composition and their functional relationship to the chemical composition in minerals of the isomorphous series. For example, the indices of refraction of the minerals of the olivine series, intermediate as far as their composition is concerned, decrease regularly from fayalite  $\text{Fe}_2[\text{SiO}_4]$  to forsterite  $\text{Mg}_2[\text{SiO}_4]$ .

The determining of optical constants is carried out mostly in transparent specimens, representing thin sections of minerals or rocks, 0.03 mm thick, attached (fixed) to the slide and closed with a cover glass with the help of Canada balsam (Fig. 44). The sections also lend themselves to the study, dimensions, the character of intergrowths and quantitative ratios of mineral grains.

Besides, optical properties of minerals are determined in immersion slide on small crystals and grains, which are submerged in immersion liquids with known indices of refraction.

Fig. 45. The diagram showing electronic transition from the basic energetic level  $E_b$  to the level of excitation  $E_e$ , with the absorption of energy, and, conversely, with radiation



## Spectroscopic Properties

Spectroscopic properties of minerals (colour, lustre and luminescence) are but external manifestations of the complex processes of interaction of the quanta with the electrons of the outer electronic atom shells. These processes are accompanied by absorption, reflection and radiation, if the electronic transitions from their basic state to the state of excitation and vice versa take place. These transitions are in accordance with the laws of quantum mechanics. They become possible on condition of resonance, i.e. when the energy of the quantum ( $E = h\nu$ ) coincides with the difference in energy between the excited ( $E_e$ ) and the basic ( $E_b$ ) states of the electrons ( $\Delta E = E_e - E_b$ ) (Fig. 45):

$$h\nu = \Delta E,$$

in which  $h$  is Planck's constant, and  $\nu$  is the frequency of light.

The energy necessary for the excitation of the electrons of outer atom shells in minerals corresponds in value to the energy of optic quanta, i.e. it occurs within the limits from several tenths up to a number of electron-volt and considerably exceeds the range of the visible section of the electromagnetic spectrum. Hence, directly observable spectroscopic properties of minerals are only part of absorption, reflection and radiation processes that become apparent not only within the range of visibility, but also in the fields adjacent to the ultraviolet and infrared regions of the spectrum.

### Colour of minerals

The colour of minerals is the most obvious and conspicuous outer property of a large number of minerals. Minerals are distinguished by an extraordinary variety of colour and shades, richness and intensity. Some mineral species are characterized by a constant colour, which enables to determine them almost unerroneously. It would suffice to adduce vermilion, golden yellow pyrite, green malachite, blue lazurite. Other minerals, such as tourmaline, beryl, garnet, fluorite, calcite may be of various colour. Thus, for instance, the crystals of tourmaline are found to be black, green, blue, brown, rose or even lacking in any colour at all.

In a large number of minerals the colour is spread evenly. However, multicoloured (polychromatic) minerals with mottled or regular zonal or sectorial distribution of different colour are also found. For instance, sometimes, one end of the tourmaline crystals is black, while the other is green, the middle part remaining colourless or rose.

Fluorite, quartz, calcite, garnet, topaz and others are also often found in the form of *polychromatic* crystals.

The intensity with which colour manifests itself depends on the aggregate condition and the character of the surface of minerals. In large crystals and coarse-grained aggregates the colour of many minerals is usually darker than in smaller grains, finely-granulated or dispersed aggregates. Thus, the outwardly black hematite in earthy aggregates is dark-red, while the almost black aegirine in finely-shaped aggregates has a light-green colour. On the other hand the golden-yellow pyrite in earthy aggregates is black. As a rule, the transparent crystals of minerals have very little colour or are achromatic (colourless) at all. In dispersed powdery, porous, earthy and fine-grained aggregates or in crystals containing many inclusions the dark minerals are usually brighter.

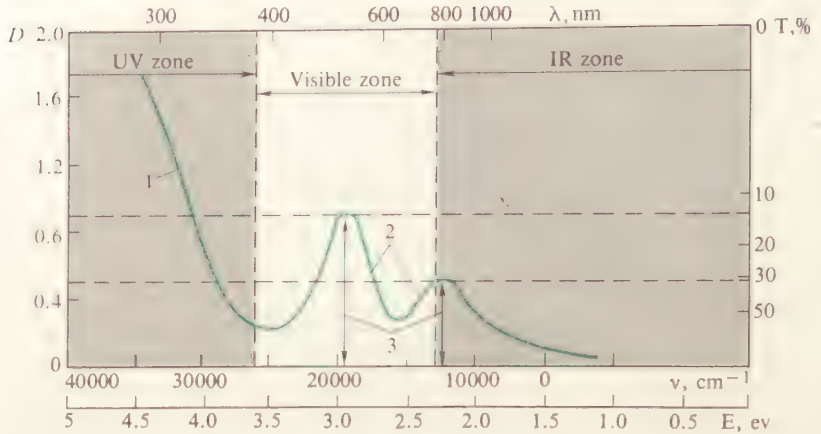
The measure of intensity of absorption or the light transmission passing through the crystal is the *transmission*  $T = I/I_0$ , where  $I_0$  is the intensity of the initial luminous flux;  $I$  – the intensity of the latter when it has passed through the crystal; and the *optical density*  $D = \lg 1/T$ . In accordance with the Bouguer-Lambert law

$$I = I_0 e^{-\alpha t}$$

where  $t$  is the thickness of the crystal (cm);  $\alpha$  is the coefficient of absorption, which characterizes the nature of the mineral.

The *reflection* of light is composed of mirror and diffuse components. The intensity of mirror reflection  $R$  for the strongly absorbing minerals is connected with Fresnel's formula with refraction

Fig. 46. The absorption spectrum of light and its parameters: 1—the edge of the fundamental band of light absorption; 2—the absorption hand; 3—absorption band maxima



indices  $n$  and absorption index  $[K]^*$ :

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

The intensity of the *diffuse reflection* is increased with the diminishing of the size of the grains in aggregates and is proportional to the coefficient of absorption. The intensity measurement of absorption and the reflection of light of minerals is conducted with the help of special instruments—*spectrophotometers*, which enable us to determine the dependence of these parameters on the wavelength of light, the graphical expression of which is termed the *optical spectrum of absorption or reflection* (Fig. 46). The maxima on the optical spectra of absorption correspond to the spectral field of absorption, while the minima correspond to the transmission of light. The position of the bands of transmission and reflection is practically the same.

The colour of minerals is of various nature. In accordance with the system elaborated by A.Ye. Fersman in his work, 'The Colours of Minerals' the following basic types are singled out: (1) the colour which is wholly conditioned by the characteristic features of the chemical composition, the crystalline structure and the presence of impurity elements—chromophores or the deficiency of minerals (idiochromatism, or colour proper); (2) the colour associated with the mechanical inclusions of brightly coloured foreign minerals (allochromatism, or the alien colour); (3) the colour which is the result of such phenomena as the scattering or the interference of light (pseudochromatism, or the false colour). Cases when the combination of all the above-mentioned types of chromatism are present in one and the same mineral are by no means exceptional.

The *idiochromatism* of minerals is determined by the degree of the overlapping of the visible field of the spectrum by the bands of the absorption of light. In compliance with the latter some minerals are either transparent or poorly coloured; the others conversely, are impervious to light, are richly coloured or possess a strong reflection

\*  $[K] = K\lambda/4\pi n$ , where  $K = \lg I_0/I - \frac{1}{t} = D/t = 0.4343\alpha$  is the linear coefficient of extinction,  $\lambda$  is wavelength.



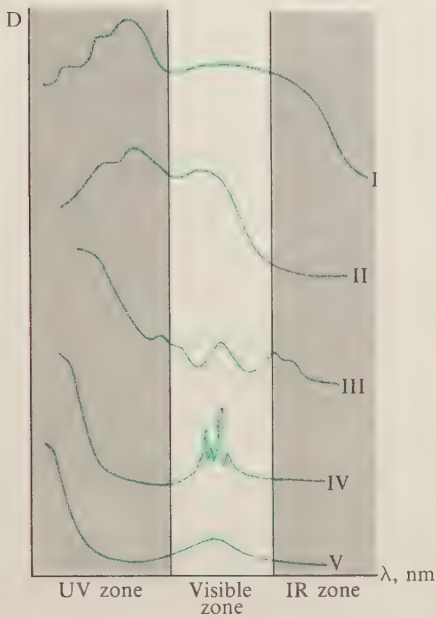
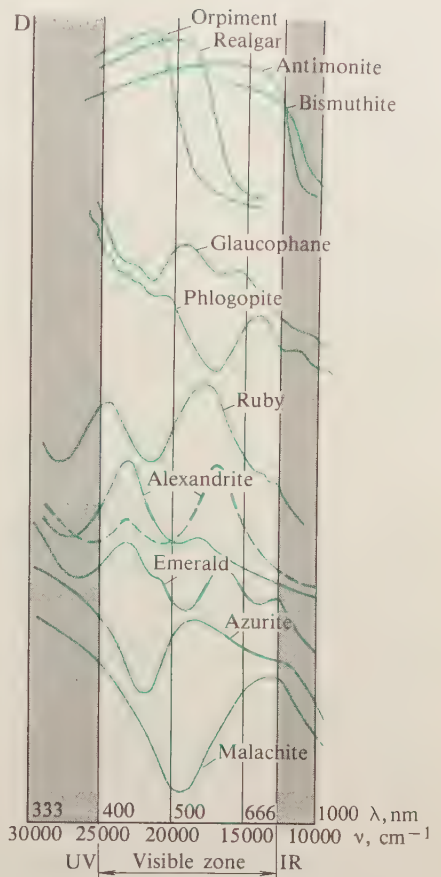


Fig. 47. Types of idiochromatic colouring of minerals and the degree of the overlapping of the visible zone of the spectrum by absorption bands:

*I*—intrinsic colour of nontransparent minerals with a powerful reflection of light and metallic lustre; *II*—intrinsic colouring with partial overlapping of transparent minerals with a powerful diamond lustre; *III*—chromophore colouring of minerals with the transition of the charge and *d*-transitions; *IV*—chromophore colouring of minerals with *f*-transitions on the ions of rare-earths; *V*—defective colouring of minerals with electronic and hole centres, molecular ions and free radicals

Fig. 48. Examples of absorption spectra of minerals with intrinsic and chromophore colouring



ranging from the steel-grey to the copper-red and golden-yellow colour.

Various colours correspond to a particular degree of the overlapping of the visible field of the spectrum by the bands of absorption of various nature (Fig. 47). In the short-wave part of the optical spectra of the minerals *the fundamental absorption band of light (the main band)* is situated. It is connected with the excitation of the valent electrons, and is characterized by a high degree of intensity. In accordance with the theory of molecular orbitals the absorption of light in this band corresponds to the transitions of electrons from the levels of the bond-forming orbitals to the levels of anti-bonding conditions. The main band of absorption, as is expounded in the zonal theory, corresponds to the transitions of electrons from the valency zone to the zone of conductance. The position of the long-wave edge of this band in the optical spectrum corresponds to the width of the forbidden zone and the minimal energy of transition. The width of the forbidden zone depends on the type of the chemical bond. With minerals of the metallic or covalent-and-metallic types of bond (most of sulphides, all metals and part of oxides) it is less than 2 eV; with minerals of the covalent bond it is 2-3 eV (some nonmetals, sulphides and oxides); with minerals of the ionic and ionic-and-covalent bonds (salts, a large

number of oxides and silicates) it is greater than 4.5 eV. Hence, with minerals of the first group the main band of absorption completely overlaps the visible field, and they are not transparent, but are characterized by a strong reflection of various colours and their shades of colour. Their variability is connected with a dissimilar reflection in different parts of the spectrum. With minerals of the second group the visible field is only partially overlapped and their colour is bright. With minerals of the third group the main band of absorption is situated far within the ultraviolet region. A considerable part of them in the visible field is either transparent or achromatic. A number of sulphides As, Sb, and Bi (Fig. 48) can serve as an example, illustrating the dependence of colour and reflection on the width of the forbidden zone and the degree of its overlapping the visible field of the spectrum.

*Bands of the charge transfer* between the species-forming or the admixing ions of various valency, as well as between anions and the metal of the transient group in complex anions are characterized by symmetry. The position of these bands in the spectrum depends on the type of the chemical bond, the coordination and the distance between ions. Partial overlapping of the visible field by the bands of the charge transfer between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  conditions the presence of brown or green colour in many ferriferous silicates. The intensity of the bands depends on the concentration of ions and their position in the crystalline structure, which explains pleochroism of a large number of minerals, as is the case with cordierite, hornblende, tourmaline, biotite and others. The transfer of the charge in complex anions conditions the bright colour in the visible field of chromates, lead molybdates and tungstates.

Electronic transitions and their corresponding absorption bands are connected with the impurities of ions of different valency in minerals, thus forming *the local donor-acceptor levels* in the forbidden zone. The energy of the transition between the donor-acceptor levels is smaller than the width of the forbidden zone, and, consequently, the bands of absorption are dislocated in respect to the main band in the long-wave field. For instance, the orange colour (band 2.42 eV) is connected with the transitions in the donor-acceptor pair  $\text{Cu}^+ - \text{Ga}^{3+}$ , the red colour of sphalerite is connected with the transitions between the valency zone and ion  $\text{Sn}^{4+}$  (band 2.18 eV) and in the pair  $\text{Cu}^+ - \text{In}^{3+}$  (band 2.35 eV).

The transitions between the levels of *d*-electrons of the elements of transition groups are connected with *the bands in the spectra of the crystalline field* which condition the presence of colour in most of the minerals with the ionic type of chemical bond as the result of partial overlapping of the visible field by one or several bands of absorption of moderate intensity. The position and the intensity of these bands of absorption in the spectra are described for minerals with a considerable ionic bond within the framework of the theory of the crystalline field of ligands and is determined by the degree of the disintegration of the *d*-levels, the distribution of electrons between them, and the probability of transitions. These parameters depend on the power of the crystalline field and its local symmetry. They are markedly influenced by the nature and the charge of ligands ( $\text{F} - \text{Cl} - \text{H}_2\text{O} - \text{S}^- - \dots$ ), interatomic distances and the ion-covalence degree of the chemical bond. This is particularly the reason why

different minerals, containing one and the same chromophore, are often distinguished by their colour (see Fig. 48). For instance, with chromeferrous minerals of the red colour—ruby, pyrope, spinel—the distance between the ions  $\text{Cr}^{2+}$  and  $\text{O}^{2-}$  is smaller than that of the green minerals—uvarovite and emerald. The bands of absorption of the green minerals are, consequently, shifted into the long-wave field so that the red part of the spectrum finds itself overlapped, and the transmission band is located in the green region of the spectrum. Similarly, the narrow band of transmission of azurite is situated in the blue part of the spectrum, while with malachite it is in the green zone. This is congruous with a greater degree of disintegration of the  $d$ -levels of the ion  $\text{Cu}^{2+}$  in the octahedral complex of azurite as compared with malachite, in which  $\text{Cu}^{2+}$  is surrounded by 4 ions of oxygen. The colour of many minerals is also connected with ions  $\text{Ti}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Ni}^{3+}$  and other transition elements.

The colour conditioned by the transitions between the levels of  $f$ -electrons of rare-earth ions and actinoids is highly characteristic. The narrow bands of absorption conditioned by the transitions on the  $\text{TR}^{3+}$  ions are responsible for the poor colouring. Wider bands are connected with the  $\text{TR}^{2+}$  ions. Both the former and the latter are responsible for the colour impurity of fluorite, anhydrite, scheelite and other minerals. Bright yellow and yellow-green colour of uranic minerals is connected with the transitions on complex ions of uranyl  $(\text{UO}_2)^{2+}$ .

The colour conditioned by electron transitions on various defects which function as *the electron-hole centres*, is characterized by wide bands of absorption in relation to a comparatively low intensity. They include: (1) centres of colour connected with anion vacancies ( $F$ -centres); they are typical of haloids (halite, fluorite); (2) impurity ions with an anomalous charge resulting from the occupation of the electrons or the hole, as is the case in amazonite  $(\text{Pb}_{\text{K}^+}^{2+}) + \bar{e} \rightarrow (\text{Pb}_{\text{K}^+}^+)^{\times}$ ; in anhydrite  $(\text{Y}_{\text{Ca}^{2+}}^{3+}) + \bar{e} \rightarrow (\text{Y}_{\text{Ca}^{2+}}^{2+})^{\times}$  etc; (3) anions which have occupied the electron or the hole, e.g. the hole centre  $(\text{O}^{2-})^{\times} + h^+ \rightarrow (\text{O}^-)$ , found in carbonates, borates and some silicates; (4) molecular ions which have occupied the electron or the hole, e.g.  $\text{S}_2^{2-} + \bar{e} \rightarrow (\text{S}_2^-)^{\cdot}$  in sodalite; (5) free radicals which have been formed as a result of capture of complex anions occupying the electron or the hole, e.g.  $[\text{CO}_3^{2-}]^{\times} + h^+ \rightarrow [\text{CO}_3^-]^{\cdot}$  in calcite.

Ionization promotes the formation of the colour of this type while heating leads to the loss of colour. The radiationally stimulated smoke-coloured morion, which is distorted in the process of heating, can serve as an example.

*The allochromatism* of minerals is conditioned by their phasal heterogeneity—mechanical inclusions that have a bright or darker colour. For instance, the eye-striking iridescence of the reddish-brown colour of aventurine is connected with the impurities of specularite flakes—hematite  $\text{Fe}_2\text{O}_3$ —in quartz. The rose colour of orthoclase is also associated with hematite impurity, which is the product of the disintegration of the solid solution. The green colour of scheelite is often connected with the impurities of malachite, coinciding with the thin fissures, while the dark-grey colour—with the smallest scales of molybdenite. The pigmenting inclusions can be evenly spread, either in spots or strictly according to the zones and sectors of the growth. In

this respect the crystals of chialstolite-andaluzite, in which the pigmenting bitumens form regular configurations are characteristic.

The *pseudochromatism* of minerals is of interferential nature and is manifested in the tarnish, opalescence and iridescence. *Tarnish* is usually the variegated or prismatic colour of minerals which becomes apparent only on the changed surface or in the spallings along fissures where a thin film of secondary minerals is formed (e.g. in oxidation). Bright violet and blue tarnish are characteristic of bornite  $\text{Cu}_5\text{FeS}_4$  to such an extent that its old name—variegated copper ore—may well be justified. Yellow, greenish and red tarnish is typical of chalcopyrite  $\text{CuFeS}_2$ , while the dark-blue colour, of antimonite  $\text{Sb}_2\text{S}_3$ . The interference on the thin films of hydroxides of iron are responsible for the attractive opalescent tarnish of quartz.

*Opalescence* is characteristic of opal which has a globular structure. Interference occurs only with the noble varieties of this mineral, which are distinguished by a regular closest packing of globules corresponding to the wavelength of visible light. Silky opalescence is sometimes found with fine-fibrous pale-coloured rubellite, in which the thickness of fibres also corresponds to the wavelength of visible light.

*Iridescence* is found in semi-transparent minerals containing oriented inclusions of foreign minerals. For instance, the bright yellow-green and blue iridescence of labradorite is connected with the interference on the minutest oriented plate inclusions of ilmenite. Sometimes iridescence occurs in finely-scaled minerals, e.g. in muskovite, as a result of the interference on the borders with other mineral inclusions or in air band. Blue iridescence of moonstone is associated with the inclusions of albite in orthoclase.

*The colour of the streak.* Minerals the hardness of which is not considerable (< 5.5-6), leave a streak on the rough surface of the porcelain plate. Sometimes its colour differs from that of the mineral. The colour of the streak, i.e. the colour of the mineral in powder-form, serves as a more reliable characteristic feature of colour and is, hence, more widely used in diagnostics. The dark-red streak of hematite and the bright golden-yellow streak of gold are typical examples.

The colour of minerals has a marked diagnostic importance since it reflects the characteristic features of the structure and composition of minerals. It is employed to determine the content, valency and forms of inclusions of elements-chromophores, as well as in establishing various imperfections in the structure of mineral individuals. Colour also helps to speak of the genetic type of the deposit, temperature or the redox conditions of mineral formation.

The colour of minerals is highly significant as an exploratory feature of various ores. The green and blue selvages of malachite and azurite help to locate copper ores, rose powdery coating of erythrite function likewise for cobalt ore, brown and rusty colours of hydroxides of iron make it possible to establish the place of oxidation of ore deposit. The blue colour of halite often serves as a feature with the help of which the presence of sylvite and carnallite is established. Black, dark-violet colour of fluorite speaks of its association with radioactive minerals. The boggy-green tourmaline in granite pegmatites may well be connected with the presence of the rare mineral caesium—pollucite etc. This what A. Ye. Fersman wrote on the colour of minerals: 'The colour of minerals should particularly be the concern of the geo-

chemist-pro prospector and the field-researcher for whom it is the primary feature serving to locate the deposit of mineral resources and what can be of more value than an experienced eye'.

### The lustre of minerals

The reflection of light from the surface of minerals is perceived as a lustre of various intensity. Lustre is related to the ability of reflection, which is expressed as a relationship of the intensity of the reflected light  $I_1$  to that of the falling light  $I_0$  (in %):  $R = I_1/I_0$  and the refraction index. On evenly cleaved spallings, on faces and on the polished surface of crystals or crystalline-granular aggregates with the size of the individuals exceeding 0.5 mm there is lustre of unequal intensity and quality. Transparent and semi-transparent minerals with a low or moderate refraction index ( $n = 1.3-1.9$ ) and low reflecting ability of light ( $R = 2-9\%$ ) are characterized by *glassy lustre*, whereas, *the adamantine lustre* is typical of minerals with a greater index of refraction ( $n = 1.9-3.2$ ) and the reflecting ability ( $R = 9-27\%$ ). Nontransparent minerals with a low refraction index and a low reflection ability are also characterized by a glassy lustre, while with greater values of  $n$  and  $R$  ( $1.9-2.6$  and  $9-20$  respectively) it is *the submetallic lustre*. The refraction index of minerals with *metallic lustre* is greater than 2.6 and other reflecting ability exceeds 20%.

On the uneven surface of the crystalline aggregates as well as on the dull surface of the cryptocrystalline and amorphous aggregates the lustre is found to be *waxy* and *dull*. *Greasy* lustre is characteristic of transparent minerals, while *resinous* is typical of the nontransparent ones. A large number of minerals with fibrous structure are found to have *silky* lustre (e.g. gypsum-selenite, chrysotile-asbestos). *Pearly* lustre is typical of scaly minerals (muscovite, orpiment, hydrargillite).

The lustre depends on the type of chemical bond. Metallic lustre is shared by minerals with metallic and covalent-metallic bond. The diamond lustre is typical of minerals with covalent bond; minerals with ionic type of bond have a glassy lustre. The lustre is the most important diagnostic feature of minerals.

### The luminescence of minerals

Some minerals when radiated or acted upon by other external factors can radiate light. The ability to do this is called the *luminescence*. Luminescence usually becomes apparent at the excitation caused by ultraviolet or visible light (photoluminescence), X-ray or cathode rays (X-ray and cathode-luminescence respectively). Thermal excitation (thermoluminescence) is always widely used in mineralogy. Luminescence can occur in the electromagnetic field (electroluminescence), as well as under mechanical deformations (triboluminescence) and the growth of crystals (crystalloluminescence) etc.

The luminescence is characterized by excitation, colour, intensity and duration. Luminescence occurs only under the absorption of energy, necessary for the electronic transitions from the levels of the basic state to the levels of excitation and the subsequent reverse transition.

*The excitation* of luminescence is determined by the optimal value of the excited energy. For photoluminescence it is several electron-volts. The corresponding bands of excitation in luminescence spectra are usually distinguished in the ultraviolet (UV) and more infrequently in

the short-wave part of the visible field. The luminescence of some minerals is excited only by the short-wave part of the UV-light, which is characteristic, for example, of scheelite. The other minerals e.g. ruby, luminesce under the radiation of the long-wave UV-light. Many minerals are brought into the state of excitation in the wide band of the long-wave range, for instance, the manganiferous calcite. The number of X-ray cathode-luminescent minerals is considerably greater than those that are excited in the ultraviolet light. Some non-luminescent minerals, after special processing become luminescent.

*The colour and intensity of the luminescence* of minerals are of various nature and cover a wide range with different kinds of mineral species. Minerals are known to be of violent luminescence (fluorite), blue (scheelite), light blue (diamond), green (autunite), yellow (powellite), orange (sodalite), red (ruby), and of all intermediate shades of colour. Cases are not rare when one and the same mineral can luminesce different colours. Calcite is found to have red, orange, yellow, green, light-blue and white luminescence. Fluorite has not only violet, but green luminescence as well. Variegated colours of luminescence have also been established for apatite, scheelite, zircon, diamond, lazurite and other minerals. Sometimes even the luminescence, different in colour and intensity, is found within the limits of even one crystal. Thus, for instance, the outer zones of the growth of calcite crystals often have a brighter orange-red luminescence than its central parts. Then the zonal crystals of molybdoscheelite are characterized by a change of the yellow luminescence to its white and light-blue varieties from the centre to the periphery. In diamond the light-blue and yellow luminescences usually coincide with various sections of the growth.

The colour and the intensity of luminescence are determined primarily by the nature of the phenomenon itself, though their direct apprehension also depends on the extent to which the bands of radiation coincide with the range of the visible field. Electronic transitions are accompanied by inevitable losses of energy, i.e. the energy of radiation is less than that of excitation. Hence, in the spectra of luminescence the bands of radiation are shifted into the long-wave field in respect to the bands of excitation and, as a rule, are wholly or partially situated in the visible field. Only in some cases the bands of radiation are located in the ultraviolet or infrared fields of the spectrum. When minerals are heated, the intensity of luminescence decreases, conversely, when the cooling process takes place, the intensity usually becomes greater. There are some minerals the luminescence of which is exhibited only at a very low temperature, e.g. wulfenite  $\text{Pb}[\text{MoO}_4]$ . In the case of thermal excitation of luminescence the intensity and the colour of luminescence change with the rise in temperature.

*The duration of the luminescence* becomes apparent on the cessation of excitation. In conjunction with the latter, *fluorescence* and *phosphorescence* are clearly set apart. If the short afterglow (usually  $\tau < n \cdot 10^{-2}$  s) does not depend on temperature, it pertains to fluorescence. If the duration of the afterglow (usually  $\tau > n \cdot 10^{-2}$  s) increases under cooling, and decreases in the process of heating, then the phenomenon dealt with is phosphorescence. Most of the luminescent minerals are characterized by fluorescence and only a part

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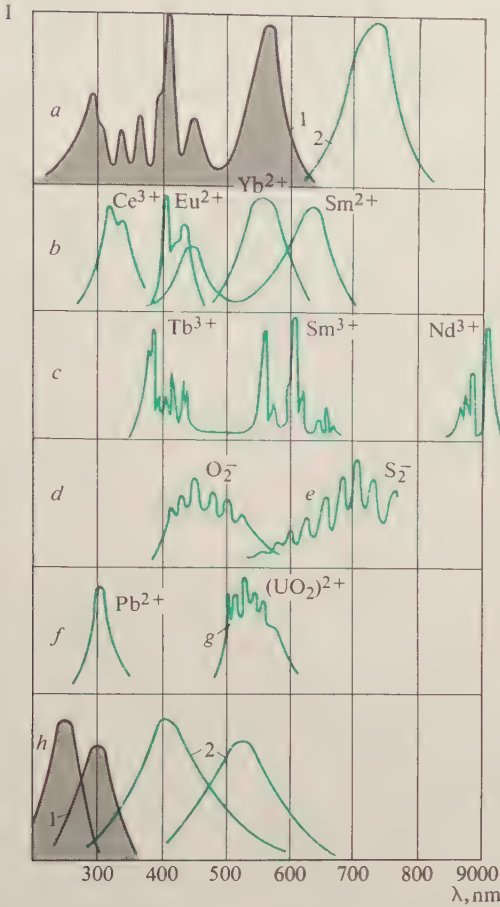


Fig. 49. Spectra of excitation (1) and radiation (2) of various centres of luminescence in minerals:

a—spectra of  $Mn^{2+}$  luminescence in calcite; radiation spectra of bivalent (b) and trivalent (c) rare-earth ions in fluorite; molecular  $O_2^-$  ions in anhydrite (d) and  $S_2^-$  in hackmanite (e),  $Pb^{2+}$  ion in calcite (f) and  $(UO_2)^{2+}$  in tuyamunite (g); (h)—luminescence spectra of tetrahedral anions  $[W^{5+}O_4]^{3-}$  in scheelite (left), and  $[Mo^{5+}O_4]^{3-}$  in powellite and molybdscheelite (right)

of them are conspicuously phosphorescent. Phosphorescence of marked duration is characteristic of calcite with white luminescence, of pseudomorphism of calcite by aragonite, of barite with yellow luminescence, of fluorite with the green luminescence, of many colourless borates etc. A large number of minerals exhibit phosphorescence under X-ray excitation.

The character and the types of electronic transitions as well as the luminescent properties of minerals related to them are determined by the nature of the centres of luminescence, which represent point, impurity, or structural defects. In some cases the processes of absorption of the excited energy and its radiation take place within the limits of the centres. In other cases, processes of this kind are connected with the transitions of energy between centres.

In most of the luminescent minerals the centres of luminescence are the ions of transition metals, such as  $Mn^{2+}$ ,  $Cr^{3+}$ , and rare earths  $TR^{2+}$  and  $TR^{3+}$ . Luminescence in these centres is connected with the electron transitions between *d*- or *f*-levels, split by the crystalline field.  $Mn^{2+}$  centres are connected with a markedly wide band of orange or red luminescence with the maximum approximately equal to 600 nm in such a widespread mineral as calcite (Fig. 49a), as well as in wollastonite, anhydrite, apatite, spodumene and others. The  $Cr^{3+}$  ions, replacing the positions of aluminium, are responsible for

the red luminescence of ruby and the noble spinel, alexandrite, emerald, cyanite and others. The band of violet luminescence with the maximum 425 nm is connected with the  $Eu^{2+}$  impurity in fluorite; the yellow-green band ( $\lambda_l = 540$  nm) is connected with the  $Yb^{2+}$  impurity, the former reaching the state of excitation only at a low temperature (Fig. 49b). The narrow lines of luminescence in fluorite, apatite, monazite, zircon, scheelite and other minerals are conditioned by the transitions on the  $TR^{3+}$  ions (Fig. 49c).

The luminescence of a large group of minerals is connected with the transition within the boundaries of the 'molecular' centres. They are represented by complex cations  $(UO_2)^{2+}$  in many hypergene minerals of uranium with brightly green luminescence (Fig. 49g), as well as by the centres  $S_2^-$  and  $O_2^-$  characteristic, for example, of barite with yellow-orange luminescence, of scapolite with red luminescence and others (Fig. 49d).

Luminescence conditioned by electronic transitions in anion oxygenous tetrahedral complexes of transitory elements is mostly characteristic of molybdates and tungstates of calcite. Wide bands of

light-blue luminescence of scheelite  $\text{Ca}[\text{WO}_4]$  and the yellow luminescence of powellite  $\text{Ca}[\text{MoO}_4]$ , as well as molybdo-scheelite  $\text{Ca}[(\text{W},\text{Mo})\text{O}_4]$  as compared with a large number of other minerals, are brought into the state of excitation only in the remote UV-field (Fig. 49h).

Special mention should be made of recombination luminescence. It takes place under the recombination of the excited donor-acceptor pairs in a number of sulphides (sphalerite, cinnabar, realgar) and diamond. The light-blue luminescence of sphalerite is connected with the transitions in the associated centre: the cation vacancy  $(V_{\text{Zn}^{2+}})''$  and the impurity  $(\text{Ga}_{\text{Zn}^{2+}}^{3+})'$ , the yellow luminescence is in the centre; the ion  $(\text{Cu}_{\text{Zn}^{2+}}^+)$  and the anion vacancy  $(V_{\text{S}^{2-}})''$ , and the red luminescence is in the centre:  $(\text{Cu}_{\text{Zn}^{2+}}^+)$  and  $(\text{Ga}_{\text{Zn}^{2+}}^{3+})'$  or  $(\text{In}_{\text{Zn}^{2+}}^{3+})'$ .

Recombination luminescence of cinnabar and realgar are connected with the donor-acceptor pairs of the type  $(V_{\text{A}})'' - (V_{\text{C}})''$ . The luminescence of diamond can be explained by the recombination transitions in the associated centres of the type  $(\text{N}_{\text{C}}^{5+})' - (\text{Al}_{\text{C}}^{3+})'$ —the line of light-blue luminescence,  $(\text{N}_{\text{C}}^{5+})' - (V_{\text{C}^{4+}})''''$ —the zone of yellow luminescence and others.

Luminescence is widely used in the diagnostics of minerals, if the centres of luminescence are the species-forming cations and anions, such as  $(\text{UO}_2)^{2+}$  in uran micas,  $[\text{WO}_4]^{2-}$  and  $[\text{MoO}_4]^{2-}$  in minerals of the scheelite-powellite series. Luminescent diagnostics is particularly reliable in the spectra of excitation and radiation. Luminescence facilitates the expressive diagnostics of minerals represented by earthy aggregates and small grains, as is the case with heavy concentrates.

Luminescent properties of minerals are employed for the assessment of the content and the discovery of the forms of inclusions pertaining to various impurities—the activators of luminescence and to determine their valency, coordination and local symmetry.

Luminescent properties serve as distinguishing features by means of which various genetic types of the deposits of scheelite, apatite, fluorite, calcite and other minerals are comparatively easily determined. The evaluation of temperature and other conditions of mineral formation are also indebted to properties of this kind.

The function of *thermoluminescence* consists in evaluating the relative age of minerals, sedimentary and magmatic rocks. The differences in luminescent properties are also employed during the sorting of diamonds, in the phase analysis of scheelite ores, as well as in their concentration.

## Electrical Properties

Minerals are acted upon by electrical potentials, the electrical and the electromagnetic fields, heating and mechanical deformations, which are accompanied by various electrical processes, as a result of which electrical charges and properties come into effect.

### Electrical conductivity,

measured in terms of specific electrical resistance  $\rho$  or the specific electrical conductivity  $\sigma = 1/\rho$ , represents one of the fundamental physical characteristics of minerals, since it directly reflects their



nature, type of chemical bond and all the characteristic features of their chemical composition, structure and defectiveness, i.e. their electronic structure. Depending on the value of electrical conductivity and the type of electronic structure described within the framework of the zonal theory all minerals are subdivided into *conductors* with  $\rho = 10^{-6}$ - $10^2$  ohms, *semiconductors* with  $\rho = 10^3$ - $10^{10}$  ohms and *dielectrics* with  $\rho = 10^{10}$ - $10^{17}$  ohms.

Mineral-conductors chiefly include native metals with the metallic type of chemical bond. The valency zone with conductors is half occupied by electrons and is partially overlapped by the zone of conductivity. The valency zone with dielectrics is wholly occupied by electrons. It is separated from the conduction zone by a wide zone of forbidden conditions, with the energy of several electron-volts. Semiconductors are distinguished by a comparatively narrow zone of forbidden conditions (usually fewer than 3 electron-volts) and a partial electron filling of the zone that is situated below the conduction zone. If the number of electrons in the partially filled zone is not great, they are referred to the *n-type with electronic conduction*. If, however, the number is predominant, they are referred to the *p-type with hole conduction*.

The electrical conductivity of metals decreases with the rise in temperature and usually increases when the concentration of impurities becomes greater. In semiconductors the electrical conductivity, to a great extent, depends on the content of impurities and on the structural defects and undergoes a marked increase with the rise in temperature. The *intrinsic* conduction of semiconductors is connected with the transition of part of the electrons, when heated, from the valency zone to the conduction zone with the formation of an equal number of free electrons and holes. The *extrinsic* conduction is conditioned by the ionization of isomorphous impurities with redundant charges. Thus, in sphalerite the impurity ( $\text{Cu}_{\text{Zn}^{2+}}^{\pm}$ ) produces a redundant negative charge, while the positive charge is produced by ( $\text{Ga}_{\text{Zn}^{2+}}^{\pm}$ ), the former and the latter being the donor and the acceptor respectively. Besides, redundant charges are found in the non-stoichiometric minerals. At high temperatures in semiconductors and dielectrics *ionic* conduction can also take place. It functions within the scope of vacancy mechanism.

To determine the type of conduction in semiconductors of minerals—sulphides and oxides—it is customary to employ the thermoelectric method. One part or end of the mineral is heated to a particular degree, while the temperature at the other end remains constant. Consequently, there is a difference of the electrical potential with the positive and the negative sign at the heated end of the mineral becomes apparent.

The dependence of electrical properties on the content of impurities and the non-stoichiometric character of the composition of the semiconductive minerals becomes pertinent to the study of the inner structure of these minerals in detail. A type of conduction bond with morphological characteristic features and a position in ore bodies and the temperature of formation has been established for certain minerals. Thus, for instance, *n*-conduction is typical of the high-temperature pyrite of the pentagon-dodecahedron habit. On the other hand, the low-temperature pyrite of the cubic habit is characterized by the

*p*-conduction which is compatible with those parts that have maximum concentration of gold.

The study of the electrical conductivity of minerals is also carried out in connection with the use of electrical methods in exploration geophysics since the ore deposits usually have maximum electrical conductivity as compared with the enclosing rocks, when electrophysical anomalies are explained it is necessary to take into account the fact that the electrical conductivity of rocks does not so much depend on the properties of minerals as on the character of intergrowths of conductive and nonconductive minerals. Some minerals, such as chalcopyrite, pyrrhotite, graphite form current-conducting intergrowths, more often than, for instance, galena and magnetite. It is also essential to consider porous solutions as electrolytes that can function as electrical conductors between ore minerals.

### **Polarization and the dielectric permeability of minerals**

are connected with a shift of positive and negative charges in different directions under the action of the electrical field. The polarization occurs in minerals-dielectrics and is not accompanied by electron conductivity. Polarization can be: electronic (asymmetrical shift of electrons in respect to the nuclei), ionic (shift of ions of different sign), orientational (orientation of dipoles). Polarization is measured in terms of *dielectrical permeability*. Impurities and defects have practically no effect upon dielectrical properties. Polarization is connected with the electrization of minerals, i.e. with the emergence of electrostatic charges of this or that sign on their surface. When the surface has an opposite charge, mineral particles in case of contact are attracted. On the other hand, conductive minerals at places of contact, for instance, with the earthed surface emit a negative charge and receive a positive one, as a result of which repulsion takes place. These distinctions between minerals-dielectrics and conductive minerals (usually ores) are used in dressing with the implementation of the method of the electrostatic separation.

Electrostatic charges on the surface of minerals-dielectrics also take place as a result of thermal and mechanical activity. It is a well known fact, for example, that the friction caused by the contact of native sulphur with wool or leather results in the electrization of the crystals. The electrostatic charge thus emerged deviates the leaves of the electroscope.

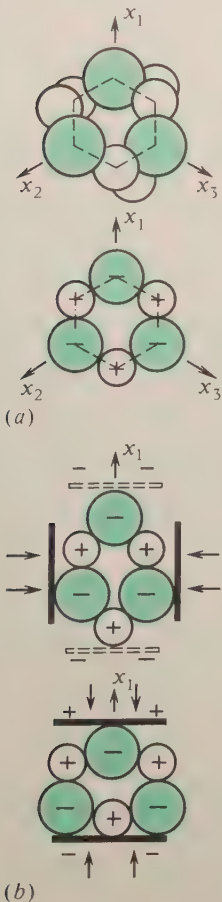
Special cases of dielectrical properties that are found in dielectrical crystals with polar axes of symmetry, i.e. with no centre of symmetry, deserve our particular attention. They are the pyro- and piezoelectrical effects.

### **Pyroelectricity**

manifests itself when charges of a different sign at the opposite ends of the crystal occur in the process of heating. Tourmaline is particularly remarkable for this property. Synthetic pyroelectrical crystals are used as means of transforming the thermal energy into electrical energy, as is the case with solar batteries. They also function as indicators susceptible to minute fluctuations of temperature and serve to transform the infrared radiation into visible light in the infrared images etc.

**Piezoelectricity**

Fig. 50. A fragment of the structure of quartz from the ions of silicon (+) and oxygen (-) (a) and the piezoelectric effect under the deformation of the quartz crystal parallel and perpendicular to the axis of the 2nd order (b)



occurs in crystals due to the mechanical effort along and across one of the polar axes of symmetry. Under compression electrical charges of a different sign appear on the opposite faces of the crystal. The sign of the charges is reversely changed under stretching. This effect was initially found on the quartz crystals. In the framework structure of the trigonal quartz the positive ions of silicon alternate with the ions of oxygen in a way which is exemplified in Fig. 50. If the external pressure is directed along the polar axis of the second order (one of the electrical axes  $x_1$ ,  $x_2$  or  $x_3$  coincides with it), the ions undergo a shift with the formation of dipoles. Consequently, charges opposite in sign appear on the faces that are normal to these directions. In those cases when the alternating current is applied to the piezoelectrical crystal, its compression and stretching take place with the corresponding frequency. Piezoelectrical crystals are used as generators of supersonic fluctuations, to stabilize the supersonic and electromagnetic waves in underwater communications and radiolocation, to measure the pressure in gun barrels, engine cylinders etc.

Among minerals possessing piezoelectrical properties the perfect crystals of quartz, rock crystal and morion, lacking in Dauphine and Brazilian twins, are of the greatest practical significance. Since natural piezoquartz is rare, the synthetic quartz is used as well as artificial compounds, mainly potassium sodium tartrate. Piezoelectrical properties have also been discovered with tourmaline, calamine, boracite and others.

**Magnetic Properties**

Magnetic properties originate and manifest themselves in the magnetic field. There are only few minerals that possess a high degree of *magnetization*, sufficient to attract the magnetic needle, magnetic powder or filings. However, most of the minerals reveal their magnetic properties only in a strong magnetic field with a high degree of intensity. Magnetic induction, which produces the magnetic field, undergoes changes in the presence of a mineral. The scope of its fluctuation is conditioned by the *magnetic permeability* of minerals  $\mu_m$  and the *magnetic susceptibility*  $\chi = (\mu_m - 1)$ , which is connected with the latter and determines the relationship of magnetization  $M$  and the magnetic intensity  $H$  in the mineral:

$$M = \chi H, \text{ or } \chi = \frac{M}{H}$$

Magnetic susceptibility, and consequently magnetization, depend on the number of unpaired electrons, each of which is characterized by a particular magnetic moment (spin), or by Bohr magneton:

$$\mu_B = \frac{e\hbar}{4m\pi}$$

where  $e$  is the charge;  $m$  is mass of the electron; and  $\hbar$  is Planck's constant. According to the value of the magnetic susceptibility and the

magnetization of minerals, as well as the character of their fluctuation in the magnetic field of various intensity when heated or cooled, several types of minerals, corresponding to various kind of magnetism, are singled out.

### Paramagnetism

Minerals-paramagnetics are characterized by the fact that their composition includes ions with unpaired electrons (primarily elements with vacant *d*- or *f*-levels) and chaotic orientation of spins. Hence, in the absence of the magnetic field the magnetic moments are compensated and minerals do not reveal any magnetization. As a result of orientation of spins in the magnetic field minerals are magnetized positively and are attracted in the direction of the magnetic field. When paramagnetic minerals are heated, following the disordering of spins, magnetization and magnetic susceptibility are decreased. With the growth of intensity in the magnetic field magnetization increases. Paramagnetics include moderately magnetic minerals: ilmenite, hematite, chromite, wolframite, siderite, pyrolusite, as well as ferriferous silicates.

### Diamagnetism

Minerals-diamagnetics are distinguished by a negative value of magnetic susceptibility, which is practically independent of the intensity of the magnetic field and temperature, decreases in the magnetic field and is driven out of it. Diamagnetic properties are most prominently manifested with native bismuth and graphite, native silver and gold, fluorite and calcite exemplify the opposite.

### Ferromagnetism

Minerals-ferromagnetics contain ions of transitory elements with unpaired spins, magnetic moments of which are oriented by the crystalline field within the limits of *magnetic domains*. They can be equated with micromagnetics of the size from a micrometre to a millimetre. In the absence of the magnetic field the magnetic moments of domains have various orientation and for this reason the magnetization of pure native iron, for example is not manifested. In the magnetic field the domains, like the spins in paramagnetics, are oriented, which causes a high degree of magnetization. After the magnetic field is relieved the disorientation of domains takes place. With some minerals this process is immediate, while with others it occurs within a certain period of time. There are cases when the *residual magnetization* remains. This is connected with a various mobility of magnetic domains in different minerals, depending on the presence of dislocations, inclusions of other minerals, such as the disintegration products of solid solutions, the zonal and mozaic character of crystals and other heterogeneities. The stability of residual magnetization finds its expression in the energy which is relevant for the process of demagnetization. It is called *the coercive force*. Minerals-ferromagnetics are characterized by a greater positive value of magnetic susceptibility, which, to a considerable degree, depends on the intensity of the magnetic field and temperature. As is the case with paramagnetics, spinal disordering takes place in the process of heating, magnetic domains are disoriented in ferromagnetics and at a certain temperature (Curie point) the magnetic moments are completely compensated and magnetization disappears – the former is transferred into a paramagnetic.

Ferromagnetics with a very high degree of magnetization include native iron, ferroplatinum, ferriferous gold.

### Antiferromagnetism

Minerals-antiferromagnetics are distinguished by the fact that under the influence of the crystalline field the spins of the neighbouring ferromagnetic ions have an antiparallel orientation. Above a certain temperature (Néel point) partial disordering takes place. It is accompanied by an insignificant increase in the magnetic susceptibility. Antiferromagnetics comprise certain sulphides, pyrite  $\text{FeS}_2$ , chalcopyrite  $\text{CuFeS}_2$ , troilite  $\text{FeS}$ ; oxides-ilmenite  $\text{FeTiO}_3$ , as well as other minerals, containing the ions of iron, manganese and a number of rare-earth elements: tourmaline, monazite, orthite, sphene, pyrochlore and others.

### Ferrimagnetism

Mineral-ferrimagnetics, just as is the case with antiferromagnetic, are characterized by the opposite orientation of spins, but are distinguished by an incomplete compensation of magnetic moments. Magnetization of ferrimagnetic is proportional to the number of redundant ions of the transition elements with unpaired spins. In magnetite  $\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4$ , for instance 8  $\text{Fe}^{3+}3d^6$  ions (C.N. = 6), 8  $\text{Fe}^{3+}3d^5$  ions (C.N. = 6) and 8  $\text{Fe}^{2+}3d^6$  ions (C.N. = 4) fall on an elementary cell. The spins of ions of iron in the octahedral and tetrahedral coordination have an opposite orientation, but they are wholly compensated only with  $\text{Fe}^{3+}$  ions (antiferromagnetism). The  $\text{Fe}^{2+}$  ions in the octahedral coordination have four electrons on the three lower  $d$ -levels. Two of these electrons are antiparallel, while on the upper levels there are two unpaired electrons, which is congruous with the high-spin configuration (see Fig. 8).

Thus, the magnetic moment of each of the 8  $\text{Fe}^{2+}$  ions is equal to the product of the four unpaired spins by the Bohr magneton. The magnetization of magnetite  $M$ , referred to the volume of the elementary cell  $V$  and equal to the product of the  $N$  number of  $\text{Fe}^{2+}$  ions by the magnetic moment of each ion ( $n\mu_B$ ), can be calculated by the formula

$$M = \frac{Nn\mu_B}{V}$$

Ferrimagnetic minerals together with the ferromagnetic ones refer to the strongly magnetized minerals, but are distinguished by the value of magnetization, which is mainly connected with the presence of nonmagnetic cations and anions. Among them magnetite possesses maximum magnetization, and easily attracts the magnetic needle.

Titanomagnetite, pyrrhotite, jacobsonite, maghemite, cubanite and other rarer minerals are less magnetic. Domain magnetic structure is typical of all of them, but the mobility of domains is exceptionally low. Hence, ferrimagnetic minerals are characterized by a high degree of *residual magnetization* and reveal magnetization in the absence of the magnetic field. The orientation of the magnetic moments in them coincides with the direction of the magnetic field at the moment of their formation.

'The magnetic memory' of minerals serves to reestablish the directions of the paleomagnetic field of the Earth, and is widely used

in reconstructing the positions of the magnetic poles in various geological epochs, as well as the classification of sedimentary and igneous rocks according to age. The diagnostic importance of the magnetic properties of minerals is restricted to the identification of only some of the strongly magnetic minerals, such as the said ferro- and ferri-magnetic substances, whose residual magnetization is high.

On the basis of a detailed study of the behaviour of minerals in the magnetic field of various intensity it is possible to subdivide minerals into para- and diamagnetics, while in paramagnetic minerals one can determine the concentration of paramagnetic ions (magnetic weighing). The study of the magnetic properties of minerals and the change of their temperature enables one to determine the content and the way the ions of various valency are distributed in the crystalline structure.

The origin of some magnetic minerals can be determined by magnetic properties. Thus, for instance, ilmenite from kimberlite, traps, alkaline rock and carbonatites are distinguished by the temperature of the ferriparamagnetic transformation (Curie point), which depends on the content of magnesium and chrome. The difference in the magnetic properties of minerals has a marked significance in geophysical explorations of the deposits of iron (magnetite) ores, diamond-bearing in kimberlites, containing magnetic ilmenite, as well as rare-metallic and magnetite-apatite ores in carbonatites and others.

The magnetic division of minerals and the concentration of ores, containing ferrimagnetic minerals, are based on the contrast of the magnetic properties and are carried out in electromagnetic separators with a regulated intensity of the heterogeneous magnetic field.

## Radioactivity and Radioactive Properties

*Radioactivity* is the transformation of unstable isotopes of one chemical element into the isotopes of other elements with the emission of radioactive particles. Natural radioactivity is shared by minerals whose composition includes radioactive-unstable isotopes of uranium, thorium, radium, radon, potassium, strontium and others. Strong natural radioactivity, connected with the radioactive isotopes of species-forming elements, serves as a diagnostic feature of the uranium and thorium minerals, for example, uraninite  $UO_2$ , thorite  $Th[SiO_4]$ , autunite etc. Moderate and weak radioactivity are caused by an inconsiderable impurity of U, Th isotopes, as well as other radioactive isotopes contained, for instance, in pyrochlore, samarskite, aeschynite, monazite.

The weak radioactivity of sylvite, microcline, muscovite and other potassium minerals is conditioned by the constant impurity of the radioactive isotope of potassium ( $^{40}K$ ). An inconsiderable impurity of radioactive elements is present in a large number of minerals, rocks and waters. There are cases when there is a concentration of radon in natural gases. All this leads to the creation of a natural radioactive background.

Radioactivity is studied by means of special instruments such as radiometers, while the distribution of radioactive minerals in rocks and ores or the radioactive elements in certain minerals by applying the method of *radiography*. The latter is based on the assumption that

radioactive radiation can illuminate photogene. If the polished specimen is closely attached to the film, the black sections, appeared on it, will correspond to the emission of radioactive minerals. The photographic density will correspond to the content of radioactive elements contained in them.

As a result of radioactive disintegration the isotope composition of elements is changed at the expense of disintegration products. For instance, when uranium is disintegrated the isotopes of lead  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and helium  $^4\text{He}$  ( $\alpha$ -particles) are formed. There is an accumulation of argon ( $^{40}\text{Ar}$ ) and calcium ( $^{40}\text{Ca}$ ) during the disintegration of radioactive isotope of potassium ( $^{40}\text{K}$ ), the disintegration of each radioactive isotope takes place at constant speed. The said speed (the period of half-life), the content of radioactive isotopes and the products of their disintegration in a mineral makes it possible to determine its age.

Minerals are characterized by various degrees of radioactive stability and permeability. Minerals containing radioactive elements or in a state of intergrowth with radioactive minerals undergo changes caused by  $\alpha$ -particles and fragments of spontaneously split nuclei. Along the trajectory of  $\alpha$ -particles there is a shift of atoms resulting in the formation of tracks characterized by a high concentration of vacancies and interstitial atoms. The concentration of tracks is proportional to the number of disintegrated radioactive isotopes, i.e. to the age of minerals.

Not infrequently the segments of radioactive deterioration are located in minerals in the form of concentric spheres corresponding to the segments of the retardation of  $\alpha$ -particles. The radius of these spheres corresponds to the maximum range of  $\alpha$ -particles and reaches approximately  $50\mu\text{m}$ . The colour of the radiative rings is connected with the ionization of the occurring defects and the formation of the radiative centres of colour. Radiative rings are particularly noticeable in micas and fluorite.

The metamict state of certain minerals, such as pyrochlore, orthite, zircon, containing radioactive elements is also connected with a high degree of radiative disintegration of their crystalline structure.

The radiative stability and variability of minerals are of particular importance in the technology of ore dressing. When the radiative methods are employed in the latter process it is not the natural, but *the induced radioactivity* that is widely used. It occurs during interaction of certain elements with the applied radiation. The radiative methods of dressing are based on the registration of neutron or secondary X-ray radiation as well as on the various ability of minerals to absorb or reflect the radioactive  $\gamma$ -,  $\beta$ -, or neutron radiation. Radiative stability and penetration of minerals are highly significant, that are used as concrete fillers, foundation and protective walls in nuclear reactors.

The variability of minerals under the influence of radiation also causes a considerable influence on some physical properties, for instance on the colour and the transparency of rock crystal, Iceland spar, optical fluorite and some of the precious stones.

## Thermal Properties

When minerals are heated the atoms entering into their composition are shifted in respect to the state of equilibrium. These shifts are mainly of fluctuating character of particular frequency. With the rise of temperature the amplitude of fluctuations is increased. The increase in the distance between the fluctuating atoms leads to changes of repulsive and attractive forces. Consequently, the kinetic energy is transformed into the potential energy, and vice versa. The equilibrium (theoretical) state in the structure corresponds to the minimal value of the potential energy for each atom (or atoms of one type). The potential energy of the fluctuating atom increases with the temperature. Variations of the vibrational energy also depends on the amplitude of vibration (i. e. on the value of the shift of atoms in respect to the equilibrium state), on the mass of atoms, the coordination number of atoms and other factors.

**Thermal capacity** of minerals  $C_v$  determines the amount of energy required to heat 1 mole by  $1^\circ$ . At absolute zero (K)  $C_v = 0$  at higher temperatures it increases proportionally to  $T^3$ , and then, beginning with a certain temperature (the Debye temperature) it becomes constant.

**Thermal expansion** is mainly determined by the growth of amplitude of fluctuating atoms when the heating of minerals takes place. Accordingly, the distance between the atoms increases, and the chemical bond becomes weaker. *The coefficient of linear expansion* is an anisotropic value and depends on the crystalline structure of minerals. Thermal expansion is also connected with a shift of atoms from the state of equilibrium and the transition to interstitial positions, i. e. with the formation of thermal defects— anion vacancies and interstitial atoms. The concentration of thermal defects is in an exponential dependence on temperature. Hence, a greater degree of thermal expansion corresponds to a greater concentration of vacancies in the structure of minerals. For example, metals with vacancies increase in volume when heated to the melting point by a tenth of a percent.

**The melting** of minerals takes place when the distance between the atoms increases and there is an increase in the specific volume of the mineral which is called *unconfined space*. Practically all the minerals melt with an increase in unconfined space by 2-6%. Ice and bismuth, whose structure is more dense in the liquid state, can be referred to as exceptions. *The melting heat* is the energy required to destroy the crystalline structure with the formation of the melt at a certain temperature immanent to each mineral, or *the melting point*. The latter decreases when the concentration of point defects and isomorphous impurities becomes greater. If melting takes place directly, by means of a transition into the liquid state with the retention of the composition, it is called *congruent*. Congruent melting is characteristic of metals simple in their composition, salts, oxides etc. In those cases when intermediate phases differing by the composition from the original mineral and melt are formed in the process of melting, the melting is called *incongruent*. The intermediate phases are usually formed during the melting of silicates, salts etc. whose composition is complex.



The temperature and the type of melting are accurately determined by experimental means presupposing absorption or emission of heat at uniform heating. Retardation in the rise of temperature at heating is connected with the processes of the absorption of melting heat. The heating of minerals is usually accompanied by the diffusive shifts of atoms. Under these circumstances in some of them disordering takes place. In others there is a homogenization of phases (the intergrowths of the products of the disintegration of solid solutions). In some of them there are phasal transformations—polymorphic transitions that are often accompanied by an increase in the volume, for example at the polymorphic transformation of aragonite  $\rightarrow$  calcite.

### Thermal decomposition

of minerals takes place when the temperature is below that of the melting point and is expressed in *thermal dissociation* of, for example, calcite  $\text{Ca}[\text{CO}_3] \rightarrow \text{CaO} + \text{CO}_2\uparrow$  or hematite  $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}^{2+} + \text{Fe}^{3+}\text{O}_4 + \text{O}_2\uparrow$ , and *thermal dehydration* of minerals, containing water, for example, gypsum  $\text{Ca}[\text{SO}_4] \cdot 2\text{H}_2\text{O} \rightarrow \text{Ca}[\text{SO}_4] + 2\text{H}_2\text{O}\uparrow$ , when heated in the open air, i.e. in the oxidizing atmosphere, some minerals are oxidized or burned. When sulphides, oxides, and salts are heated, the metal bead is produced in the conditions of recovery.

### Sublimation,

or vaporization, of minerals when they are heated is found to be typical of native mercury, cinnabar, realgar, orpiment, as well as graphite, bismuth, gold and other metals, particularly in the restoring conditions or in vacuum. The heating of metamictic minerals is accompanied by the liberation of energy of crystallization, leading to their excessive overheating and a bright glow, which becomes particularly noticeable in pyrochlore, samarskite etc.

It is also necessary to lay particular stress on the influence of heating on the colour of minerals. Under heating some colourless minerals of iron (siderite) darken, which is connected with oxidation  $\text{Fe}^{2+}$ .

Minerals with radiation colour usually change their colour or become colourless under heating. Thus, for instance, the radiation colouring of the green spodumene, when heated to  $250^\circ\text{C}$  becomes purple; further heating of spodumene up to  $500^\circ\text{C}$  makes the mineral lose its colour altogether.

The study of thermal properties and phenomena, which, in the process of heating, are accompanied by absorption or emission of heat, as well as by a loss or gain of mass, is carried out by employing the methods of thermal analysis with the help of special instruments—pyrometers, thermographs, thermoscales and more complex apparatuses. Microcalorimeters are used to measure the exact thermal constants—the heat of melting, dissolution et al.

The study of thermal properties of minerals and the phenomena pertaining to them is of great significance in the diagnostics of minerals, when their content and form of finding water, the valency of ions, in the measuring of the temperature of phasal transformations, dissociations, dehydration and melting takes place. The acquisition of thermal constants is necessary to interpret the reactions of native mineral formation.

The knowledge of the thermal stability of minerals is also important

so as to ascertain the conditions of their formation and it is particularly important in the technological processing of mineral raw materials.

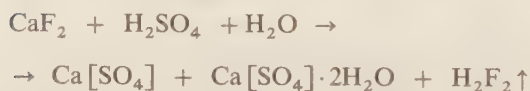
## Physicochemical Properties and the Stability of Minerals

When minerals interact with various chemical reagents—in liquid, gaseous and even solid states—there is a change or disintegration (decomposition) of minerals, uneven as far as its character and degree are concerned. The chemical stability of minerals depends on their constituent features and the selectively acting parameters of the chemical environment—concentration, acidity-and-alkalinity, redox potential, temperature and pressure. Under the influence of the chemical environment minerals are either partially or completely dissolved, hydrated, oxidized or reduced, evaporated, and enter into chemical reactions with the formation of new forms of matter.

### The solubility

of minerals is usually determined in relation to water and water solutions of acids (sulphuric, nitric, hydrochloric, hydrofluoric, acetic), alkali (KOH, NaOH) and various salts (mainly  $\text{Na}_2\text{CO}_3$ ). Minerals that are hard to dissolve in aqueous solutions are first melted with sodium carbonate, phosphate, borax, or sodium fluoride in order that alloys soluble in water or aqueous solutions of acids or alkali could be produced.

The rate at which minerals are dissolved depends on the size of grains. Hence, they are first grounded and grinded with a pestle. In the process of heating the solubility of minerals increases. There are instances when the solubility of minerals is accompanied by the formation of microcrystals of newly-formed substances at the surface of the grains. These microcrystals may prevent solubility. Thus, for instance, when fluorite is dissolved in the solutions of sulphuric acid the crystals or radiated aggregates of anhydrite or gypsum appear on the surface according to the reaction



It is equally difficult to dissolve the sulphates of alkaline-earth and other elements (Sr, Ba, Pb) and consequently sulphuric acid is hardly used in mineralogical research. In sodium solutions on the surface of fluorite and scheelite grains microcrystals of calcite are formed. Insoluble substances are hardly ever formed when the minerals are dissolved in hydrochloric acid. Most of the carbonates with the formation of bubbles of carbon dioxide, some sulphides with the liberation of hydrogen sulphide, as well as hydrated oxides with the liberation of chlorine (for example, when pyrolusite  $\text{MnO}_2$  is dissolved) are particularly soluble.

For the solution of sulphides nitric acid is usually used, sometimes mixed with hydrochloric acid; in the heated mixture  $3\text{HCl} + \text{HNO}_3$  (the aqua regia), which is the strongest oxidizer, even gold and platinum are dissolved. Silicates are dissolved with the help of

hydrofluoric acid. Due to the formation of easily volatile silicon tetrafluoride  $\text{SiF}_4$  most silicates are easily destroyed even in the vapour of hydrofluoric acid.

Minerals are less soluble in water. Those that are easily dissolved in water include nitrates, chlorides, fluorides, borates, sulphates and the carbonates of alkali and some other metals. Minerals dissolved in water are characterized by a specific taste—salty (thenardite), saline (halite), bitterly saline (sylvite), stingingly saline (carnallite), astringent (chalcantite) etc.

The faces of different simple forms of one and the same mineral have various solubility. The solubility of minerals is effected by various structural defects and impurities. This becomes particularly apparent and is employed in the process of mineral *etching* in solutions and oxygenous steam. Selective solution on the surfaces of spallings enable us to discover the zonal and other features of the inner structure of magnetite, arsenopyrite, garnet, pyrite, the twinned structure of quartz, dislocations and tracks on the spallings and faces of many minerals, different configuration of etching, which may also help to define the symmetry of crystals, to specify right and left varieties of quartz, etc.

Various solubility of minerals is used in diagnostics. The results of the investigation into mineral solubility are employed when analyzing the conditions of mineral formation and in the technology of processing the mineral raw materials.

## Redox reactions

between minerals and various reagents take place in those cases when the composition of minerals contains atoms of elements that can change their charge. Oxidation or reduction of minerals is accompanied by their partial or complete destruction and the formation of new substances, with liquescency, volatility or solubility as their distinguishing features. Infrequently they are characterized by a specific odour and bright colour and, hence, are employed for diagnostic purposes.

Redox reactions in solutions are often accompanied by the formation of coloured products of the reaction. Thus, when scheelite is dissolved in a heated hydrochloric acid in the presence of a reducer, such as metallic zinc, hydroxides with pentavalent and tetravalent tungsten of blue colour are formed. Identical reaction may take place if a drop of hydrochloric acid falls on the surface of scheelite and then is energetically grinded by a steel needle.

In most cases heating serves to promote processes of oxidation. There are instances, however, when, as a result of thermal dissociation processes with the extraction of oxygen, there is a reduction of ions, as is the case in the example discussed above. Here the reaction leads to the transformation of hematite into magnetite.

Redox reactions are widely spread in nature, particularly in the oxidation zone. The study of the oxidation processes and the reduction of minerals is significant in the technology of mineral raw-material processing.

## The Surface Properties

The change and destruction of minerals as a result of various external factors usually begins with the surface of mineral grains. The impact of these forces on minerals is determined by the micromorpho-

logical and crystallochemical characteristic features of the surface and largely depends on its macro- and micro-heterogeneity as well as defectiveness. The differences in the surface properties of various minerals can roughly be determined by touch or while rubbing the powder minerals between fingers. Minerals are said to be 'dry' or 'scraggy', similar to chalk. They are unpleasant to the touch for their coarseness or dryness (the sulphur powder, hydroxides of iron etc.). On the other hand, minerals like talc are referred to the so-called 'fat' minerals. Their smallest scales are known to stick to fingers when touched (kaolinite, montmorillonite, molybdenite) etc.

### The adsorptional ability

of minerals is varied in its nature and is manifested in that minerals adsorb on their surface molecules and ions. The adsorptional ability is particularly great with the dispersed minerals due to a large density surface, measured in the units of area by the units of mass ( $\text{cm}^2/\text{g}$ ). Adsorption is said to be *chemical* if strong chemical bonds are formed between the adsorbent and the adsorbate. *Physical* adsorption is the other type of adsorption, which is characterized by the fact that the adsorbent molecules can be easily scaped. In the first case adsorption can be likened as to the formation of chemical composition, containing combined atoms, belonging to both the adsorbent and the adsorbate simultaneously. In the second case these compositions are not formed. *Hygroscopicity*, i.e. the adsorption of moisture from the air by the insoluble minerals can be referred to as an example of physical adsorption of water (kaolinite, halloysite, and other clay minerals). These minerals stick to the tongue or the lips. As distinct from the latter some easily soluble minerals are hygroscopic to such extent that become dissolved (carnallite, bishofite and others).

### The wettability

of minerals wholly depends on the crystallochemical characteristics and type of non-compensated chemical bond typical of the surface of chippings. *Hydrophilic* minerals are easily wetted in water as compared with the *hydrophobic* ones, that are not wetted and are driven out as to the borderline separating the liquid from the air. This property of the minerals is used when the *floatation enrichment of ores* takes place. Mineral particles with natural *floatability*—hydrophobic ore minerals—become adhesive to air-bubbles, come on the surface and concentrate in the foam, which together with the ore minerals is mechanically separated from the hydrophilic minerals. Hydrophobic minerals include metals with fully compensated charges (gold, copper, platinum and others), layered minerals with a markedly perfect cleavage and the molecular crystals with weak hydrogen bonds or van der Waals bonds (graphite, talc, molybdenite, sulphur, realgar and others). Weak hydrophobic minerals include minerals-semiconductors with a complete or partially compensated covalent or covalent-metallic bonds (sulphides—galena, sphalerite, pyrite, chalcopyrite and others, as well as diamond). Natural floatability is not characteristic of hydrophilic minerals—dielectrics with uncompensated strong ionic or ionic-covalent bonds (barite, calcite, quartz, scheelite, feldspar, spodumene etc.).

The use of various floatation reagents makes it possible to change (or vary) the natural floatability of minerals which enables one to separate hydrophilic minerals from one another in the process of

enrichment. The use of apolar reagents (organic oils, kerosene and others) improves the floatability of hydrophobic minerals, which are adhesive to the drops of these substances.

The chemical adsorption of polar anion and cation reagents is used in the floatation of weak hydrophobic and hydrophilic minerals. The former are attached to the surface of the minerals with redundant negative charges, while the latter to the positive ones. As a result each grain is found to be in the environment of molecules, the free ends of which are not wetted by water, and consequently the hydrophobic nature and the floatability of the mineral is increased. Various surface defects, due to the locally uncompensated charges linked with them, exercise a considerable influence on the adsorption of floatability of minerals. Since most of the mineral chippings occur along the more defective directions of crystalline grains, the concentration of defects on the surface of fractured mineral particles can be highly substantial.

Floatation, at present, is the most widespread means of enriching mineral raw material: 90% of all nonferrous and rare metal ores are enriched by means of floatation, which makes it possible to process the exceptionally poor, with complex content as finely impregnated ores of copper, lead, zinc, molybdenum, tungsten, tin and other metals.

## The Methods of Mineralogical Research

### The Study of Minerals in Field-Work Conditions (Methods)

Any geological survey or thematic mineralogical study begins with geological observations of natural and artificial exposures, loose deposits, the walls of exploratory prospecting, core samples or the slime of boreholes. A detailed description in the field diary is made along with meticulous drawings and photography, the scale of which depends on the particular task set before the researcher and the range of the investigation. At first a general drawing should be made, e. g. of ore vein or contact zone, so as to show in what rocks the given mineral body is deposited, and to characterize its form and thickness. Then it is found useful to make a detailed documentation on the scale of 1:10 or even 1:1 to illustrate the interrelationship of minerals and their aggregates that have been the object of research.

Field diagnostics presupposes the study of external physical features and morphological characteristics, the use of such implements as the magnifying-glass, the sharp end of a pocketknife or a steel needle, and a porcelain plate. In order that the results of the diagnostics could be verified or the unfamiliar minerals determined and their chemical composition, structural and physical properties studied the selection of lumps of ore is made. Small pieces are cut off and samples are thus produced. The singling out of monomineral fractions implies the preparation of samples of a larger size. Samples obtained by the use of geological hammer and a chisel should be both representative and convenient, as far as their size is concerned, for transportation and storage. Unique samples of druse can be of a large size. However, care should be taken not to damage the specimens when they are being prepared or transported.

When specimens are selected, care should be taken that an exact location of their exposure, with the type of rock to which they belong, its characteristic features, colour, texture features, the size of grains, mineral composition etc. be registered in the field diary.

Entries are made in the diary at each exposure and at the selection of each specimen. The data thus recorded should be quite explicit. It is also necessary to record questions that arise during the procedure. For instance, cases of similarities that might exist between the given specimen and those dealt with earlier, the possibility of discovering a mineral that has so far not been found in the given mineral association, special relationship of minerals to certain types of rock and others.

When the research is being conducted in itinerary conditions, it is essential that all points of observation and the places of specimen selection should be registered on a map. This equally applies to quarries and exploitation openings where the specimens are selected.

Field specimens should be labelled. Each label should contain the name of the administrative body responsible for the research, the number of the specimen itself, the place of the finding and the working definitions of the specimen. All this should be written in soft pencil or ball-point pen, dated and signed. The label is then folded, wrapped and placed in the corner of a sheet of paper into which the specimen is neatly wrapped. If cotton bags are available, it would be better to put both the specimen and its label into each of these bags. Each bag should contain the number of the specimen written in inky pencil, soft-tip or ball-point pen. To preserve the brittle specimens of the dendritic aggregates and crystals card-boards, tin or plastic boxes are used. In those boxes the specimens are packed with thin paper, cotton or fastened by ropes or threads. Hygroscopic and easily soluble minerals are placed into polyethylene bags, hermetic plastic or glass containers.

At the base or in the camp the selected specimens are processed and sorted. When it is necessary, they are examined under a binocular microscope or in the ultraviolet light. For the verification of mineral diagnostics with the help of polarized microscope and a set of immersion liquids the refraction indicators and other optical constants are determined. The simplest chemical experiments, particularly of rare minerals are carried out too.

After processing the specimens should be registered in special diaries (the specimen catalogues) or in a card catalogue. Then they are neatly wrapped and packed into boxes. On the lid of each box there is the name of the field-crew and its address. Each box also contains a list of specimens.

To conduct chemical analyses, the study of physical properties and special investigations of minerals it is necessary that pure monomineral material be extracted, in sufficient quantity. If in ore or stock the mineral forms large crystalline grains and is present in vast quantities, its preliminary extraction is carried out under a pump test which is followed by the study of the selected fractured material under the binocular microscope.

To separate minerals that are found to be in close intergrowths as well as rare and accessory mineral samples of rocks and ores weighing 10-20 kg and more (depending on the content of minerals presenting special interest) samples are gradually crushed on the jaw or roll

crusher, filtered through the sieve, classified, and then as a result of the use of various methods, monomineral fractions are received.

The monomineral fractions of magnetic minerals—magnetite, titanomagnetite, pyrrhotite—are received by the method of wet magnetic separation on the electromagnet. The electric separator separates sphalerite from galena, cinnabar from antimonite etc. The floatation method is used to separate feldspar, quartz, molybdenite, pyrite, chalcopyrite and other minerals. Complex methods are employed to separate biotite, muscovite, garnets, olivine, pyroxenes, amphiboles, chrome-spinellides, sphalerite, galena, some carbonates and other minerals.

Depending on the type of rock or ore, their distribution in minerals, as well as on the properties of the minerals themselves, the separation designs of monomineral fractions can be varied.

Pure monomineral fractions set for control are examined under binoculars and, if necessary, subjected to hand cleaning. Then their morphological characteristics, colour, size, the presence of zonality or deformation, the character and the degree of mineral variability are described in detail, to be followed by chemical analyses and other forms of investigation.

## Methods of Studying Heavy Concentrates

*Heavy concentrate* is a concentrate of heavy minerals which results from the washing of friable natural deposits or dwarfed rocks and ores. The study of heavy concentrates is one of the methods in prospecting mineral resources, e.g. gold, diamonds, platinum, scheelite, cassiterite, cinnabar and others. The method of heavy concentrates is also widely used for the correlation of barren deposits by the mineral composition of heavy fractions.

The material scattered and grounded into powder is washed in an iron pan or a wooden trough. For this purpose the trough loaded with rock (10-20 kg) is submerged into water and its contents are elaborately and uninterruptedly stirred and washed. The trough being smoothly moved from side to side, forwards and backwards, the light minerals are washed away. This results in that only a small number of heavy minerals are left in the trough. The washed sample (heavy concentrate) is then removed into a bowl, dried, placed into a special package and sent to the laboratory.

The colour of the heavy concentrate depends on the prevalence of this or that mineral. Magnetite, ilmenite, chromite give the heavy concentrate a black colour; red is associated with garnet, while the light-brown colour is conditioned by the presence of zircon. If the heavy concentrate consists of lightly-coloured minerals (quartz, feldspar, and others), its colour is light. Same may be said of poorly washed specimens, i.e. those containing a considerable number of minerals with low density.

The mineral composition of heavy concentrates depends on the composition of original rocks. Each rock or placer corresponds to its own association of minerals. Alluvial placers, formed in the valleys of large rivers, washing away rocks of various composition are an exception. Heavy concentrates, taken from these deposits, can contain several mineral associations at the same time.

For the mineralogical analysis of the heavy concentrate to be complete an average sample of 5-10 g will suffice. The heavy concentrate analysis consists in a segregation of the heavy concentrate into fractions, determining the minerals and the quantity of mineral content in the heavy concentrate and in the rock.

The division of the heavy concentrate into fractions is based on various physical properties of the minerals: magnetization, density and others; fractions are also distinguished by the size of grains.

Minerals selected from the heavy concentrates are determined by their morphology, colour, luminescence, density, magnetic and crystalloptical properties with the help of spot and microchemical reactions and more complex methods of analysis.

The general network of the mineralogical analysis of the heavy concentrate includes the following operations:

1. washing in the trough;
2. weighing of the heavy concentrate;
3. sieve separation and weighing of selected fractions;
4. study of a large fraction under binoculars;
5. taking of average sample from fine fraction;
6. the division into magnetic and nonmagnetic fractions by a permanent magnet;
7. study of the magnetic fraction under binoculars and its weighing;
8. the division of the nonmagnetic fraction in heavy liquids with the extraction of light and heavy fractions;
9. the division of the heavy fraction into electromagnetic and nonelectromagnetic fractions by the electromagnet;
10. the microscopic study of fractions;
11. determination of minerals by outer properties, under the microscope, with the help of chemical reactions. The study of radioactivity, luminescence and magnetic properties; the carrying out of spectral analysis;
12. determination of mineral content in heavy concentrates.

*The washing in the trough* is called for in those cases when the heavy concentrates delivered to the laboratory are found to be clogged with clay particles and poorly washed in the field. The heavy concentrate is emptied out into the trough, which is placed into a large enamel vessel filled with water. Under the water the heavy concentrate is stirred with a glass stick, the heavy minerals remaining on the bottom of the trough. By slanting the trough on to one side and carefully shaking it, we relieve the contents of light minerals, which are coalesced and sedimented on the bottom of the vessel. This results in the remaining on the bottom of the trough only an inconsiderable part of the heavy concentrate (heavy minerals). The heavy concentrates are dried and further subjected to processing.

*The weighing of the heavy concentrate* and all selected fractions is accurate to 0.01 gram.

*The sieve analysis*, or the separation of the specimen according to the size of the grains, is used in those cases when the specimen consists of grains of different coarseness. Heterogeneously coarse material hampers the processing and makes it impossible to properly carry out separation of minerals by applying magnet, electromagnet or solid liquids. The sieve analysis presupposes the use of laboratory sieves of



various construction (design). One sieve is inserted into the other, thus forming a whole set. The lowest sieve is placed on the bottom plate into which the smallest grains are discharged. The top sieve must have a lid. Thus, all sieves form a column with the sieve with large meshes on the top followed by those whose meshes gradually decrease in diameter. The specimen is discharged into the top sieve and the whole set is shaken within 5-10 minutes, till the separation is completed. After that, the sieves are separated one by one in decreasing order and each fraction is weighed.

The large fraction is weighed, divided by the magnet and studied under the binocular.

*The average sample* is a small quantity of heavy concentrate corresponding to the average composition of the whole sample. The average sample is taken from the uniform grained material and its weight conditioned by a complete mineralogical analysis should comprise 5-10 g. Sometimes, the mass of the average sample must be increased up to 15-20 g (when the heavy concentrate contains a large number of magnetic minerals) and even up to 100 g (in those cases when rare minerals are to be determined).

There are various methods of sample reduction, but the most accessible one is that of *quartering*, which is widely used in practice. Sometimes, special equipment is employed for the reduction of samples.

*The extraction of the magnetic fraction* is carried out with the help of constant magnets. Magnetic minerals entering into the magnetic fraction are: magnetite, titanomagnetite, pyrrhotite, as well as intergrowths of magnetic minerals with other minerals. The extraction of magnetic fraction can be carried out with the help of a horseshoe magnet, but more conveniently and in a shorter period of time magnetic separation can be achieved by applying the multipolar permanent self-releasing magnet. After the magnetic fraction has been extracted the nonmagnetic remainder undergoes further separation with the help of electromagnet or solid liquids.

*The electromagnetic separation* is the separation of the heavy fraction of the specimen according to the degree of the magnetic permeability of minerals which is smaller than that of magnetite. There are various types of electromagnets, but at present electromagnets with the strength of current ranging up to 2 and even 8 A are more often used. With the help of electromagnets, by changing the strength of current, it is possible to single out three electromagnetic fractions: strong-, mid-, and weak-magnetic fractions. The strong electromagnetic fractions include the following ferruginous minerals: hematite, ilmenite, goethite, chromite and others. The mid-electromagnetic fraction comprises ferruginous silicates: amphiboles, pyroxenes, garnet, epidote, biotite and others. The weak electromagnetic fraction contains the following remaining minerals: sphene, monazite, orthite, xenotime and others.

*The division of minerals according to density* is carried out by means of applying heavy liquids, heavy alloys and a special contrivance for mechanical blowing. These methods are based on the difference in density with minerals. Heavy liquids should be transparent, easily concentrated and dissolved by any solvent and should not enter into chemical reactions with minerals undergoing separation or be

disintegrated when processed. The separation of heavy concentrates presupposes the use of various heavy liquids: bromoform (density 2.65-2.9), Thoullet solution (density 3.4), methylene iodide (density 3.33), ethylene bromide, acetylene tetrabromide and others, as well as heavy alloys: mercurious nitrate, Brion mixture and others. All heavy liquids are toxic and it is possible to work with them only in the fume cabinet or in a well-aired room.

Bromoform is used more often and proves to be more handy. In the process of bromoform separation the minerals with density  $< 2.9$  (quartz, feldspar, zeolite and others) enter into the light fraction. Minerals with density  $> 2.9$  remain in the heavy fraction. As a rule, the light fraction does not present any interest to the analyses of mineral resources and does not undergo further investigation. The heavy fraction can be divided into even a greater number of fractions with the help of heavy liquids with a greater density, as compared with bromoform and with the use of heavy alloys. Thus, if methylene iodide, mercurious oxide and Brion mixture are employed, it is possible to single out fractions with the following densities:  $< 2.9$ ; 2.9-3.3; 3.9-4.3; 4.3-5.0 and  $> 5.0$ . Thus, each of the extracted fractions contains a limited number of mineral species, which considerably facilitates their determination. For the separation of minerals with approximately equal densities the thermogravimetric separation is employed.

*Electrostatic separation* is based on the difference in the electrical conductivity of minerals. According to the degree of electrical conductivity the minerals fall into three groups, viz. good, middle, and bad conductors. This method is most successfully employed when zircon is separated from cassiterite, monazite from tourmaline, wolframite from quartz etc.

For the extraction of monomineral fractions there are other methods too. They are: *dielectric separation, vibrational method, the method of blowing* and others.

After the heavy concentrate is divided into fractions and certain minerals are determined the content of minerals in the heavy concentrate and in the rock are determined. The balance method is the one that is most widely used. The method consists in weighing the extracted mineral on the analytical scales with the accuracy up to the fourth sign. Then minerals are measured in grammes per cubic metre or one ton of rock.

## Laboratory Methods of the Study of Minerals

Laboratory investigations are carried out to diagnose minerals, study their chemical compositions, physical properties, crystallo-chemical characteristic features, defectiveness and other heterogeneities essential to the solution of various theoretical, genetic and applied problems.

A brief outline of the most important laboratory methods of mineral analysis is given below.

*The chemical method* calls for a considerable amount of mineral matter (ranging from 0.5 to 5 g), the extraction of which in pure form

is not always simple, for the reason that they usually have a heterogeneous structure, are zonal, and contain smaller inclusions of other minerals etc. At a high degree of accuracy and a marked susceptibility to other elements (up to  $10^{-7}\%$ ) the method is comparatively cumbersome and expensive. Hence, microanalytical methods have recently gained more ground.

*Emission spectral analysis* is conducted to determine the chemical composition of minerals in qualitative and quantitative terms. This method is expressive and cheap and only an inconsiderable amount of mineral matter (approximately 0.05 g) suffices for its application. The susceptibility of spectral analysis for most minerals is  $10^{-3}$ - $10^{-5}\%$ . Spectral analysis implies the burning of a mineral sample in the electric arc of direct or alternating current, as well as in the high-voltage spark. During the evaporation of the sample there occurs an excitation of the atoms which results in radiation. The latter, with the help of prismatic or diffraction spectrographs is decomposed into a spectrum which is registered on a photographic plate or by a photoelectric method.

The interpretation of spectrograms is carried out on spectroprojects or microphotometers.

In order that the composition of minerals with grains of up to 50-100  $\mu\text{m}$  could be studied, the laser installations of local spectral analysis are employed.

*Flame photometry* represents one of the types of emission spectral analysis. The source of excitation is the flame of a gas burner working on a gas (acetylene, propane and others). It is a time-saving and comparatively simple method of determining the number of elements with the accuracy of 2-4% and sometimes 0.5-1%. It is usually used to determine alkaline and alkaline-earth elements. The sample under analysis is transmitted into a solution which is injected into the flame of the burner in a pulverized form. The radiation occurring in the flame is decomposed into a spectrum with the help of a spectrograph, and falling on a photoelement or photoamplifier through light filters causes a photocurrent which increases and is measured or registered by a recorder. The intensity of the photocurrent is proportional to the concentration of a particular element.

*Atomic-absorption analysis* enables us to determine the alkaline and alkaline-earth elements Sb, Bi, Pt, Ag, Sn, Co, Ni, Pb, Zn, Cd, Hg, Mo, Se, Te, as well as some other elements.

The sample is transposed into a solution, which, in the form of aerosol is injected into the flame of the burner, standing on the way of the rays of the standard source of light. The absorption of radiation, proportional to the content of the element to be determined, is registered by the photoamplifier, enhanced and measured or registered.

*The X-ray spectral analysis* helps to determine the elements when their content in the object whose investigation is in average not less than hundredths of one per cent.

The specimen in the form of a tablet is placed in the vacuum object camera of the instrument, and is subjected to radiation by an electronic beam of high energy. Under its action a secondary X-ray radiation, whose spectrum is characteristic of every element, takes place. The intensity of X-ray spectral lines of the corresponding elements are registered by the recorder and figureprinting appliances.

*X-ray spectral microanalysis* is basically analogous to the X-ray spectral method, but is conducted on a special appliance—an X-ray spectral microanalyzer. The electron-optical system of the instrument makes it possible to conduct the X-ray spectral analysis on an area of 3-5  $\mu\text{m}$  and, besides, to receive a vivid picture of the distribution of elements on the surface of the specimen under analysis on the TV screen.

*Radiometric methods* are employed to determine the intensity of the  $\alpha$ -,  $\beta$ - and  $\gamma$ -radiation of the radioactive elements. The measurements take place with the help of  $\alpha$ -,  $\beta$ -,  $\gamma$ -meters, the multichannel analyzers and other appliances.

*Radioactivation analysis* is based on the nuclear reaction of elementary particles with the elements entering into the composition of minerals. Its susceptibility of identification is exceedingly high (up to  $10^{-8}\%$ ). The specimens under investigation are placed into a channel of nuclear reactor to be radiated. The concentration of elements is determined by measuring the radioactivity of the specimens with the help of meters on special spectrometers with multichannel analyzers of impulses.

*X-ray diffraction methods* of studying minerals are based on the phenomenon of diffraction of X-ray beams, the length of which is commensurable with the interatomic distances (from 0.01 up to 1.0 nm). In mineralogical practice the powder method is commonly used. It helps to receive diffractograms in the form of X-ray powder pattern (Debye crystallogram—named after the scientist P. Debye). When this method is used, the powder of the mineral, attached to the steel thread in a colloidal vessel or rolled into a rubber ball, is placed into a cylinder chamber in which a photofilm is spread around its walls. The X-ray beams are registered on it after diffraction. After the film is developed, the X-ray powder pattern serves as a device for measuring the distances between the lines and the intensity of their darkening, and these data help to determine the interplanar distances and the parameters of the elementary cell of minerals.

By means of a special appliance—the *X-ray diffractometer*—the registration of the diffracted X-ray beams is carried out with the help of electronic photoamplifier, and is registered on the tape of the recorder in the form of a *diffractogram*.

*Electronic microscopy*, with the help of electronic microscope, makes it possible to study the most hyperfine morphological features of the smallest particles of minerals, the surfaces of faces and splittings, the investigation of the inner structure, discover dislocations and investigate the structure of minerals. When magnified  $10^4$ - $10^5$  times and more it becomes possible to study the structure of the finely dispersed, cryptocrystalline and amorphous aggregates of minerals (clay minerals, ferric, manganese, aluminium, silicon hydrous oxides). For the study of minerals with the help of transparent electronic microscope the material in the form of suspension is spread on the colloidal foundation and after drying is inserted into the vacuum chamber under a bundle of electrons that is either partially or completely absorbed by the mineral. The shadow is projected upon the luminescent screen of the microscope. In other cases it is not the mineral that is observed but its trace on the colloidal film, which is shadowed by powdering of carbon, gold or platinum in the vacuum.

With the help of a *scanning electronic microscope* the image of the surface of the specimen covered with a thin layer of gold (powdered in vacuum) can be received on the television screen.

*The thermal method* makes it possible to study the changes that the minerals undergo when heated. The specimen is placed into a special stove the temperature in which gradually rises at a constant rate. By applying thermocouples the changes in temperature are registered. They are connected with the processes of absorption or emission of heat under dehydration, oxidation, dissociation, phase transformations etc.

As a result of thermal analysis thermograms are received. They characterize the matter itself and reveal changes that take place in it. Modern appliances for the thermal analysis synchronically register the changes in mass that occur in the minerals when heated.

The thermal method is particularly widely used in the study of sea minerals, the silicates of the layered structure (e.g. clay minerals), bauxites, some iron ores, carbonates and others.

*Infrared spectroscopy* is based on the study of vibrational spectra of the absorption of the infrared light by the minerals. The measurement of infrared spectra (the IR spectra) is carried out on the IR spectrometers. The intensity and the position of the absorption bands in the IR spectra are connected with the structure and the chemical composition of the minerals. The IR spectroscopy is a method of structural analysis of minerals containing water, hydroxyl groups and complex anions.

*Optical spectrophotometry* is based on the study of electronic spectra of absorption or reflection by minerals of the visible ultraviolet and shortwave infrared light (up to 2  $\mu\text{m}$ ) which are received by using spectrophotometers. The intensity and the position of the absorption bands in the spectrum are connected with the characteristic features of the composition, structure and the defectiveness of minerals. The optical absorption is studied on the transparent plane-polished plates or in the section. The spectra of diffusive reflection are received on the powder-like or specially rubbed minerals.

*Fluorometric analysis* makes it possible to evaluate the characteristic features of the composition of minerals, their structure and defectiveness by studying radiation spectra, excitation and the scope of luminescence. Ultraviolet sources of light excitation in conjunction with light filters, passing only UV-light or with quartz monochrometer are usually used in luminescence spectrophotometers. Besides, to excite luminescence X-ray, cathode and lazer radiation are employed. Thermoluminescence analysis of minerals is based on the luminescence which occurs at uniform heating and is registered in the form of curves showing the dependence of intensity on temperature. They enable us to evaluate the defectiveness and the relative age of minerals.

*Resonance spectroscopy.* The method of electronic paramagnetic resonance (EPR) enables us to determine in minerals the concentration, coordination and valency of paramagnetic ions of transition elements and the structure of various defects. It is based on the splitting of spin and electronic levels in the magnetic field of variable intensity and the registration of the transitions between them.

Nuclear magnetic resonance (NMR) appears in the constant

magnetic field during the splitting of spin levels into atomic nuclei.

The gamma-resonance method is based on the Mössbauer effect (isotopic shift of the nuclei occurring at  $\gamma$ -radiation); it is used to determine the valency and the form of entering the ions of iron and some other elements into minerals. It is also used for the express determination of tin.

*Mass-spectrometry* is the method of measuring the relative content of isotopes of chemical elements with the help of mass-spectrometers. The study of isotopes of chemical elements in natural objects is significant in determining the absolute age of minerals and the assessment of the temperature and conditions of their formation.

*The thermobarometric analysis* is carried out with the aim of determining the temperature of other physical and chemical conditions of mineral formation. The determining is based on the microscopic study of gas and liquid inclusions in minerals with the help of thermo-chambers. The investigation of multiphase inclusions when the specimen is heated makes it possible to determine the temperature of homogeneity which corresponds to the minimal temperature of mineral formation. In a number of cases the character of the change of phases at heating enables us to evaluate the pressure. The study of inclusions is used in the exploration of mineral resources.

## Part II

# Systems of Minerals (An Outline)

Modern classification of minerals is based on the crystallochemical principles which take into account the more substantial features of mineral species, viz. their chemical composition and crystalline structure. In accordance with this classification minerals may be represented by the following classes:

1. *Native elements*, or simple substances. Besides native metals, semimetals and nonmetals this class tentatively includes the rare nitrides, carbides, phosphides, silicides.
2. *Sulphides and their analogues*, e.g. arsenides, antimonides, bismuthides, tellurides, selenides.
3. *Halides*. This class comprises not only chlorides, fluorides, bromides and iodides, but also oxy- and hydrohalides.
4. *Oxides and hydroxides*.
5. *Silicates, aluminosilicates and their analogues* represented by borosilicates, titanosilicates, zirconium silicates, and beryllium silicates.
6. *Borates*.
7. *Carbonates*.
8. *Nitrates*.
9. *Phosphates and their analogues*, e.g. arsenates and vanadates.
10. *Sulphates and their analogues*, e.g. tellurates and selenates.
11. *Molybdates and tungstates*.

These classes are divided into subclasses, the structural type of minerals being the feature of their classification. Most of these classes lend themselves to a further subdivision of minerals with coordination, island, chain, layered or skeleton structures. A more subtle division of the subclasses is carried out in compliance with the characteristic features of the chemical composition, its relative complexity, the presence of additional anions of water. Consequently, in a large number of classes simple, complex, aquatic minerals as well as those with additional anions are singled out. Among them, in their turn, families and groups of minerals are brought out. In some families amalgamation is typical of minerals of variable composition but of approximately the same structure. In others it concerns minerals of identical composition but of different structure. Minerals of similar composition and with approximately the same structure are referred to particular groups. The intraspecific subdivision of minerals is based on the singling out of chemical, structural, morphological and physical

characteristic features. It should be borne in mind that together with the crystallochemical systematization of minerals there exist other classifications based on different principles. Thus, for instance, in the genetic classification it is the type of genesis of minerals that serves as the distinguishing feature. In the chemical classification minerals are grouped according to the main chemical elements or their associations. In the technology of ore processing the classification based on their physical (discriminating) properties is found to be useful. This is exemplified by magnetization, density, solubility, fusibility and other features.

An outline of minerals pertaining to the most important classes with the exception of an inconsiderable number of chromates (crocoite  $\text{Pb}[\text{CrO}_4]$ ), iodates, and oxalates is given below. The consistency with which minerals are described in classes is congruous with the systematization which comes with the description of each class. The description includes minerals that are most widely spread, are of practical importance or interest as far as their genesis is concerned.

## Native Elements

Minerals of this class are composed of atoms that are either the same or approximately such in terms of their structure and the properties of chemical elements, e.g. metals (Cu, Ag, Au, Fe, Co, Ni, Os, Ir, Pt, Hg, Zn, Sn and others), semimetals (As, Sb, Bi) and nonmetals (C, S, Se, Te and others).

The type of chemical bond in minerals of the class of native elements determines their crystallochemical peculiarities. Most of the native metals with the metallic type of bond are characterized by a coordinate structure with closest cubic or hexagonal packing of atoms. Only the atoms of iron form a less close volume-centered cell. All native metals possess a high degree of thermal and electric conductivity, and are distinguished by a strong metallic lustre, high density, depending on the atomic mass of the elements. Most of the native metals are characterized by a high degree of malleability and moderate hardness (3-4). The more covalent osmiridium is distinguished by a high brittleness and hardness (up to 6).

Native metals are characterized by substantial isomorphic replacements. Sometimes the latter are accompanied by the formation of mineral species of intermediate composition, with a regular structure and the disintegration of solid solutions.

Native semimetals (metalloids) with a mixed covalent-and-metallic bond and an increasing part of covalence in the series Bi—Sb—As are characterized by a deformed coordination structure with a layered motive. Hardness increases from bismuth to arsenic, and the metallic lustre becomes metalline. A markedly high degree of electric conductivity as well as perfect cleavage by pinacoid are conditioned by the residual bonding between the layers.

The degree of covalence with native nonmetals increases from tellurium to sulphur and reaches its maximum in diamond. In accordance with the electronic structure of elements in the crystalline structure of sulphur, selenium and tellurium, each atom is bound to two other atoms, which is conditioned by the hybridization of the  $p^3$ -bond. In



the structure of selenium and tellurium they form spiral chains, while in the structure of native sulphur the chains are enclosed in the 8-member rings, connected with one another by the van der Waals bonds. Hence, the low degree of hardness and the high degree of brittleness of these minerals.

Carbon minerals are represented by a number of modifications. In diamond (cubic system) and lonsdeilite (hexagonal system) the hybridized  $sp^3$ -electrons of carbon atoms with four binding orbitals take part in the bonds. They have tetrahedral orientation and thus the fourth coordination (see Fig. 4). However, in graphite only three  $sp^2$ -electrons are hybridized with each atom of carbon. They form three orbitals which have a plane orientation determining the triple coordination of carbon and the layered structure (see Fig. 5). Low hardness and perfect cleavage by pinacoid are conditioned by weak residual binding between the layers, while their metallic character is responsible for the high electric conductivity of graphite. Excessively marked covalent bonds are characteristic of very rare minerals representing combinations of metals with carbon, nitrogen, phosphorus, silicon, e.g. carbides, nitrides, phosphides, silicides. By their properties they resemble the nonmetals.

Most of native metals are of rare occurrence; however, noble native metals as well as diamonds, which are precious stones of the highest class, are extracted in large quantities. Among nonmetals only graphite and native sulphur are comparatively widespread, thus forming considerable deposits.

The origin of metals, semimetals, and nonmetals varies. The formation of most of them is connected with endogenic processes (diamond in kimberlite, platinum in ultrabasic rocks, gold in hydrothermal veins etc.). The origin of graphite is associated with metamorphic processes. Native sulphur is of volcanic (exhalational) nature or is formed in hypergene processes with the participation of sulphate reduction bacteria and at the expense of gypsum. Native iron is a typical mineral of meteorites. The hexagonal modification of carbon, lonsdeilite, has a cosmogenic origin; it is found in impactites, i.e. rocks of meteorite craters. Carbides, phosphides, and nitrides of metals, uncommon on Earth, are characteristic of meteorites and are also found in lunar rocks.

## Systematization\*

### Metals of Coordination Structure

*The group of copper*  
(cubic)

COPPER Cu,  
SILVER Ag,  
GOLD Au,  
electrum (Au, Ag),  
cuproaurite  $Au_2Cu_3$  and others.

*The group of platinum*

PLATINUM Pt (cubic),  
iridium Ir (cubic),

\* Italicized minerals are those that are described in the present manual.

<i>The group of iron</i> (cubic)	polyxene Pt <sub>3</sub> Fe (cubic), osmium Os (hexagonal), ruthenium Ru (hexagonal), nevyanskite Ir <sub>2</sub> Os (hexagonal) and others. telluric iron, or ferrite (Fe, Ni), nickel telluride, or souesite (Ni, Fe); meteorite iron (Fe, Ni):
<i>The group of mercury</i>	kamacite with about 6-9% of Ni, and taenite with usually 30-40% of Ni. mercury Hg (liquid and hexagonal-R at -39.5°C), amalgam Au <sub>2</sub> Hg <sub>3</sub> ; kongsbergite (Au, Hg) with up to 31% of Hg (cubic) and others. Lead Pb (cubic), zinc Zn (hexagonal), tin Sn (tetragonal), aluminium Al (cubic), indium In (tetragonal) and other natural metals and alloys are also found in native state.

### Semimetals of the Layered Structure

<i>The group of arsenic</i>	arsenic As (hexagonal-R), antimony Sb (hexagonal-R), allemonite SbAs (hexagonal), bismuth Bi (hexagonal-R).
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### Nonmetals of Coordination and Layered Structures

<i>The group of carbon</i>	DIAMOND C (cubic), lonsdeilite C (hexagonal), GRAPHITE C (hexagonal), and its polytypes.
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### Nonmetals of Cycle and Chain Structures

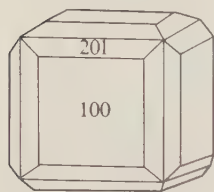
<i>The group of sulphur</i>	sulphur [S <sub>8</sub> ] (monoclinic), SULPHUR [S <sub>8</sub> ] (orthorhombic).
<i>The group of selenium</i>	selenium Se (hexagonal-R), tellurium Te (hexagonal-R). Carbides, silicides, phosphides and nitrides are represented by coordination moissanite SiC, fersilicide FeSi (cubic), schreibersite (Fe, Ni, Co) <sub>3</sub> P (tetragonal), osbornite TiN (cubic), and cohenite Fe <sub>3</sub> C (orthorhombic) and others.

### Metals of Coordination Structure

#### GOLD Au

In nature chemically pure gold is practically never found. It contains small quantities of Ag, Cu, Fe and more seldom other metals with which it forms solid solutions. The crystalline structure is a closest cubic packing with face-centered elementary cell.

Fig. 51. Gold crystal



The system is cubic. It is rarely found in crystals (Fig. 51). In most cases it occurs in the form of small grains and scales in quartz. Sometimes it forms flattened and nodular dendrites, whisker fine wires and nuggets of irregular shape (Fig. 52).

The colour is goldish-yellow. Gold containing silver is of lighter hue. Its colour becomes reddish when the copper admixture is introduced. The streak is of a shiny, goldish-yellow colour. The lustre is metallic. Hardness is between 2 and 3. Gold is very ductile and viscous. Its fracture is hackly. The density depends on admixtures; for pure gold it is 19.3. It is characterized by a high electric conductivity, chemical stability and is not dissolved in acids (with the exception of aqua regia).

*Variety.* *Electrum* is gold containing more than 20% of silver.

*Origin.* Gold is genetically connected with acid intrusives, and its hydrothermal origin in quartz veins is found to be most characteristic. Here the associated minerals of gold are pyrite, arsenopyrite, galena, grey ores, chalcopyrite, bismuthine, and tellurides. Besides, gold is found in the ore deposits of polymetals, copper, rare metals, uranium and others, from which it is simultaneously extracted.

Being chemically resistant, gold is accumulated in placers where it is found in rounded and flattened grains and in nuggets. The largest samples weighing 74.6; 70.8 and 69.7 kg were found in Australia. The 36.2 kg ('Bolshoi treugolnik') the biggest of the nuggets that has been preserved was discovered in the Miass district of the southern Urals in the middle of the last century. Together with the other gold nuggets and diamonds it forms part of the USSR Diamond Treasury in the Kremlin.

*Deposits.* In the USSR primary deposits are located in Central Asia (Muruntau), in the Middle Urals (Berezovskoye), the Southern Urals (Kochkar), in Kazakhstan (Maikain), in Kuznetsk Alatau (Berikul), in Eastern Siberia (Darasun, Balei), on the Aldan and in the north-east of the USSR (Karamken). Placer deposits are situated in the Urals, Altai, Sayany Mts., in the Yenisei Taiga, the Irkutsk region (the Lena mines), along the Aldan and the Amur rivers and in the north-east of the USSR.

The deposits outside the USSR that should be mentioned include the renowned Witwatersrand deposit in South Africa, connected with old conglomerates. The second largest gold-bearing region is Australia, with Bendigo, Ballarat deposits and rich placers. Gold deposits in Canada, India (Kolar), and Ghana should also be mentioned here.

*Practical use.* Gold is the most important currency metal. It is widely used in jewelry, electronics, instrument making, in medicine, and in the production of reagent groups. Its world output is approximately 1 000 tons per year.

### SILVER Ag

Silver often contains Au, Cu, Hg, and thus forms solid solutions. The crystalline structure is the same as that of gold.

The system is cubic. It is usually found in the form of dendrites, thin plates, reticulated and wire varieties (Fig. 53).

Its colour is silver-white. The surface is sometimes yellowish or with black tarnish. The streak is silver-white and glossy. The lustre is

Fig. 52. A gold nugget (weight 12 kg). The Urals. 1/3 of the actual size (according to A. P. Smolin)

Fig. 53. Native silver on calcite (half the size)



metallic, with hardness 2.5 and density 10.5. Silver is very ductile, its fracture is hackly, and it is distinguished by a high degree of electric conductivity.

*Origin.* Native silver is found in hydrothermal veins with sulphides in the oxidation zone of silver and some other polymetallic deposits, where it is formed at the expense of argentite and complex sulphosalts of silver.

*Deposits.* The extraction of silver is mainly carried out along with the melting of polymetallic ores (Altai) into which it is found in the form of sulphide impurities.

In other countries large deposits of silver are in Mexico (Pachuca, Veta-Madre and others). Deposits in Bolivia, Saxony and Norway (Kongsberg) have been known for a long time.

*Practical use.* Silver is employed in jewelry, the minting of coins, in various alloys, photography and electrical engineering.

### COPPER Cu

Copper usually does not contain any isomorphous impurities. Fe (up to 2.5%), As (up to 4%), Au (up to 3%) are sometimes present in it in small quantities. The crystalline structure is analogous to the structure of gold and silver.

The system is cubic. The crystals of the cubic shape are usually rare. More often copper is found in the form of dendrite flattened aggregates, wire-like or sponge secretions in block masses.

The colour is copper-red and the streak is brilliant. The lustre is

metallic. The surface of copper is often covered with a crust of secondary minerals. Hardness is 2.5-3, density 8.9. Copper is ductile and malleable. The fracture is hackly. Its electric conductivity is high. *Origin.* 1. The origin is said to be exogenetic when copper is mainly found in the oxidation zone of copper deposits in association with chalcocite, cuprite, bornite, limonite, malachite, and calcite. 2. Copper of hydrothermal origin is rare. Besides, the latter is always of low temperature.

*Deposits.* Copper is rather widespread mineral. In the USSR large nuggets (weighing several tons) were discovered in the Degelen Mountains (Kazakhstan). Beautiful crystals of copper are known from the Turyinsk Mines (the Urals). Along the Sarkhoi River in the Eastern Sayany copper was found in placers.

The hydrothermal deposit of copper in the district of the Lake Superior (Michigan, USA) has undergone mining operations for about 100 years. Nuggets weighing up to 450 tons were found there. Native copper is associated with zeolites, calcite, and copper sulphides. *Practical use.* The basic consumption of copper is shared among electrical, machine-building, instrument making engineering and ship building industry. Various alloys with Sn, Zn, Ni (bronze, brass, German silver) are widely used.

#### PLATINUM Pt

In its pure form platinum is not found. It usually forms solid solutions with iron, iridium, palladium, rhodium, osmium, copper, and other metals. This leads to the singling out of iridioplatinum, palladium, rhodium, and other types of platinum. *Polyxene* (Pt, Fe) with 9-11% of iron, is the most widespread type in nature. The structure of platinum is similar to that of gold.

The system is cubic. It usually occurs in irregular grains and nuggets.

The colour is steel-grey. The streak is lustrous and white. The lustre is metallic. Hardness—4-4.5. Platinum is ductile, and its fracture is hackly. The distinguishing features are: a high degree of density (15-19), infusibility (melting point is 1771°), high electrical resistance and chemical inertness. Platinum is dissolved only in aqua regia. *Origin.* The origin of platinum is magmatic. It is genetically associated with ultrabasic rocks (dunites, peridotites, pyroxenites), thus forming in them dissemination or schlieren. Minerals associated with platinum are: olivine, pyroxene, chromite, and magnetite. The weathering of ultrabasic rocks results in that platinum is accumulated in placers and is mined by washing.

*Deposits.* Platinum placers of the Urals have a world-wide renown. The 9.6 kg nugget of platinum (the largest in the world) was found here. There are placer deposits in Columbia. The by-output of platinum from the magmatic copper and nickel deposits in the USSR, Canada (Sudbury), South Africa (the Merensky Reef) are of great significance.

*Practical use.* Platinum is one of the currency metals. It is used in manufacturing chemical pottery (crucibles, spatulas, cups), as a catalyzer in chemical industry, and as a noble metal in jewelry and medicine.

## Nonmetals of Coordination and Layered Structures

### DIAMOND C

Its inner structure is particularly strong. Each atom of carbon is connected with four other atoms that are tetrahedrally situated round it (see Fig. 4).

The system is cubic. The shape of crystals is mostly octahedral (Fig. 54). Faces of rhombic dodecahedron and cube are of rare occurrence. Not infrequently the edges are curved, and the crystals seem to be fused.

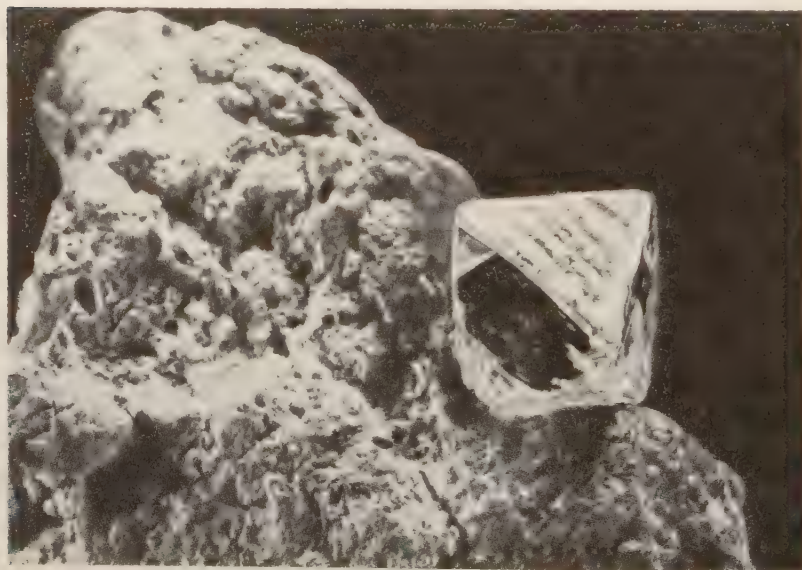
The colour is variable. Pure varieties are colourless, water-prismatic, and sometimes have shades of brown, red, yellow, blue, and other colours. Diamond is fairly brittle. Its cleavage by  $\{111\}$  is perfect. The luminescence is either blue or yellow. Density is 3.5. Its hardness is 10, the highest as compared with other minerals. It is distinguished by a very bright (adamantine) lustre.

Diamonds are measured in carats. One metric carat equals 0.2 g. Diamonds weighing more than 100 carats present a particular rarity and bear their own names.

*Varieties.* There are gem and industrial diamonds.

*Origin.* The formation of diamonds is primarily connected with the crystallization of the residual magma of the ultrabasic composition, rich in volatile compounds. It is assumed that the crystallization of diamonds takes place some time before the eruption of magma begins. Moreover, the following specific conditions are found to be relevant for the process discussed: very high pressure (approximately 60-80 thousand atmospheres) and a comparatively low temperature (about 1 000°C). Olivine, pyrope, ilmenite, diopside, chlorite and other minerals are found among the fragments of various rocks in kimberlites. Besides, diamonds and lonsdeilite are formed as a result of shock metamorphism of rocks during the fall of the large meteorites.

Fig. 54. The octahedral crystal of diamond in kimberlite from the 'Mir' pipe (Yakutia).  
Scale: 10:1



*Deposits.* In the kimberlites of South Africa the largest diamonds in the world were found, e.g. 'Cullinan' (3 024.75 carats), 'Excelsior' (995.3 carats), 'Jonker' (726 carats) and others. In South Africa, placers in the drainage basins of the Vaal and the Orange rivers are being exploited. Namibia is particularly rich in diamonds. Their output here is related to the near-shore sands and river and marine terraces. In 1976 Namibia yielded 1.7 million carats of diamonds, the greater part of which were precious stones.

At present, Zaire, with its rich diamond placers, and where the main output is that of industrial diamonds (Shaba Province) with approximately 30% of world's production has gained one of the leading places in the world. The diamond placers of Ghana, Sierra Leone, Angola and the kimberlites of Tanzania are of enormous industrial importance. Africa, in general, yields approximately 80-95% of all the diamonds in the capitalist countries.

Diamond deposits are also known in Brazil, India, Australia, and Indonesia. Indian diamonds are known to have been recovered in ancient times. The first largest diamonds come from India. They include the 'Orlov' (194.8 carats) and 'Shakh' (88.7 carats). They are now in the Diamond Treasury of the USSR.

The primary deposits of diamonds in the USSR are being mined in Yakutia (the kimberlite pipes 'Mir', 'Aikhal', 'Udachnaya', and 'Internatsionalnaya'). The weight of the largest diamonds found in Yakutia, equals 106 carats ('Mariya'), 121 carats ('Shestdesyat let Oktyabrya'), 232 carats ('Zvezda Yakutii'). One of the largest diamonds has recently been found. Its mass is 342 carats. It bears the name of the '26th Congress of the CPSU'.

There are diamond deposits in the Urals and elsewhere. The impactite deposit (with lonsdeilite) in large meteorite craters is of particular interest. A number of placer deposits are connected with it. *Practical use.* Industrial diamonds account for about 75-80% of all the diamonds produced in the world. Approximately 15% of all industrial diamonds are intended for the diamond drilling (diamonds here are inserted into drilling bits). Industrial diamonds are also used as cutting tools and drills (shaped diamonds), for the stretching of the thinnest wires (drawing diamonds or drawholes) and for a large number of other purposes. Diamonds of low quality are widely employed as abrasive material. Pure, or evenly coloured transparent diamonds are precious stones of the first class. Cut diamonds are classified as gem stones.

At present there are means of producing diamonds artificially. This is basically the result of catalytic reactions at high temperatures and pressures between graphite and some other metals (iron, nickel, cobalt, chromium, platinum) as well as by using explosives.

## GRAPHITE C

As compared with diamond, graphite represents a hexagonal modification of carbon (see Fig. 5).

The system is hexagonal. Graphite is found in the form of small hexagonal crystals. Its aggregates are compact, flaky, black, and spherical.

The colour is iron-black. The streak is black and bright. The lustre is metallic. Hardness is 1. The cleavage of graphite is perfect, parallel

to {0001}, and its density equals 2.2. It conducts electricity, and is both fireproof, and acidproof. Graphite differs from molybdenite, which resembles the former, in a greater degree of brittleness and in the colour of the streak which is black on paper for graphite and bluish for molybdenite.

*Varieties.* There are crystalline, flaky and amorphous types of graphite. The first represents aggregates of fibrous crystals, the second has the form of scales and plates, and the third is compact and cryptocrystalline. *Shungite* is the amorphous variety of carbon formed within the metamorphic process of hard coal.

*Origin.* 1. Contact-metamorphic. 2. Metamorphic, in marble, gneiss and schist. 3. During the metamorphism of hard coal (in contact with traps).

*Deposits.* In the USSR: Botogol - in the Eastern Sayany (crystalline graphite), Zavalievskoye and Zhdanov deposits in the Ukraine (flaky graphite of metamorphic origin in gneissess), Tas-Kazgan - in Kara-Kalpakia (metamorphic deposit), Noginsk and Kureisk in the lower reaches of Yenisei River ('amorphous') graphite resulting from the metamorphism of coal.

Outside the USSR, there are graphite deposits in North Korea, South Korea, Sri Lanka, Madagascar, Australia, and Czechoslovakia.

*Practical use.* Graphite is used in metallurgy (melting pots, casting), as lubricant, in the manufacturing of paints and pencils, and in electric industry (electrodes). At present the use of graphite produced from anthracite in the electric stoves is on the increase.

## Nonmetals of the Cycle Structure

### SULPHUR [ $S_8$ ]

Sulphur occasionally contains the admixtures of Se. Its crystalline structure is characterized by molecular eightfold rings (Fig. 55).

The system is orthorhombic. The crystals are dipyramidal with truncated dipyramids (Fig. 56), thus forming beautiful druses. Sulphur is often found in block masses and sinters.

The colour is yellow, brown and black as a result of bitumen inclusions. The streak is light-yellow. The crystals are translucent. The lustre is glassy (approaching adamantine) on faces and greasy and resinous in the fracture. The fracture is uneven till shelly. Sulphur is

Fig. 55. The structure of sulphur:

*a* - the molecular ring  $S_8$  in plane and *b* - in cross section; *c* - the character of the packing of molecular rings of sulphur in the sulphur orthorhombic structure

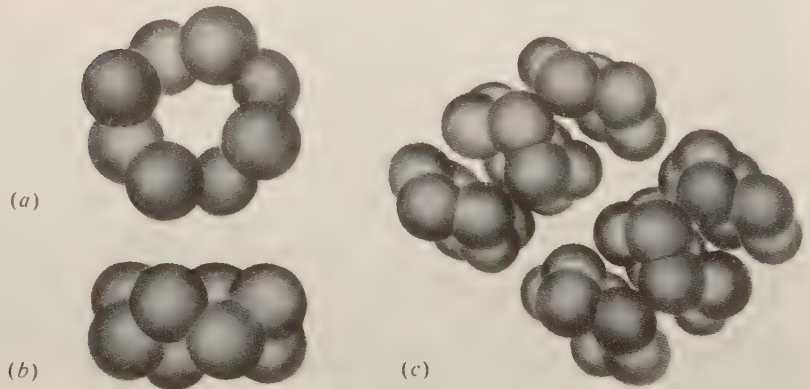
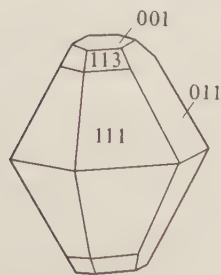




Fig. 56. Sulphur crystal



very brittle; its hardness equals 1.5-2; cleavage is absent, and density is 2.07. Sulphur is easily melted and at  $270^{\circ}$  burns with a blue flame and yields  $\text{SO}_2$ . It is a dielectric which becomes negatively charged when rubbed.

*Origin.* 1. The origin of sulphur is sedimentary and biochemical. It is formed partly by the living activity of sulphur bacteria, and is associated with gypsum and bitumens. 2. During the disintegration of gypsiferous strata. 3. In the oxidation zone of sulphides. 4. As a result of sublimation during the volcanic activity it bears powder-like coatings, crusts and sinters.

*Deposits.* In the USSR the known sedimentary deposits are in Turkmenia (Gaurdak), Uzbekistan (Shorsu), the Volga River region (Aleksievskoye). The deposits of volcanic origin are in the islands of Ebeko, Paramushir, and Kunashir (the Kuril Islands).

In countries other than the USSR, Italy (Sicily) and Poland are rich in sulphur. There are large sedimentary deposits in the states of Texas and Louisiana in the USA.

*Practical use.* The most important use of sulphur is connected with sulphuric acid, which forms the basis of chemical industry. Sulphur is also used in textile and rubber industries, in the manufacturing of paints, explosives, and the production of pesticides. Native sulphur meets the requirements of practically half of world's production. The other half is recovered in the processing of sulphide ores and from natural gas.

## Sulphides and Their Analogues

This class includes mineral species representing compounds of metals and semimetals of transitory elements with sulphur, arsenic, selenium, and tellurium. The species-forming elements, besides sulphur and arsenic, are basically Fe, Cu, Zn, Pb, Sb, Ag, Au, Bi, Co, Ni. Others are found primarily in a dispersed state and very seldom form independent species of minerals (Cd, In, Ga, Ge, Se, Te, and others).

Sulphides and their analogues are characterized by a prominently expressed covalent type of chemical bond between the atoms entering into their composition with a donor-and-acceptor character of its manifestation and a substantial number of metallic and residual bondings. The donor-and-acceptor bondings are prevalent in sulphides containing metals with a filled *d*-coating. They aim at establishing a stable 18-electron configuration ( $10 + 4 \times 2$ ), which is realized by the interchange between the metal and the  $\text{S}^{2-}$  ions of the four pairs ( $4 \times 2$ ) of electrons. As a result of this four bondings of different direction occur. They help to establish the tetrahedral coordination of the ions of sulphur and the ions of the type:  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Ge}^{4+}$ , etc.

The metallic bond is usually manifested in sulphides containing metals with an unfilled *d*-coating. The stability of the 18-electron configuration is further achieved at the expense of the electrons of the metallic bond, during the interchange of electrons of the intercoordinate *d*-orbitals of the neighbouring atoms of iron, surrounded by six ions of sulphur, as was the case, in particular, with pyrrhotite  $\text{Fe}_{1-n}\text{S}$ . The atoms of other metals of transitory elements in

most of the sulphides are also surrounded by six atoms of S or As. The distorted octahedral coordination (3 + 3) can also be exemplified by the atoms of Pb in galenite and other minerals. In sulphides Hg, Cu, Ag metals, excluding those of the fourth order, can occur in a double coordination with the formation of spiral chains. In sulphides As, Sb, and Bi metals are in a ternary (umbelliferous) surrounding of the sulphur atoms. Similar coordination takes place in the anion radicals of sulphosalts. In sulphides, where the covalent-molecular type of chemical bond is prevalent, the formation of groupings with a paired coordination is customary. The latter is realized, for instance, in the ring molecules of realgar  $[\text{As}_4\text{S}_4]$ .

The iso- and heterodesmic character of the chemical bond determines the variety of structural types and motifs in sulphides. Most of them have coordination, island, chain and layered structures.

Most of the sulphides are characterized by a wide development of iso- and heterovalent isomorphism. In sphalerite, for example,  $\text{ZnS}$   $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  form an isovalent admixtures; the inclusion of the pair  $\text{Cu}^+$  and  $\text{Fe}^{3+}$  or  $\text{Ag}^+$  and  $\text{Ga}^{3+}$  takes place according to the pattern of heterovalent isomorphism ( $2\text{R}^{2+} = \text{R}^+ + \text{R}^{3+}$ ). The admixture  $\text{Ag}^+$  and  $\text{Sb}^{3+}$  (or  $\text{Bi}^{3+}$ ), usual for galenite  $\text{PbS}$ , is also found to be congruous with the heterovalent isomorphism. Isomorphic replacements are also characteristic of anions. For instance, in the said galenite  $\text{Se}^{2-}$  and  $\text{Te}^{2-}$  are often present (isovalent isomorphism), in pyrite  $\text{FeS}_2$  one may often find the  $\text{As}^{3-}$  admixture, usually in the pair with  $\text{Co}^{3+}$  (heterovalent isomorphism according to the pattern  $\text{R}^{2+} + \text{A}_2^{2-} \rightarrow \text{R}^{3+} + \text{A}_2^{3-}$ ), in grey ores the replacements in anion radicals take place according to the pattern of isovalent isomorphism  $[(\text{As}_{1-n}\text{Sb}_n)\text{S}_3]^{3-}$ .

The crystallochemical peculiarities of sulphides and their analogues of each structural type depend on whether they are compounds of metals with anions or molecular constructions. In accordance with the structure of anion radicals and molecular groupings the following can be singled out among sulphides and their analogues: (1) monosulphides and their analogues (anions  $\text{S}^{2-}$ ,  $\text{As}^{2-}$  and others); (2) disulphides and their analogues (anions  $[\text{S}_2]^{2-}$ ,  $[\text{As}_2]^{3-}$ ,  $[\text{AsS}]^{3-}$ ,  $[\text{As}_4]^{4-}$ ); (3) island sulphides and their analogues (ring molecules  $[\text{As}_4\text{S}_4]$ , complex anions of the type  $[\text{AsS}_3]^{3-}$ ,  $[\text{SbS}_3]^{3-}$ ,  $[\text{AsS}_4]^{3-}$ ); (4) chain-like sulphides and their analogues (simple and more complex heteroanion chain radicals of the type  $[\text{Sb}_2\text{S}_4]^{2-}$ ,  $[\text{Sb}_4\text{S}_{11}]^{10-}$ ) and (5) layered sulphides and their analogues.

Sulphides and their analogues marked by crystallochemical peculiarities, the types of chemical bond and the variability of the chemical composition determine the physical properties and the crystallomorphic features characteristic of sulphides.

Most of the sulphides with covalent-metallic chemical bonds are characterized by a metallic lustre, a high electric conductivity, and the properties of semiconductors. Their colour is grey, yellowish or bronze-yellow. The hardness of layered and chain sulphides is low (between 1 and 2.5). The hardness of coordinate monosulphides is moderate (2-4), while disulphides and their analogues with a greater degree of covalency have hardness which reaches 6-6.5. Covalent monosulphides with coordinate (sphalerite), chain (cinnabar),

molecular-layered (orpiment), molecular-island (realgar), and island (proustite) structures are distinguished by an adamantine lustre, semitransparency, bright colours, a high degree of brittleness, low and moderate hardness. The density of the greater part of sulphides is high (up to 8.5).

Sulphides usually form solid crystalline grained masses, dissemination or are found in the form of crystals. Sulphides with chain structure are often represented by aggregates of elongated-and-prismatic and fine-acicular crystals with perfect cleavage by elongation (antimonite, bismuthine, and sulphosalts of lead). Layered sulphides and their analogues are characterized by an elongated-and-tabular form of crystals and a most perfect cleavage in one direction (molybdenite, tetradyomite, orpiment).

Sulphides are basically of hydrothermal origin. Besides, they are formed within magmatic processes and occasionally in hypogene conditions in the zone of the secondary sulphur dressing, and in sedimentary rocks. Sulphides have been discovered in meteorites and in samples brought from the Moon. In surface conditions sulphides and their analogues are not stable and are easily destroyed. In the process of their oxidation they mainly become soluble sulphates. At their expense various secondary minerals are formed, e.g. oxides, carbonates, sulphates, arsenates, silicates, as well as native metals.

At present among sulphides and their analogues there are all in all more than 250 mineral species. However, not more than 20 of them are spread and form considerable accumulations. Sulphides and their analogues are the most important ores of nonferrous, noble and many rare metals.

## Systematization

### Sulphides and Arsenides of the Coordination Structure

Sulphides with Singular Anions of the Type  $S^{2-}$   
(Monosulphides)

#### Simple

- The group of chalcocite* CHALCOCITE  $Cu_2S$  (monoclinic),  
argentite  $Ag_2S$  (orthorhombic) and their polymorphic modifications.
- The group of galena*  
(cubic) GALENA  $PbS$ ,  
alabandite  $MnS$ ,  
altaite  $PbTe$ , etc.
- The group of sphalerite* SPHALERITE  $ZnS$  (cubic),  
wurtzite  $ZnS$  (hexagonal), and its polytypes;  
metacinnabarite  $HgS$  (cubic),  
CINNABAR  $HgS$  (hexagonal-R).  
troilite  $FeS$  (hexagonal),  
*The group of* PYRRHOTITE  $Fe_{1-n}S$  (monoclinic) and its modifications,  
*pyrrhotite* NICCOLITE  $NiAs$  (hexagonal), etc.
- Complex**
- The group of* CHALCOPYRITE  $CuFeS_2$ ,  
*chalcopyrite* STANNITE  $Cu_2FeSnS_4$ ,  
*(tetragonal)* BORNITE  $Cu_5FeS_4$ ,

	gallite $\text{CuGaS}_2$ ,
	germanite $\text{CuGeS}_2$ , etc.
<i>The group of cubanite</i>	cubanite $\text{CuFe}_2\text{S}_3$ (orthorhombic).
<i>The group of pentlandite</i>	PENTLANDITE $(\text{Fe}_4\text{Ni}_4)$ $(\text{Fe}, \text{Ni}, \text{Co})\text{S}_8$ (cubic).

Sulphides and Arsenides with Anions of the Type  $[\text{S}_2]^{2-}$ ,  $[\text{AsS}]^{2-}$ ,  $[\text{As}_2]^{3-}$ ,  $[\text{As}_4]^{4-}$  (Disulphides and Their Analogues)

**Simple**

<i>The group of pyrite:</i>	PYRITE $\text{Fe}[\text{S}_2]$ (cubic), MARCASITE $\text{Fe}[\text{S}_2]$ (orthorhombic).
<i>The group of sperrylite</i>	sperrylite $\text{Pt}[\text{As}_2]$ (cubic).
<i>The family of sulpho-arsenides and arsenides Fe, Co, and Ni</i>	ARSENOPYRITE $\text{Fe}[\text{AsS}]$ (monoclinic), COBALTITE $\text{Co}[\text{AsS}]$ (cubic), gersdorffite $\text{Ni}[\text{AsS}]$ (cubic), löllingite $\text{Fe}[\text{As}_2]$ (orthorhombic), safflorite $(\text{Co}, \text{Fe})[\text{As}_2]$ (orthorhombic), rammelsbergite $\text{Ni}[\text{As}_2]$ (orthorhombic), skutterudite $\text{Co}_4[\text{As}_4]_3$ (cubic), SMALTITE $(\text{Co}, \text{Ni})_4[\text{As}_4]_3$ (cubic), chloanthite $\text{Ni}_4[\text{As}_4]_3$ (cubic), etc.

**Sulphides of the Island Structure**

Sulphides with Isolated Molecules

**Simple**

<i>The group of realgar</i>	REALGAR $[\text{As}_4\text{S}_4]$ (monoclinic).
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Sulphides with Isolated Complex Anions of the Type  $[\text{AsS}_3]^{3-}$ ,  $[\text{AsS}_4]^{4-}$ , etc. (Sulphosalts)

**Simple**

<i>The group of red silver ores (hexagonal-R)</i>	PROUSTITE $\text{Ag}_3[\text{AsS}_3]$ , PYRARGYRITE $\text{Ag}_3[\text{SbS}_3]$ .
<i>The group of enargite</i>	ENARGITE $\text{Cu}_3[\text{AsS}_4]$ (orthorhombic).

**Complex**

<i>The group of grey ores (cubic)</i>	TENNANTITE $\text{Cu}_{10}^+\text{Cu}_2^{2+}[\text{AsS}_3]_4\text{S}$ , TETRAHEDRITE $\text{Cu}_{10}^+\text{Cu}_2^{2+}[\text{SbS}_3]_4\text{S}$ etc.
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**Sulphides of the Chain Structure**

Sulphides with Simple Chains

**Simple**

<i>The group of antimonite (orthorhombic)</i>	ANTIMONITE $\text{Sb}_2\text{S}_3$ ,
<i>The group of millerite</i>	BISMUTHINE $\text{Bi}_2\text{S}_3$ .
	millerite $\text{NiS}$ (hexagonal-R).

**Simple and Complex***The group of jamesonite**The group of cosalite**The group of bournonite*

(orthorhombic)

## Sulphides with Complex Chains (Sulphosalts)

JAMESONITE  $\text{Pb}_4\text{Fe}[\text{Sb}_6\text{S}_{14}]$  (monoclinic),  
 BOULANGERITE  $\text{Pb}_5[\text{Sb}_4\text{S}_{11}]$  (monoclinic),  
 berthierite  $\text{Fe}[\text{Sb}_2\text{S}_4]$  (orthorhombic),  
 cosalite  $\text{Pb}_2[\text{Bi}_2\text{S}_5]$  (orthorhombic),  
 bournonite  $\text{CuPb}[\text{SbS}_3]$ ,  
 aikinite  $\text{CuPb}[\text{BiS}_3]$ .

**Sulphides of the Layered Structure****Simple***The group of orpiment*  
(monoclinic)*The group of molybdenite**The group of tetradymite*

(hexagonal-R)

**Complex***The group of covellite*ORPIMENT  $\text{As}_2\text{S}_3$ .

MOLYBDENITE  $\text{MoS}_2$  (hexagonal),  
 TUNGSTENITE  $\text{WS}_2$  (hexagonal), and their polytypes.  
 tetradymite  $\text{Bi}_2\text{Te}_2\text{S}$ ,  
 tellurobismuthite  $\text{Bi}_2\text{Te}_3$ ,  
 joseite-A  $\text{Bi}_4\text{TeS}_2$  etc.

COVELLITE  $\text{Cu}_2^+\text{Cu}^{2+}\text{S}[\text{S}_2]$  (hexagonal).**Sulphides of the Coordination Structure****Sulphides with Singular Anions of the Type  $\text{S}^{2-}$  (Monosulphides)****Simple**CHALCOCITE (copper lustre)  $\text{Cu}_2\text{S}$  (Cu 79.8%)

The name comes from the Greek word '*chalcos*', which means 'copper'. The low-temperature modification has a distorted closest hexagonal packing of S atoms. The coordination number of Cu atoms equals 2. The high-temperature modifications are close to antifluorite structure and are characterized by the scarcity of copper. Their composition corresponds to the formula  $\text{Cu}_{2-n}\text{S}$ .

The system is monoclinic. Crystals are rare, and are usually found in block masses. Chalcocite is compact.

The colour and the streak are lead-grey to black. The lustre is metallic, which becomes tarnished with time. The cleavage is imperfect. Hardness is 2.5-3; density equals 5.7. It is a semiconductor of the *n*-type. Chalcocite is characterized by the following features: low hardness, malleability and dark grey colour.

*Origin.* Chalcocite is formed in the zone of the secondary sulphide enrichment (the cementation zone) of copper deposits as a result of the reactions of the solutions of copper sulphates with unoxidized sulphide ores. The hydrothermal origin is comparatively rare. It associates with bornite, grey ores, covellite, chalcopyrite, and other sulphides. In the process of oxidation malachite, cuprite, native copper

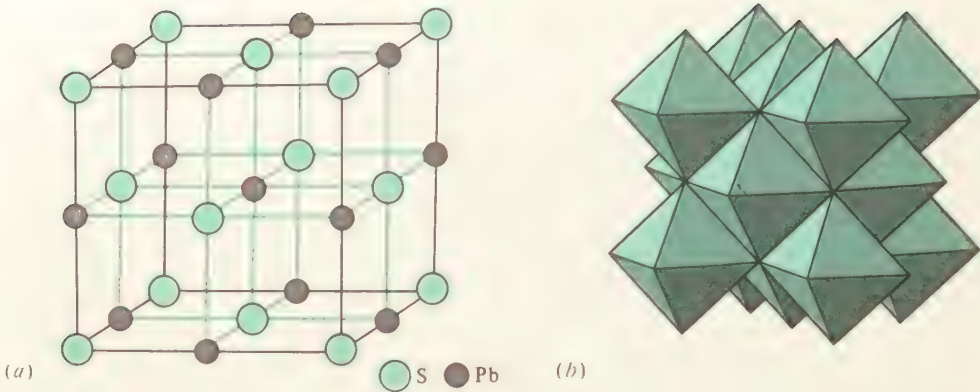


Fig. 57. Galena structure in globular (a) and polyhedral (b) models

and other minerals are developed at the expense of chalcocite. *Deposits.* In the USSR: the Dzhezkazgan and Kounrad (Kazakhstan), Almalyk (Uzbekistan), the Turinskii Mines (the Urals). In other countries: in the USA—Butte (Montana), Bingham (Utah), Bisbee (Arizona); in Yugoslavia—Bor. *Practical use.* Chalcocite is an important ore of copper.

**GALENA** (lead lustre)  $\text{PbS}$  (86.6% of Pb)

Galena often contains isomorphic Ag, Sb, Bi. The crystalline structure is of the type NaCl (Fig. 57).

The system is cubic. Crystals of the cubic octahedral habit are predominant (Fig. 58). It usually forms grained massive aggregates.

The colour is lead-grey. The streak is greyish-black. The lustre is prominently metallic (occasionally tarnish on faces). Galena is characterized by a perfect cubic cleavage. It is brittle; its hardness equals 2.5, and its density is 7.5. It is a semiconductor of *n*- and *p*-types. Galena is recognized by its colour, perfect cleavage, low hardness and a considerable degree of density.

*Origin.* 1. The hydrothermal (the mid- and low-temperature varieties) is found in veins, metasomatic bodies, as well as in skarns. There exists a close association of galena with sphalerite in the sulphides of silver and copper in polymetallic ores. It is also found together with pyrite, pyrrhotite, and other sulphides, with barite, quartz and calcite. 2. The sedimentary origin forms dissemination, mainly in bituminous carbonate rocks. In the oxidation zone galena lacks stability and is easily destructible with the formation of cerussite, anglesite, pyromorphite and other minerals.

*Deposits.* In the USSR: the skarn deposits covers Verkhneye (Primorski Krai), Kansai, Altyn-Topkan, and Kurgashinkan (Soviet Central Asia). There are hydrothermal, veined and metasomatic deposits in the Northern Caucasus (Zgid), and volcanic-sedimentary ones in the Altai (Leninogorsk, Zyryanovka, Belousovo and others), the deposits of the Nerchinsk group (the Transbaikal region), Corevka (the Yenisei Ridge), the low-temperature deposits in carbonate rocks: Central Kazakhstan and the Karatau Range (Zhairesm, Mirgalimsai, Achisai). Outside the USSR there are deposits in Sullivan (Canada), Broken Hill, Mac-Arthur (Australia), the Three-State district (in the states of Missouri, Kansas, Oklahoma in

Fig. 58. Galena crystals

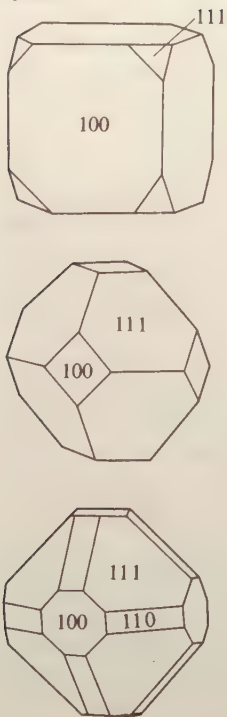
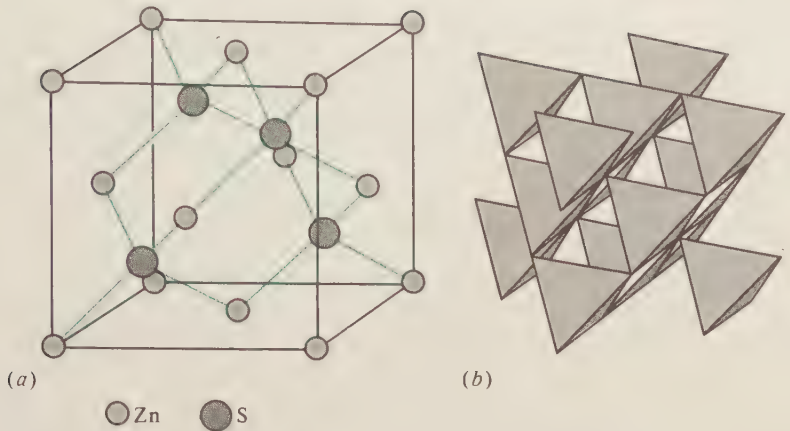


Fig. 59. Sphalerite structure in globular (a) and polyhedral (b) models



the USA), as well as in Poland, Czechoslovakia (Kutná Hora), Mexico, Chile, and other countries.

*Practical use.* Galena is the most important ore of lead, from which silver, bismuth, and other metals are recovered as by-products.

#### SPHALERITE (zinc blende) $ZnS$ (up to 67.1% of $Zn$ )

In the form of isomorphic impurities sphalerite contains iron (up to 30%), manganese (up to 5%), cadmium (0.5-1%), indium (up to 0.1%), gallium (up to 0.1%), and germanium (up to 0.3%). The crystalline structure is similar to that of diamond. In the closest cubic packing the atoms of sulphur and zinc are in a tetrahedral coordination (Fig. 59). The other polymorphic modification  $ZnS$ , wurtzite, is characterized by a hexagonal closest packing. Rhombohedral polytypes are also often found. They are distinguished by the order in which the layers with cubic and hexagonal closest packings succeed one another.

The system is cubic. The crystals have a tetrahedral shape (Fig. 60). They are sometimes twinned. The aggregates are solid, granular, massive and banded. The cryptocrystalline and reniform crystals are of more rare occurrence.

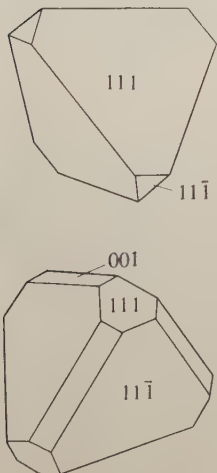
The colour is mainly brown, from brown to black, and from yellow to colourless. Sphalerite is transparent or translucent. With its colourless and the yellow varieties the streak is bright, dark-brown is characteristic of the black varieties. The cleavage is rhombododecahedrally perfect. The lustre is adamantine. Hardness equals 3.5-4, and density is 3.9-4.1.

*Varieties.* The high-temperature ferriferous variety of the black colour is called *marmatite*. The low-temperature colourless or the bright-yellow sphalerite without any impurities of iron is known as *cleiophane*, while the cryptocrystalline and reniform variety is called *brunkite*.

*Origin.* 1. Sphalerite of the hydrothermal origin with galena, chalcopyrite, pyrite and other minerals, is widely spread in metasomatic deposits and ore veins. 2. The exogenetic origin is confined to sedimentary rocks, and occasionally in coal deposits. In the process of oxidation sphalerite is transformed into smithsonite and calamine.

*Deposits.* In the USSR: there are polymetallic deposits in the Altai,

Fig. 60. Sphalerite crystals of the tetrahedral habit



Central Asia, the Transbaikal district, and those of the pyrite type in the Urals. In the Dalnegorsk deposit of the Primorski Krai sphalerite is found in beautiful druses. Outside the USSR, there are large deposits (together with galena) in the Three-State (Missouri, Kansas, and Oklahoma) and other districts of the USA, as well as in Canada, Australia, Poland, Spain, and Japan.

*Practical use.* Sphalerite is the most important ore of zinc, and also of rare metals and trace elements.

#### CINNABAR $\text{HgS}$ (86.2% of Hg)

The crystalline structure of cinnabar is close to that of the trigonally-deformed structure of the galena type, in which the Hg and S atoms with coordination number equals 2, form continuous spiral chains along the *C* axis. The cubic polymorphic modification  $\text{HgS}$ -metacinnabarite—has the structure of sphalerite.

System is hexagonal-R. It is chiefly found in the form of granular aggregates and dissemination, block or earthy masses, crusts and powdery coatings. The crystals are of isometric form occasionally of twinned intergrowth.

The colour of cinnabar in crystals is bright dark-red: in earthy masses, the colour is scarlet. The streak is red. In thin fragments, cinnabar is transparent. The lustre is adamantine, sometimes with a weak lead-grey tarnish. Hardness is 2-2.5, and density equals 8. *Origin.* Cinnabar is characteristic of a low-temperature hydrothermal process; it is usually found together with antimonite, realgar, fluorite, barite, and chalcedony, sometimes with native drop-liquid mercury and corderoite  $\text{Hg}_3\text{S}_2\text{Cl}_2$ . Cinnabar occurs in carbonate rocks, and occasionally in sandstone and shale, thus forming dissemination and veinlets.

*Deposits.* In the USSR: the Khaidarkan and Chauvai in Kirghizia, Nikitovka in Donbass, Aktash and Chagan-Uzun in the Altai, Plamennoye in the Chukotka Peninsula, and elsewhere. In other countries, there are deposits in Almadén (Spain), Monte Amiata (Italy), as well as in Idria (Yugoslavia), the province of Hunan in China, and in California and Nevada (USA).

*Practical use.* Cinnabar is the most significant mineral of mercury ores and valuable native paint. Mercury is employed in electrical engineering, instrument building, in explosives, chemical industry, medicine, etc.

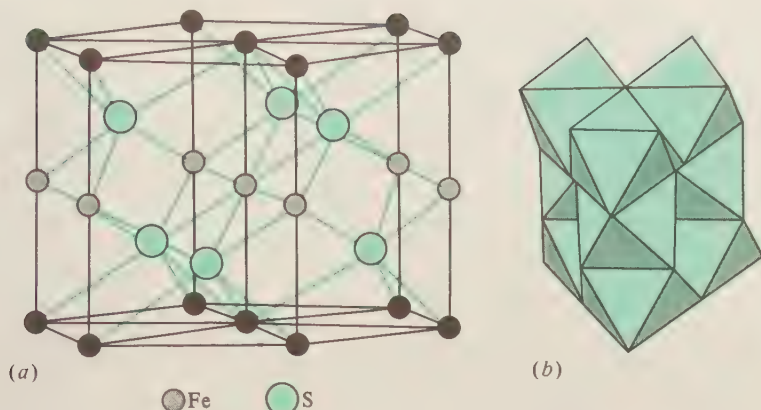
#### PYRRHOTITE (magnetic pyrite) $\text{Fe}_{1-n}\text{S}$

Pyrrhotite sometimes contains the impurities of Cu, Ni, and Co. It is represented by a number of modifications, which are distinguished by the content of iron and the defectiveness of the structure. In troilite  $\text{FeS}$  the atoms of sulphur form a closest hexagonal packing, in which the atoms of iron are found to be in an octahedral coordination (Fig. 61). In the high-temperature modification  $\text{FeS}$  the atoms of sulphur are brought together, while one of the sulphur positions remains vacant. In hexagonal and monoclinic pyrrhotite there is an alternation of the layers of troilite type of various degree of defectiveness with the formation of polytypes of non-stoichiometric composition, conditioned by the scarcity of Fe atoms on block boundaries.

The crystals, usually of a hexagonal shape, are comparatively rare.



Fig. 61. Troilite structure in globular (a) and polyhedral (b) models



As a rule, they form either block or fine grained masses and disseminations.

The colour is bronze-yellow, sometimes irridescent. The streak is grey-black. The lustre on the new surface is metallic, occasionally tarnish. Pyrrhotite is to a variable extent susceptible to magnetism. It is brittle, its hardness equals 4, and the density is 4.5. This mineral is a semiconductor.

*Origin and deposits.* 1. The magmatic origin is connected with the basic rocks in association with pentlandite and chalcopyrite (the Norilsk deposit and the Monchetundra deposit in the Kola Peninsula). 2. The contact-metasomatic or skarn deposit is related to the polymetallic ores, in crystals (Verkhneye in the Primorski Krai, and Trepcha in Yugoslavia). 3. Hydrothermal. 4. Finally, it is found among metamorphic and sedimentary rocks; in the oxidation zone it undergoes destruction resulting in the formation of sulphides and hydrous ferric oxides.

*Practical use.* Pyrrhotite is used on the production of sulphuric acid.

#### NICCOLITE NiAs (43.9% of Ni)

Niccolite contains impurities of Fe, Co, Sb, S. The crystalline structure is similar to that of troilite.

The system is hexagonal. The crystals are rare. It is found in block masses, disseminations, in nodular zonal-concentric intergrowths. Crystals are rare.

The colour is light copper-red. The streak is brownish-black, and the lustre is metallic. The cleavage is none. The fracture is uneven. Hardness equals 5-5.5. The density is up to 7.8. It differs from bornite in a greater degree of hardness, and the absence of tarnish. *Origin.* The hydrothermal origin is associated with the carbonate veins together with other sulphides and arsenides of nickel and cobalt. *Deposits.* In the USSR the deposits of niccolite are located in the Kho-vuaksy (Tuva). In other countries, niccolite is found in Ore Mountains (GDR, Czechoslovakia).

#### Complex

##### CHALCOPYRITE (copper pyrite) $\text{CuFeS}_2$ (34.6% of Cu)

Chalcopyrite often contains the isomorphic impurity of Ag. Its structure is similar to that of sphalerite, in which the elementary cell is

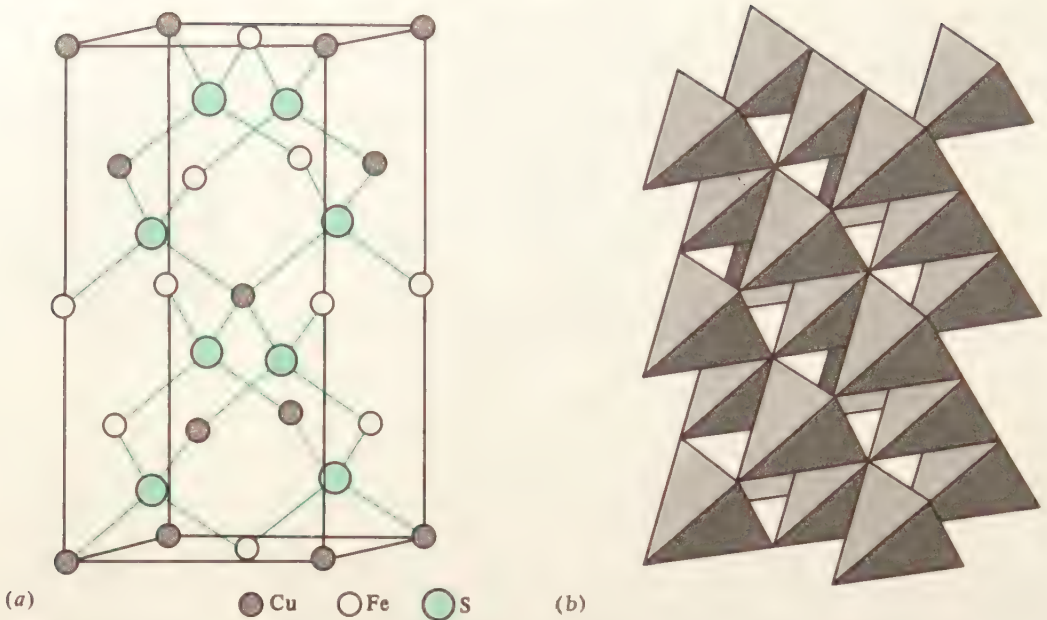


Fig. 62. Chalcopyrite structure in globular (a) and polyhedral (b) models

doubled, while the positions of each pair of zinc atoms are alternatively occupied by the atoms of copper and iron (Fig. 62). In the polymorphic cubic modification, talnakhite, the distribution of Fe and Cu atoms is irregular.

The system is tetragonal. The crystals are usually of the tetrahedral type and are found rare. They mainly form dissemination as well as block masses.

The colour is brass-yellow. The streak is black or greenish-black. The lustre is metallic. Chalcopyrite is brittle, its hardness equals 3.5-4, and the density is 4.2. It is a semiconductor of the *n*-type. Variegated tarnish is occasionally found to be typical. It differs from pyrite in that its hardness is lower.

*Origin.* 1. The magmatic origin is found to be in association with pyrrhotite and pentlandite. 2. The skarn origin is connected with andradite, magnetite, scheelite, and pyrrhotite. 3. The hydrothermal origin is related to pyrite, pyrrhotite, and the sulphides of Pb, Zn, Cu, etc. 4. The exogenetic origin is associated with sedimentary rocks. In the oxidation zone, and at the expense of the destruction of chalcopyrite the following minerals are formed: native copper, chalcocite, covellite, cuprite, malachite, azurite, chrysocolla, etc.

*Deposits.* In the USSR: Norilsk and Talnakh (magmatic); the Turyinsk mines in the Urals (skarn); the Kounrad deposit in Kazakhstan, and the Almalyk deposit in Uzbekistan (hydrothermal), the Degtyarsk, Kalatinsk, Komsomol, Sibai, Gai, 'the 50th Anniversary of the October Revolution', in the Urals, the Alaverdy deposit in Armenia (the copper-pyrite type), the Dzhezkazgan in Kazakhstan and Udokan deposits in the Chita Region (cupreous sandstone). In countries other than the USSR there are magmatic deposits in Sudbury (Canada), in Bingham (Utah, USA), Chuquicamata and others in Chile (the type of disseminated and veinlet-disseminated hydrothermal ores), the deposits of Zaire and Zambia (cupreous sandstone).

*Practical use.* Chalcopyrite is the most important ore of copper: its by-products comprise silver, indium and other metals.

STANNITE (tin pyrite)  $\text{Cu}_2\text{FeSnS}_4$  (27.61% of Sn, and 29.58% of Cu) Stannite occasionally contains some per cent of the impurity of zinc. Its structure is similar to that of sphalerite with a four-fold elementary cell, in which the positions of the four zinc atoms are occupied by the atoms of copper, iron and tin.

The system is tetragonal. The crystals are rare. Irregular grains and solid granular masses are characteristic of stannite.

The colour is steel-grey, and the streak is black. Stannite is brittle, its hardness is approximately 3.5, and the density equals 4.4. The greenish tinge of the mineral in a fresh fracture serves as a reliable diagnostic feature. It helps to distinguish stannite from the grey ores that closely resemble it.

*Origin.* The hydrothermal (sulphide-cassiterite formation) is found together with cassiterite, sphalerite, chalcopyrite, pyrrhotite, and other sulphides.

*Deposits.* Stannite is of rare occurrence. In the USSR it is known in a fairly large number of deposits in the Primorski Krai, and the Eastern Transbaikal region. However, its quantities here are insignificant. In Bolivia, stannite is used together with cassiterite as a tin ore.

BORNITE (variegated copper ore)  $\text{Cu}_5\text{FeS}_4$  (up to 64% of Cu) Sometimes, bornite contains isomorphous impurities of Ge, Re, Se, and Te. It is found in four polymorphic modifications. The structure of the high-temperature cubic modification, stable over 228 °C, is of the anti-fluorite type; there is an octahedral coordination of the atoms of iron and a double one of copper for the low-temperature tetrahedral modification. Intermediate hexagonal-R modifications are characterized by a tetrahedral coordination of Cu and Fe atoms in layered blocks  $[\text{Cu}_3\text{FeS}_4]^{2-}$  with the structure of sphalerite, connected by the cations  $\text{Cu}^+$ , their formula being  $\text{Cu}_2[\text{Cu}_3\text{FeS}_4]$ . The characteristic feature of the structure throw a sufficient amount of light on the isomorphism of the high-temperature modification with chalcocite, and the intermediate modification with chalcopyrite, which are often present in the form of inclusions of disintegration of solid solutions.

The crystals of cubic and octahedral shape are found rarely. They usually form solid masses and dissemination.

The colour is dark, bronze-red with a bright blue or violet tarnish. The streak is greyish-black. The lustre is semimetallic. The fracture is uneven and shelly. Bornite is brittle, its hardness is 3, and the density equals 5.52.

*Origin.* The origin of bornite is related to: 1. hydrothermal copper-porphyrus, pyrite and polymetallic deposits; 2. the zone of the secondary sulphide enrichment of copper ores; 3. copper sandstones.

*Deposits.* In the USSR bornite is found in the pyrite deposits in the Urals (Levikha), Caucasus (Alaverdy, Urup, etc.), in the cupreous sandstones of Dzhezkazgan (Kazakhstan) and elsewhere. In other countries the deposits are located in Bor (Yugoslavia), Colorado (Mexico), Chuquicamata (Chile), Pioneer (Arizona, the USA), Tsumeb (Namibia), etc.

*Practical use.* Bornite is a valuable ore of copper.

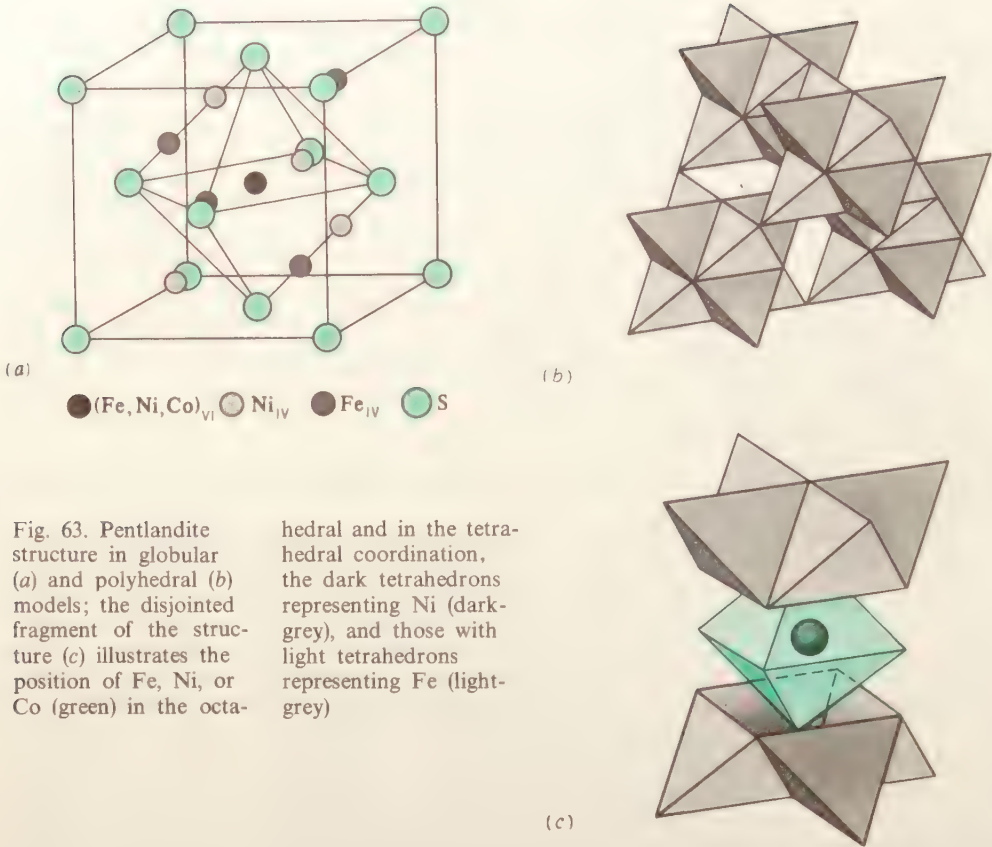


Fig. 63. Pentlandite structure in globular (a) and polyhedral (b) models; the disjointed fragment of the structure (c) illustrates the position of Fe, Ni, or Co in the octa-

hedral and in the tetrahedral coordination, the dark tetrahedrons representing Ni (dark-grey), and those with light tetrahedrons representing Fe (light-grey)

#### PENTLANDITE (Fe<sub>4</sub>Ni<sub>4</sub>) (Fe, Ni, Co)S<sub>8</sub> (22-42% of Ni)

Pentlandite contains impurities of Co. Its crystalline structure is coordinate with a frame motif. In the closest cubic packing of S atoms the eight cations (4Fe + 4Ni) occupy the position in the centre of eight tetrahedrons with common edges. The octets are directly connected with one another by the common apexes of the said tetrahedrons. Within each of the octets there is an octahedral void which can be occupied by the atoms of iron, nickel, or cobalt (Fig. 63).

The system is cubic. Pentlandite usually forms solid granular masses, occasionally coarse-grained aggregates, in which the size of the grains reaches 4-5 cm.

The colour is light-bronze, though lighter than the colour of pyrrhotite. It also differs from the latter in the absence of magnetic properties. Its lustre is metallic, hardness equals 3.5-4. The cleavage is good with characteristic triangular cavities of chipping. The density is 4.9. The mineral is a semiconductor.

*Origin.* The origin of pentlandite is magmatic, which is connected with the ultrabasic and basic rocks (peridotites, gabbro-norites, and others). A close association of pentlandite with pyrrhotite and chalcopyrite is found to be characteristic. The presence of the two latter minerals among ultrabasic rocks indicates the proximity of pentlandite.

*Deposits.* In the USSR the deposits are situated in the following parts

of the country: the Krasnoyarski Krai (Norilsk, Talnakh), in the Murmansk region (Pechenga). Outside the USSR large deposits are located in Canada (Sudbury) and the SAR (Bushveld).

*Practical use.* Pentlandite is the most important ore of nickel. Nickel is employed as an additive to steel and in alloys (brass, German silver, bronze, etc.).

## Sulphides and Arsenides with Anions

of the Type  $[\text{S}_2]^{2-}$ ,  $[\text{AsS}]^{2-}$ ,  $[\text{As}_2]^{3-}$ ,  $[\text{As}_4]^{4-}$   
(Disulphides and Their Analogues)

### Simple

PYRITE (iron pyrite)  $\text{Fe}[\text{S}_2]$  (46.0% of Fe; 53.4% of S)

Pyrite often contains the impurities of Cu, Au, As, Co, and Ni. Its crystalline structure is of the NaCl type, in which the positions of the Cl atoms occupy twinned anions  $[\text{S}_2]^{2-}$ , oriented along the axes of the third order, while the  $\text{Fe}^{2+}$  ions are in the centre of the octahedrons (Fig. 64).

The system is cubic. Crystals are in the form of cubes with reciprocally perpendicular striation on the faces (see Fig. 18). Occasionally the crystals acquire the form of pentagon-dodecahedrons and octahedrons. They form solid granular masses and dissemination.

The colour is straw-yellow. The streak is black, and the lustre is metallic. There is an absence of cleavage. The fracture is uneven, and sometimes shelly. Hardness is 6-6.5, and the density is 5. It is a semiconductor of the *n* and *p* types. Pyrite is easily discerned by its colour, the form of crystals and a high degree of hardness.

*Origin.* Pyrite is the most widespread sulphide. It is formed within various geological processes, such as, magmatic, hydrothermal, sedimentary, and metamorphic. In the oxidation zone pyrite loses its stability and is transformed into the brown oxides of iron (limonite) with the retention of sulphur in gypsum and other sulphates. Cases of pseudomorphism of limonite by pyrite are often registered. The gossans of ore deposits are formed mainly when pyrite is disintegrated. *Deposits.* In the USSR, the deposits of pyrite (and chalcopyrite) are confined to a strata of metamorphosed effusive and sedimentary rocks of Palaeozoic age, stretching in the form of a band along the Ural Ridge for 300 km. The most significant deposits are those of Kalatinsk and Uchalinsk. In other countries, there is a deposit of pyrite in Rio Tinto (Spain), which is of hydrothermal origin, a magmatic deposit in Sulitjelma (Norway) and elsewhere.

*Practical use.* Pyrite is most valuable in the production of sulphuric acid, when pyrite is processed, the impurities of Cu, Zn, Au, Se, are also occasionally made use of. Roasting cinder is used as an iron ore.

### MARCASITE $\text{Fe}[\text{S}_2]$

Marcasite often contains the As, Tl and other impurities. In its crystalline structure the  $\text{Fe}^{2+}$  ions are situated in the centre of the octahedrons, while the  $[\text{S}_2]^{2-}$  dumbbells, as distinct from the structure of pyrite, are situated in a plane, parallel to  $\{001\}$ .

The system is orthorhombic. Marcasite differs from pyrite in that it is never found in cubic crystals. It usually has the form of nodules,

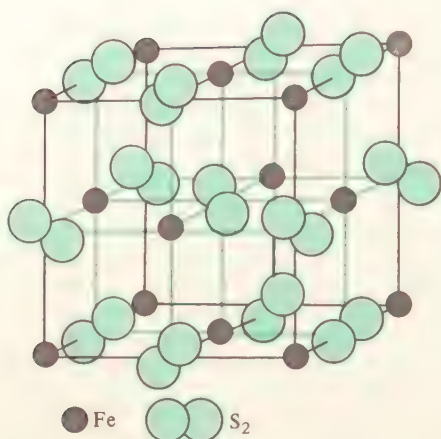


Fig. 64. Pyrite structure

concretions, spherulite crusts, comb-shaped and spear-like aggregates. There is a close resemblance of marcasite to pyrite, as far as their physical properties are concerned. However, the former differs from the latter in morphology, and in that it is less stable under morphology, and in that it is less stable under oxidation.

*Origin.* The origin is basically exogenetic. Marcasite is occasionally formed in low-temperature hydrothermal deposits. It is often found in carbonaceous rocks, sand and clay sediments, and in the oxidation zone of ore deposits.

Marcasite does not have deposits of its own. Both marcasite and pyrite are harmful impurities in coals and refractory clays, thus lowering the refractoriness of the latter.

**ARSENOPYRITE** (arsenical pyrite)  $\text{Fe}[\text{AsS}]$  (34.3% of Fe; 46.0% of As; 19.7% of S)

The crystalline structure is similar to that of marcasite.

The system is monoclinic. The crystals are prismatic. Sometimes, they are elongated, rod-like with a characteristic striation due to oscillatory combinations, and also trillings. The aggregates are compact and granular.

The colour is tin-white. The streak is greyish-black, lustre is metallic. Arsenopyrite has an imperfect  $\{101\}$  cleavage; it is brittle, with hardness 5.5-6, and density 6. It is a semiconductor. When this mineral is struck by a gliding steel object, sparks, a characteristic fume and the garlic odour of arsenic become apparent.

*Origin.* In a vast number of cases the origin is hydrothermal (high- and mid-temperature). The associated minerals of arsenopyrite are cassiterite, galena, sphalerite, wolframite, the ores of gold, silver, and copper. The contact-metasomatic (skarn) origin is also possible. In surface conditions, arsenopyrite is replaced by scorodite.

*Deposits.* In the USSR there are deposits in the Urals (Kochkar and Dzhettygara); in Central Asia (Uch-Imchak) and in eastern Siberia (Darasun and Zapokrovsk). In other countries arsenopyrite is mined on Sweden and a number of other countries.

*Practical use.* Arsenopyrite is the most important arsenic mineral, which is used in agriculture, as a pesticide, and seed dressing, as well as in leather, paint, and other branches of industry.

**COBALTITE** (cobalt lustre)  $\text{Co}[\text{AsS}]$  (35.4% of Co; 45.3% of As) It usually contains the impurity of Fe. The crystalline structure is similar to the structure of pyrite (see Fig. 64).

The system is cubic. The crystals are of the cubic and octahedral shape. The aggregates are granular and compact.

The colour is white, steel-grey with a peculiar pink tinge (significant for diagnostic purposes). The streak is grey-black. The lustre is metallic. The cleavage is medium. Hardness equals 5.5 and the density is 6.3.

*Origin.* Cobaltite (cobalt lustre) is found in the veins with arsenopyrite, the arsenide of cobalt and nickel, chalcopyrite, native silver, argentite, uraninite, siderite, calcite, as well as in skarns with glaucodot, magnetite and other minerals. In the oxidation zone cobaltite is not stable and is transformed into erythrite of pink colour.

*Deposits.* In the USSR, the deposits are located in the Transcaucasus (Dashkesan). In countries outside the USSR cobaltite deposits are situated in the Cobalt (Canada), and Sonora (Mexico), as well as in Zaire, in Norway, and Czechoslovakia.

*Practical use.* Cobaltite is a valuable ore of cobalt, which is used in the metallurgy of high-quality steels and in alloys, as well as in the production of blue glass and porcelain.

#### SMALTITE $(\text{Co}, \text{Ni})_4[\text{As}_4]_3$

Smaltite is an intermediate member of the isomorphic series skutterudite  $\text{Co}_4[\text{As}_4]_3$ —chloanthite  $\text{Ni}_4[\text{As}_4]_3$ ; it often contains the impurities of Fe and S. In its crystalline structure the cations occupy the nodes of the eight primitive cubic cells, six of which are centred by the square-prismatic anions  $[\text{As}_4]^{4-}$  with a reciprocally perpendicular orientation.

The system is cubic. Smaltite forms massive, fine granular aggregates. It is, sometimes, found in the form of crystals, mainly of the cubooctahedral habit, often with curved faces.

The colour is from tin-white to steel-grey. The streak is greyish-black. The lustre is metallic on faces and newly-formed spallings, and tarnish on the changed surface. Smaltite is brittle, its cleavage is imperfect; the fracture is uneven. Hardness equals 5.5-6, and the density is approximately 7.

*Origin.* The origin is hydrothermal of mid-temperature type. The arsenides Co and Ni are characteristic of the deposits of the five-element Ag—Bi—U—Co and Ni formations, in which together with native silver, bismuth, arsenic, red silver ores, pitchblende and other minerals. Arsenides have also been discovered in the late formations of skarn ferriferous deposits. In the oxidation zone arsenides Co and Ni are replaced by annabergite and erythrite.

*Deposits.* The Khovuaksky deposit (Tuva) of the Co—Ni—As-formation in carbonate cross veins of skarns is the one that is most widely known in the USSR. In other countries there are deposits in Morocco, the Cobalt (Canada), Ore Mountains (Czechoslovakia, GDR) and elsewhere.

*Practical use.* Smaltite is an important component of Co—Ni-ores.

## Sulphides of the Island Structure

### Sulphides with Isolated Molecules

#### Simple

REALGAR  $[\text{As}_4\text{S}_4]$  (70.1% of As, 29.9% of S)

In the core of the crystalline structure there are molecular eight fold rings  $[\text{As}_4\text{S}_4]$ , similar molecules  $[\text{S}_8]$  in the structure of sulphur (see Fig. 55).

The system is monoclinic. The crystals are short prismatic and form druses. Realgar is also found in granular and earthy aggregates, and in the form of coatings.

The colour is bright-red to orange-red. The streak is light-orange. The lustre is adamantine. Under continuous and powerful illumination realgar loses its brightness and colouring, becomes disintegrated and is transformed into orpiment  $\text{As}_2\text{S}_3$  and arsenolite  $\text{As}_2\text{O}_3$ . It is brittle. Its hardness equals 1.5-2 and its density is 3.5.

*Origin.* The origin is hydrothermal (low-temperature). Realgar usually associates with orpiment and other minerals of arsenic and with antimonite  $\text{Sb}_2\text{S}_3$ . It is present in some silver, gold and polymetallic deposits (with marcasite, calcite, aragonite, and chalcidony). Realgar is found as a sublimate in the time of volcanic activity.

*Deposits.* In the USSR there is a Lukhum deposit in western Georgia. In other countries, the deposits are found in Turkey. There are some silver and polymetallic deposits in Czechoslovakia, Romania, Greece, Italy, and the USA.

## Sulphides with Isolated Complex Anions of the Type $[\text{AsS}_3]^{3-}$ , $[\text{AsS}_4]^{4-}$ , etc. (Sulphosalts)

### Simple

PROUSTITE  $\text{Ag}_3[\text{AsS}_3]$  (65.4% of Ag) and PYRARGYRITE  $\text{Ag}_3[\text{SbS}_3]$  (59.7% of Ag)

are the extreme members of the isomorphic series of *red silver ores*. The crystalline structure represents a trigonally deformed structure of the NaCl-PbS type, in which the ions  $\text{Ag}^+$  (coordination number equals 2) and the island pyramidal radicals  $[\text{AsS}_3]$  alternate along the *C* axis, thus forming a spiral chain motif.

System is hexagonal-R. It is usually found in block crystalline masses in the form of short-columnar crystals.

The colour is cinnabar-red to dark-red with pyrargyrite. The streak is from brick-red to purple-red. When light falls on their surfaces, the two minerals become darker. The lustre is adamantine. They are both transparent and translucent, also brittle. Their cleavage is indistinct, and their fracture is shelly. Hardness is 2-2.5, and the density is 5.6; with pyrargyrite it is up to 5.8. The minerals is photoconductive.

*Origin.* The origin is mid- and low-temperature hydrothermal. They are found with other minerals of the five-element Ag—Bi—U—Co—Ni-formation, and in polymetallic deposits.

*Deposits.* In the USSR there is a Mangazei deposit in Yakutia. In countries outside the USSR the two minerals are found in the silver ore deposits in Pachuca, Chihuahua, and elsewhere in Mexico, Casapalca (Peru), Potosí (Bolivia), and also in Chile.

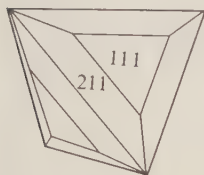
*Practical use.* Proustite and pyrargyrite are valuable minerals of silver ores.

ENARGITE  $\text{Cu}_3[\text{AsS}_4]$  (48.3% of Cu)

Enargite contains impurities of Sb, Se and Fe. Its crystalline structure is derived from the structure of wurtzite. In the positions of the three atoms of Zn there are  $\text{Cu}^+$  ions with coordination number 4. The isolated island radical  $[\text{AsS}_4]^{3-}$  occupies a fourfold position.



Fig. 65. Tetrahedrite crystals



The system is orthorhombic. It is usually found in block masses and less often in the form of tabular crystals.

The colour is from steel-grey to iron-black. The streak is greyish-black. The lustre is from metallic to tarnish. The cleavage is perfect and clear. Enargite is brittle; its hardness is 3-3.5, and its density equals 4.4. The mineral is a semiconductor. It differs from sphalerite in colour, lustre, and the colour of streak. Perfect cleavage distinguishes it from grey ores.

*Origin.* The origin is mid- and low-temperature hydrothermal, which is usually associated with other copper sulphides. In the oxidation zone enargite is replaced by malachite, azurite and other minerals.

*Deposits.* In the USSR enargite is found in the copper-porphyrus deposits in Kounrad (Kazakhstan). In other countries it is known to occur in the large polymetallic deposits of Tsumeb (Namibia) and is the most important ore mineral of copper. Enargite forms a considerable part of ore deposits in Butte (USA), Bor (Yugoslavia), and the basic minerals of the copper-molybdenite deposit of Chuquicamata in Chile.

*Practical use.* Enargite is an important mineral of copper ores.

### Complex

TENNANTITE  $\text{Cu}_{10}^+\text{Cu}_2^{2+}[\text{AsS}_3]_4\text{S}$  and TETRAHEDRITE  $\text{Cu}_{10}^+\text{Cu}_2^{2+}[\text{SbS}_3]_4\text{S}$

are the most widely spread representatives of the *grey ores* family. They often contain up to 17% of Ag (freibergite), up to 20% of Hg (schwazite), up to 10% of zinc and other elements. In the crystalline structure of grey ores the 6 tetrahedrons of  $\text{Cu}^+\text{S}_4$  have common apexes and form a sphalerite motif. Four anions  $[\text{AsS}_3]^{4-}$  (isolated trigonal pyramids) and an additional S atom, surrounded by six  $\text{Cu}^{2+}$  ions, are inscribed in it. The system is cubic. Tetrahedrite is found in clearly expressed crystals, viz. tetrahedrons (Fig. 65), but more often grey ores form block masses and disseminations.

The colour is from steel-grey to iron-black, with the same kind of streak. The lustre is metallic on faces, and tarnish on spallings and not fresh surface. There is no cleavage, the fracture is uneven. Hardness equals 3-4, and the density is 4.5-5.0. The minerals are brittle.

*Origin.* 1. The tennantite  $\text{Cu}_{10}^+\text{Cu}_2^{2+}[\text{AsS}_3]_4\text{S}$  is found together with pyrite, chalcopyrite, galena, native gold, barite, calcite, and other minerals. 2. Exogenetic origin is related to the cementation zone of sulphide deposits. The two minerals under discussion form no deposits of their own. They are characteristic of copper (the Turyinskii mines) and the gold-coating (Berezovsk, Darasun) deposits.

*Practical use.* Grey ores together with other minerals of copper enter into the composition of copper ores.

## Sulphides of the Chain Structure

### Sulphides with Simple Chains

#### Simple

ANTIMONITE (antimonial lustre, stibnite)  $\text{Sb}_2\text{S}_3$  (71.4% of Sb)  
Antimonite contains inconsiderable impurities of As, Pb, Ag, and

Fig. 66. The radiate aggregates of antimonite crystals in a quartz vein. (Half the size)



others. The crystalline structure represents zigzag chains in the form of ribbons, which consist of alternating S and Sb atoms, in which Sb is found to be in a triple (umbelliferous) coordination.

The system is orthorhombic. The crystals are elongated-and-prismatic (Fig. 66), columnar, with a rough striation along their length. They are often deformed.

The colour is lead-grey to steel-grey. The streak is of the same colour. The lustre is metallic with occasional blue tarnish. The cleavage is perfect and parallel to  $\{010\}$ . On the cleavage planes a thin twinned striation oriented across the line of elongation often becomes apparent. Hardness is 2, and the density equals 4.6. The mineral is semiconductor.

*Origin.* Antimonite is formed in the hydrothermal low-temperature deposits together with cinnabar, pyrite, fluorite, calcite, quartz, barite, and chalcedony. In the process of oxidation antimonite is replaced by antimonite ochres of a light-yellow colour.

*Deposits.* In the USSR, there are deposits in Kirghizia (Kadamzhai), in the Krasnoyarskii Krai (Razdol'ninsk) and in Yakutia (Sarylakh). In other countries the antimonite deposits are situated in the Hunan Province in China, in the Ishinokawa Mines in Japan.

*Practical use.* Antimonite is the most important ore of antimony. The latter finds its application in the alloys with lead and tin (bearings, batteries, printing type).

#### BISMUTHINITE (bismuth lustre) $\text{Bi}_2\text{S}_3$ (81.2% of Bi)

The crystalline structure is analogous to the structure of antimonite.

The system is orthorhombic. The crystals are prismatic, columnar, elongated to acicular with a characteristic vertical striation.

The colour is lead-grey to tin-white. The streak is lead-grey. The lustre is metallic, which is here more powerful than that of antimonite. The cleavage is perfect; hardness equals 2, and density is 6.6. Bismuthinite is a semiconductor.

*Origin.* It is found in high-temperature hydrothermal veins and greisens with native bismuth, pyrite, wolframite, chalcopyrite, cassiterite, quartz, topaz and other minerals. Besides, bismuthinite is

found in skarns. In the oxidation zone it is transformed into bismuth ochres of a greenish-yellow colour.

*Deposits.* Bismuthinite does not practically have any deposits of its own. In the USSR it is found in the hydrothermal deposits in Central Asia (Ustarasai and Adrasman), in the wolframite deposits of the Transbaikal region (Belukha, Bukuka and others), and in Kazakhstan (Akchatau). In other countries bismuthinite is found in Bolivia (Tacna) and Peru.

*Practical use.* Bismuthinite is the most important ore of bismuth. The latter finds its application in alloys with a low melting point.

## Sulphides with Complex Chains (Sulphosalts)

### Simple and Complex

BOULANGERITE  $Pb_5[Sb_4S_{11}]$  (55.4% of Pb) and JAMESONITE  $Pb_4Fe[Sb_6S_{14}]$  (40.1% of Pb)

are the most widespread varieties of the chain sulphides, and have very much in common as far as their outer forms are concerned. They contain 55.4% and 40.1% of Pb respectively. In the crystalline structure of these sulphosalts the pyramidal anions of the  $[SbS_3]$  or the  $[AsS_3]$  groups form infinite chains or ribbons, elongated along the *C* axis.

The system is monoclinic. The two minerals are found in the form of fibrous, acicular or radiated aggregates.

The colour is lead-grey to iron-black. The streak is greyish-black. The lustre is metallic; in fibrous aggregates it is silky. The fracture is hackly. The cleavage is perfect along the line of elongation: with jamesonite it is also parallel to  $\{001\}$ . Hardness equals 2.5-3, and the density is 6.2. The two minerals under discussion resemble the finely fibrous aggregates of antimonite.

*Origin.* The boulangerite is found on the veins of galena, sphalerite, antimonite, grey ore, arsenopyrite and carbonates.

*Deposits.* In the USSR the deposits are in the Transbaikal region (Algacha, Klichka, Zerentui, and others).

*Practical use.* There are cases when boulangerite and jamesonite enter into the composition of lead ores.

## Sulphides of the Layered Structure

### Simple

ORPIMENT  $As_2S_3$

In the crystalline structure of orpiment the corrugated lattices, consisting of the atoms of sulphur and arsenic, are interlayered in such a way that each As atom finds itself in an umbelliferous coordination with coordination number 3.

The system is monoclinic. The crystals are wedge-like with striated faces. It is usually found in the form of foliated, mica-like, granular aggregates and earthy masses.

The colour is orange on the faces of crystals; at the surface of cleaved spallings it is either lemon-yellow or golden-yellow. The streak is of the same colour, only brighter. The lustre is glassy on faces, and

adamantine purple on the planes of cleavage. The latter is absolutely perfect and parallel to  $\{010\}$ ; the leaves are flexible, though not elastic. Hardness equals 1.5-2, and the density is 3.5.

*Origin.* The origin is low-temperature hydrothermal. It is found together with realgar. Orpiment 'effloresces' with time, and is transformed into arsenolite  $\text{As}_2\text{O}_3$  in the process of oxidation.

*Deposits.* In the USSR there are the following deposits: Lukhum (Georgia), Dzhulfa (Nakhichevan ASSR), and in Yakutia. In other countries, the deposits are located in Mercur (USA) and in Greece; together with realgar it is found in a number of deposits in Rumania, Turkey, and Iran.

*Practical use.* In those cases when there are substantial accumulations of orpiment and realgar, the two minerals are used as ores of arsenic. Orpiment is also employed in the production of the yellow paint to be used by the artists.

### MOLYBDENITE (molybdenum lustre) $\text{MoS}_2$ (60% of Mo)

Molybdenite often contains the impurities of Re, Fe. The crystalline structure represents alternating packings, consisting of layers of molybdenum atoms, 'armoured' from both sides by hexagonal lattices in such a way that each molybdenum atom finds itself in a trigonally prismatic environment (Fig. 67). In the hexagonal 2H-molybdenite the same orientation is shared by each of the third packings, while in the rhombohedral 3R-molybdenite, same may be said of every fourth packing. The bonds between the packings are residual.

The system is hexagonal. The crystals form tabular, more often thin, occasionally hexahedral leaves with an absolutely perfect cleavage parallel to  $\{0001\}$ . The aggregates are foliated, scale and stellar (Fig. 68).

The colour is steel-grey. The streak on paper is bluish-grey. The lustre is strongly metallic. Hardness equals 1. When we touch the mineral our fingers get dirty and greasy. Its density is 4.7. The mineral is a semiconductor of the *n*- and *p*-types. It differs from graphite by the bluish colour of the streak made on paper.

*Origin.* The molybdenite is found in the form of dissemination in granites and granodiorites. It is known to occur in pegmatitic veins, usually in greisens with wolframite, cassiterite, bismuthinite, arsenopyrite and others. The industrial deposits are related to greisens and hydrothermal formations in quartz veins, often with chalcopyrite, in skarns with hedenbergite, garnet, scheelite, chalcopyrite and others. There are deposits where molybdenum is finely dispersed in quartz, thus attributing to it grey, faintly bluish colour. Molybdenite oxidation products are ferrimolybdate and povellite.

*Deposits.* In the USSR, there are deposits of the skarn type in the Northern Caucasus (Tyrnyauz); in greisens in Kazakhstan (the Eastern Kounrad); the copper-molybdenum deposits are situated in Armenia (Kadzharan) and in the Krasnoyarskii Krai (Sora); the quartz-molybdenum deposit can be found in the Transbaikal region (Davenda and Shakhtama). The largest molybdenum deposit in the world is in Climax (Colorado, USA), where molybdenite is found in the quartz veinlets and in the granitoids that have undergone changes. Molybdenite deposits are known in China, Morocco and other countries. In Mongolia, there is a large copper-molybdenum Erdenet deposit.

Fig. 67. Molybdenite structure in globular (a) and polyhedral (b) models

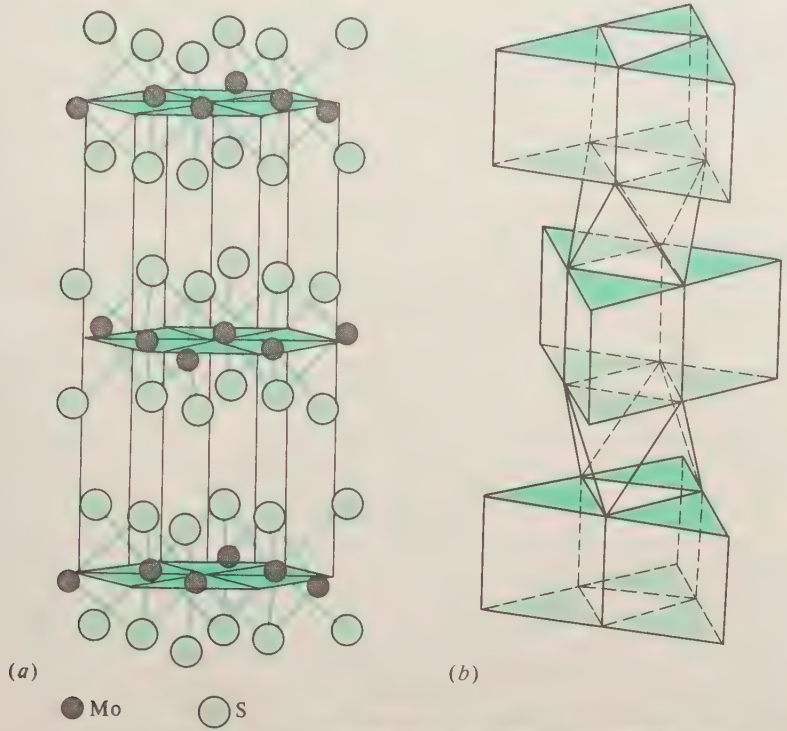
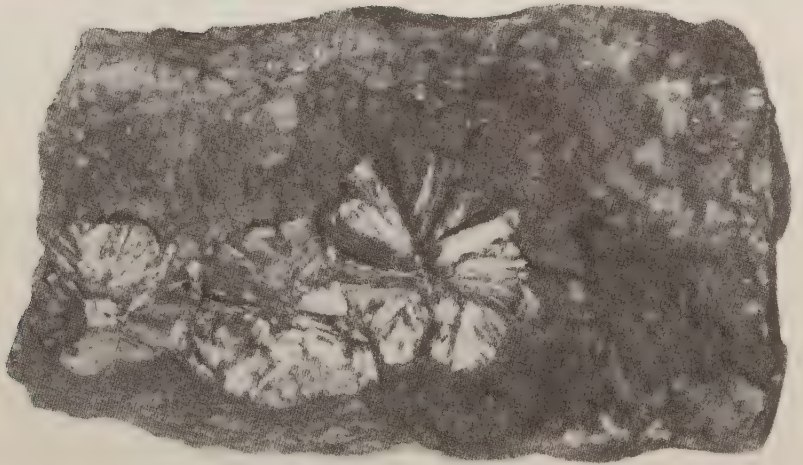


Fig. 68. Molybdenite in a quartz vein. Natural size



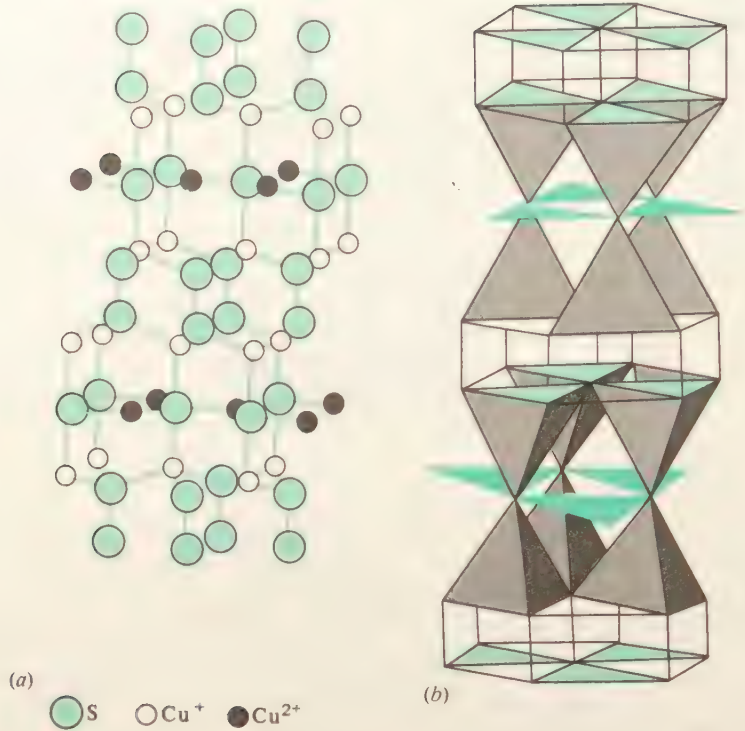
*Practical use.* Molybdenite is the main mineral of molybdenum ores. Molybdenum is used in the production of special kinds of steel remarkable for their great hardness. The mineral is also used in electrical engineering.

### Complex

COVELLITE (copper indigo)  $\text{Cu}_2^+\text{Cu}^{2+}\text{S}[\text{S}_2]$  (or  $\text{CuS}$ )

In the crystalline structure of covellite two-fold layers of  $\text{Cu}^{2+}\text{S}_4^-$

Fig. 69. Covellite structure in globular (a) and polyhedral (b) models



tetrahedrons are connected in the apexes by the common atoms of sulphur, in the planes of which the Cu<sup>+</sup> atoms are located. The S atoms composing the bases of the tetrahedrons of the neighbouring packets are brought together, thus forming the dumb-bell pairs [S<sub>2</sub>]<sup>2-</sup> (Fig. 69).

The system is hexagonal. Covellite forms thin selvages, powdery and sooty masses. Compact crystalline masses are of rare occurrence.

The colour is blue to dark-blue. The lustre is submetallic and dull. Hardness equals 1.5-2. The crystalline masses are malleable. The density is 4.6.

*Origin.* The origin is basically exogenetic, and is attributed to the zone of the secondary sulphide enrichment of a large number of copper deposits. It is found together with bornite Cu<sub>5</sub>FeS<sub>4</sub>, chalcocite Cu<sub>2</sub>S, chalcopyrite CuFeS<sub>2</sub>, enargite Cu<sub>3</sub>[AsS<sub>4</sub>] and hydrous ferric oxide.

*Deposits.* Hypogene covellite is a composite of the Butte ore deposit in the USA. Crystalline covellite is also found in the Bor mines in Yugoslavia.

*Practical use.* Together with other ore minerals of copper covellite enters into the composition of copper ores.

## Halides

Halides comprises compounds of F, Cl, Br, and I with alkaline and alkaline-earthly metals, as well as aquatic and complex heteroanion compounds, viz. alumofluorides of alkaline metals and rare earths and oxy- or sulphohaloid compounds of Cu, Pb, Ag, Hg, and other metals.

The bonds of ionic type are prevalent in halides, while in more complex compounds, those of ionic-covalent type, there is a marked increase in covalency from light to heavy halogenous anions or the substitution Ag and other metals for alkaline. Isodesmic bonds are characteristic of halides of simple composition, while heterodesmic bonds are found to be typical of aquatic and those whose composition is more complex.

In accordance with the prevalent type and character of chemical bond and the characteristic features of anion structure, halides have been classified into a number of structural types. Most halogen compounds of simple composition have a coordination structure. Halides of island, chain, and particularly layered and frame structure are more rare.

In halides of coordination structure with the closest packing of atoms, large univalent cations  $K^+$  and  $Na^+$  are in an octahedral surrounding of  $Cl^-$  and  $F^-$  anions, while in ammonium chloride  $(NH_4)Cl$  with the structure of the type  $CsCl$  the complex anion  $(NH_4)^+$  has its coordination number 12. Ion  $Ca^{2+}$  in fluorite is in a cubic coordination (coordination number is 8).

According to the prevalent type of chemical bond, and the crystallochemical peculiarities most of the halides are referred to dielectrics with glassy lustre. They are transparent, and their hardness is low or medium. Chlorides are easily soluble in water. A greater degree of stability and hardness is attributed to the less widely spread halides with complex anions. Only cerargyrite  $Ag(Cl, Br)$  and those minerals that are closely related to it substantially differ from other halides in strong adamantine lustre and malleability. The density with halides is not great and depends mainly on the atomic mass of elements entering into their composition. Halides with rare exceptions, are found in the form of isometric crystals of the cube system and crystalline-granular aggregates. Perfect cleavage is usual.

The most widely spread chlorides are formed in hypogene conditions, mainly during the steaming of sea basins (halite, sylvite, carnallite, bishofite). A considerable part of chlorides (halite, ammonium chloride, sylvite), as well as complex fluorides are formed as a result of sublimation during the volcanic eruptions, and are also accumulated in gaseous-and-liquid inclusions in minerals of the hydrothermal origin. Halides of chalcophile elements are formed in the oxidation zone of ore deposits. Most of the fluorides are connected with endogenetic processes. Villiaumite  $NaF$  is characteristic of nepheline syenites, fluorite, as well as a considerable part of complex alumofluorides and their analogues are formed in pegmatites, greisens, skarns and hydrothermal veins.

Approximately 100 species pertaining to halides are known at present. Among them only several are widely spread and have considerable accumulations of practical value. First and foremost it concerns halite, sylvite, carnallite, and bishofite, which form strong salt-bearing masses of sedimentary origin, and are the raw materials of chemical industry. The main part of halite is used in food industry, sylvite and carnallite function as agrochemical raw materials, and bishofite serves as a magnesium ore. Fluorite is used in the production of artificial cryolite as a burden for the melting of aluminium from bauxite. Transparent crystals find their application in optics. Besides, fluorides serve as a source of rare earths.

## Systematization

### Halides of Coordination Structure

#### Simple

<i>The group of fluorite</i>	FLUORITE $\text{CaF}_2$ (cubic), ytrofluorite $\text{YF}_3$ (orthorhombic).
<i>The group of halite (cubic)</i>	HALITE $\text{NaCl}$ , SYLVITE $\text{KCl}$ , villiaumite $\text{NaF}$ .
<i>The group of ammonium chloride</i>	ammonium chloride $(\text{NH}_4)\text{Cl}$ (cubic).
<i>The group of cerargyrite</i>	cerargyrite $\text{Ag}(\text{Br}, \text{Cl})$ (cubic), iodoargyrite $\text{AgI}$ (hexagonal).

#### Complex and with Additional Anions

<i>The group of gagarinite</i>	gagarinite $\text{NaTRCaF}_6$ (hexagonal-R).
<i>The group of corderoite</i>	corderoite $\text{Hg}_3\text{Cl}_2\text{S}_2$ (monoclinic).

#### Aquatic

<i>The group of carnallite</i>	BISHOFITE $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (monoclinic), CARNALLITE $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ (orthorhombic), tachyhydrite $\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ (hexagonal-R).
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### Halides of Island Structure

<i>The group of avogadrite</i>	avogadrite $\text{K}[\text{BF}_4]$ (orthorhombic).
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### Halides of Chain Structure

<i>The group of sellaite</i>	sellaite $\text{MgF}_2$ (tetragonal).
<i>The group of cryolite</i>	cryolite $\text{Na}_2[\text{NaAlF}_6]$ (monoclinic).

## Halides of Coordination Structure

### Simple

FLUORITE (fluorspar)  $\text{CaF}_2$

Fluorite often contains the isomorphic impurities of Y and TR. In its crystalline structure the  $\text{Ca}^{2+}$  ions are in the cubic coordination of  $\text{F}^-$  ions. The coordination cubes occupy the space in a chess-board arrangement (Fig. 70).

The system is cubic. The crystals have the form of cubes, octahedrons, cubic octahedrons, and more rarely that of rhombododecahedrons (Fig. 71). Sometimes the crystals form very attractive-looking druses. Fluorite is massive and veined, represented by spherulites or rhythmically banded spherulite aggregates (Fig. 72).

The mineral is mostly colourless or white, purple and green. Not infrequently polychromatic zonal crystals are found. The cleavage is



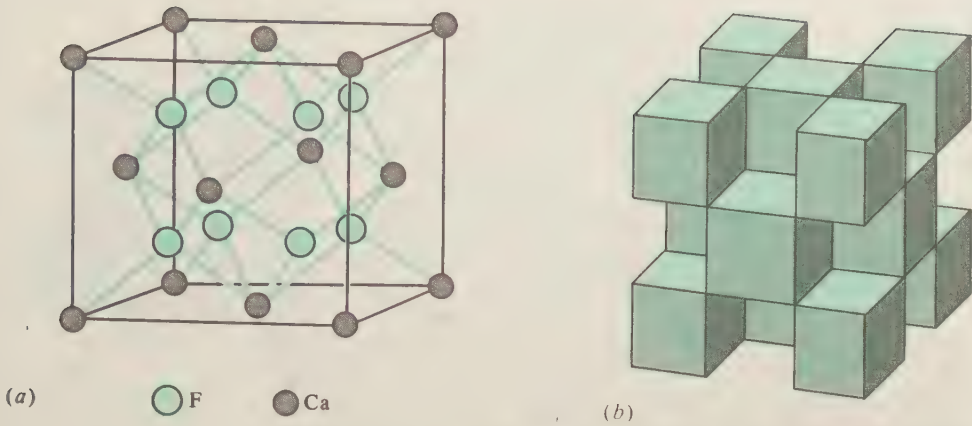


Fig. 70. Fluorite structure in globular (a) and polyhedral (b) models

Fig. 71. Fluorite crystals

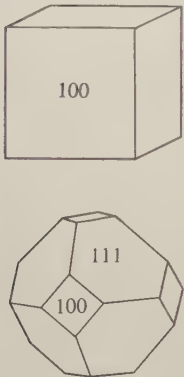


Fig. 72. Spherulitic concentrically-zonal crust of fluorite. Kalangui deposit (the Transbaikai region). Dim. by 1.5 times

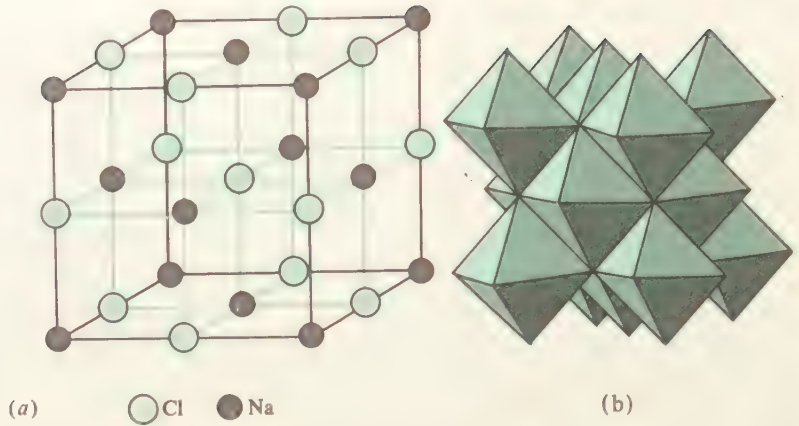


perfect, parallel to octahedron  $\{111\}$ . The lustre is glassy. Hardness is 4, and density equals 3.18. Fluorite is characterized by purple or blue luminescence.

*Varieties.* The *optic fluorite* is transparent and colourless variety of fluorite. *Ratofkite* is an earthy, pale-purple fluorite found in marly rocks and dolomitized limestones.

*Origin.* The hydrothermal, industrial origin is usually that of low-temperature. The skarn origin in greisens is of less often occurrence, and the ratofkite origin is sedimentary. The associated minerals of fluorite in quartz veins are: barite, calcite, sulphides of Pb, Zn, Sb and other metals; in greisens fluorite is associated with muscovite, topaz, tourmaline, wolframite and cassiterite, and with garnet, calcite, and quartz in skarns.

Fig. 73. Halite structure in globular (a) and polyhedral (b) models



*Deposits.* In the USSR, the deposits are located in the Transbaikalian region (Kalangui), in Central Asia (Aurakhmat) and in the Arkhangelsk region (Amderma). Outside the USSR there are deposits in Mongolia, in Kentucky and Illinois in the USA, and in other countries.

*Practical use.* Fluorite, in its bulk, is used as a flux in the production of aluminium, as well as a source of various fluorine compounds, the optical fluorite is an optical material of great value.

#### HALITE (rock salt) NaCl

The crystalline structure represents a closest packing of chlorine ions, in which all the octahedral voids are occupied by Na ions (Fig. 73).

The system is cubic. The crystals are in the form of cubes, and usually form solid, compact granular masses, and infrequently crusts, coatings and blooms.

The colour is white, grey, often colourless and occasionally bluish. The mineral is either transparent or translucent. Its lustre is glassy; the cubic cleavage is perfect. The hardness equals 2, and the density is also 2. Halite is soluble in water, and salty when tasted.

*Origin.* Halite is a typical chemical sediment of seas and lakes. It is formed in the drying out salt-bearing lakes and shallow-water lagoons, separated from the sea by bars. It is found together with sylvite, gypsum, anhydrite, carnallite, and sometimes with borites, thus forming thick masses. Under the pressure of the overlying rocks the salt becomes plastic, and can be driven out and come through the said rocks, which results in the formation of salt domes and stocks. In small quantities halite forms efflorescence and sublimation products resulting from volcanic activity.

*Deposits.* In the USSR, there are the following deposits: Artemovsk (Donbass), Sototvino (Transcarpathians). Deposits of the salt-dome type include those that are situated in the western Kazakhstan and Yakutia; the contemporary salt deposited lakes of Elton and Baskunchak in the Region of Lower Volga, the salt springs of Usolie Sibirskoye in the Irkutsk Region and elsewhere. The Solikamsk deposit in the Urals is the largest in the world, and it is remarkable not only for halite, but for potassium and magnesium salts as well. In other countries, there are deposits in Poland (Welichka), as well as in

North India, Egypt, and in the southern states of the USA. *Practical use.* Halite is the most important food product and the basic raw material of chemical industry. It is used in the production of hydrogen chloride, sodium carbonate, chlorine, etc.

#### SYLVITE KCl

The structure is of the NaCl type.

The system is cubic. Solid, compact, granular masses, more seldom cubic and cubooctahedral crystals are typical of both halite and sylvite. The mineral sometimes contains the inclusions of ammonium chloride and hematite.

The colour is white, grey. The mineral is often colourless, though sometimes reddish as a result of mechanical impurities of hematite  $\text{Fe}_2\text{O}_3$ . Sylvite is usually transparent and translucent, its lustre is glassy, and the cubic cleavage is perfect. Hardness equals 2, and the density is also 2. The mineral is easily soluble in water, when tasted, it is bitter and salty.

*Origin.* Sylvite, as well as halite, is a typical mineral of the chemical sediments of seas and lakes. It is usually found together with halite, gypsum, anhydrite, carnallite and other halides and sulphates, as well as borates. It forms sublimations during the eruptions of volcanoes.

*Deposits.* In the USSR, there is Solikamsk deposit in the Urals, where sylvite is found together with halite. There is also a large Starobinsk potassium salt deposit in Byelorussia (Soligorsk). In countries other than the USSR, the largest potassium deposit is that of Strassfurt in GDR. It differs from the Solikamsk deposit in that the sulphates there are found in much greater quantities than the haloids.

*Practical use.* Sylvite is a raw material used in the production of potassium fertilizers.

#### Aquatic

##### BISHOFITE $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

Bishofite often contains the impurities of Br (up to 1%). In its crystalline structure the Mg ions are in the octahedral environment of  $\text{H}_2\text{O}$  molecules and two  $\text{Cl}^-$  ions, centering the opposite faces of the octahedrons. Six more Cl ions form a hexagonal ring in the plane perpendicular to the C axis.

The system is monoclinic. The crystals form granular, fibrous or foliated aggregates and solid masses.

The minerals is either white or colourless. Sometimes it is red. The lustre is glassy or dull. Bishofite is brittle, its fracture is uneven, with hardness 1-2, and density is 1.6. It is hygroscopic and becomes blurred in air. Bishofite is easily soluble in water, its taste is very bitter.

*Origin.* The origin is chemogenically-sedimentary. The mineral is one of the last that crystallizes from the brines and is accumulated in the upper regions of salt deposits. Besides, it is formed in the process of carnallite decomposition.

*Deposits.* In the USSR, there are large deposits in the Saratov and Volgograd regions. In other countries, mention should be made of the Strassfurt deposit in GDR.

*Practical use.* Bishofite is a highly valuable raw material in the production of metal magnesium and magnesium salts.

**CARNALLITE**  $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ 

In the crystalline structure the bishofite 'molecules' alternate with  $\text{K}^+$  ions, that are in the octahedral environment of  $\text{Cl}^-$  ions.

The system is orthorhombic. It is found in block granular masses.

The colour is white, pink and red resulting from the hematite  $\text{Fe}_2\text{O}_3$  inclusions. The mineral is sometimes colourless. It is brittle; its hardness is 1-2 and the density is 1.6. The taste is acrid and bitter. It is easily soluble in water, hygroscopic, and loses its configuration of humid air. The sound of friction is produced when the mineral is rubbed.

*Origin.* The origin is a chemical sediment. It is one of the last to leave the solution and thus characterizes the upper limits of the salt deposits. The alternation of layers from bottom to top has the following sequence: gypsum, anhydrite, halite, sylvite, carnallite, and bishofite.

*Deposits.* In the USSR there are the following deposits: Solikamsk (the Urals), Starobinsk (Byelorussia), and Kalush (Transcarpathians). Outside the USSR there is the Strassfurt deposit in GDR.

*Practical use.* Carnallite serves as a raw material in the production of metal magnesium and potassium fertilizers.

## Oxides and Hydroxides

Oxides comprise minerals, that are in themselves compounds of metals and semimetals with oxygen. Hydroxides contain the OH group, additional anions and/or water.

In oxides there is a predominance of the ionic type of chemical bond with an inconsiderable inclusion of covalent and metallic bonds, mainly in minerals of the complex composition, containing Fe, Ti, Nb, Ta, etc. In hydroxides there is, in addition, a substantial impact of hydrogen bonds.

In terms of their chemical composition the minerals under discussion lend themselves to a clear-cut classification into those that are simple and complex. The simple oxides are characterized by a marked restriction of isomorphic replacements. The content of impurities in them does not usually exceed 1%, and goes beyond this figure only in those cases when heterovalent isomorphism is present.

Oxides, that are more complex, as far as their composition is concerned, and containing cations of different charge, are sometimes regarded as compounds, transitory between oxides and salts of the oxygen acids. This concerns spinel and magnetite to a lesser extent. However, with complex oxides, containing Ti, Nb, and Ta, the problem of referring them to oxides or to oxygenous salts can be solved only if their crystallochemical characteristic features and physical properties are taken into account. Irrespective of this, it is customary to label them respectively as titanates, niobates, and tantalates. These very features make it possible to refer wolframite ( $\text{Fe, Mn}\text{WO}_4$ ) also to complex oxides.

All complex oxides are usually characterized by wide isomorphic replacements. Isovalent isomorphism is common, e.g. to magnetite  $\text{FeFe}_2\text{O}_4$  and chromite  $\text{FeCr}_2\text{O}_4$ , in which  $\text{Fe}^{2+}$  is replaced by ions

$Mg^{2+}$ ,  $Mn^{2+}$ , while  $Fe^{3+}$  and  $Cr^{3+}$  are replaced by ions  $Al^{3+}$ ,  $Mn^{3+}$ , and  $Ti^{4+}$ .

Restricted heterovalent isomorphism is found in cassiterite, containing in small quantities  $Fe^{3+}$  and  $Nb^{5+}$  replacing  $Sn^{4+}$  positions according to the pattern:  $Sn_{1-2n}(Fe_{3n^{3+}}^{3+})_n(Nb_{3n^{5+}}^{5+})_nO_2$ . Heterovalent replacements are particularly characteristic of complex oxides Ti, Nb, and Ta. For instance, in samarskite  $Y^{3+}$  is partially replaced by  $U^{4+}$  or  $Th^{4+}$ , while  $Nb^{5+}$  is respectively replaced by  $Fe^{3+}$  in accordance with pattern  $Y_{1-2n}^{3+}(U_{2n}^{4+})_n(Nb_{2-n}^{5+})(Fe_{n}^{3+})_nO_6$ .

In terms of their structure the simple and the complex oxides are represented by various types. Coordination structures are more characteristic of simple oxides, in which the coordination number of the cations is 8 and 6, for example in uraninite  $UO_2$  and periclase  $MgO$ . Same can be said of minerals with closest hexagonal packing of oxygen, in which the cations replace 2/3 of the octahedral positions, as is the case with corundum  $Al_2O_3$  and hematite  $Fe_2O_3$ . Coordination structure is also shared by complex oxides with closest packing of oxygen, in which the cations occupy a part of the tetrahedral and octahedral positions.

Insular structures are practically not typical of oxides. Rare minerals with molecular-insular structure, e.g. arsenolite  $As_2O_3$  and senarmontite  $Sb_2O_3$  can be regarded as exceptions.

In the chain structure of oxides the cations are distributed in octahedral voids of the closest hexagonal packing of oxygen in the form of linear (in cassiterite) or zigzag (in columbite) alternating chains.

Ribbon and layered structures are characteristic of hydroxides. Their core is constituted by a closest hexagonal packing of  $OH^-$ -groups, in which the cations are distributed in octahedral coordination.

In oxides of the frame structure the atom groupings in the form of tetrahedrons  $[SiO_4]$  (in quartz), octahedrons  $[TiO_6]$  or  $[NbO_6]$  (in perovskite and pyrochlore) are connected with each other by the common ions of oxygen. In complex salt-like oxides of titanium, niobium and tantalite the voids in the frame are occupied by large cations.

The physical and morphological characteristic features of oxides and hydroxides are wholly congruous with their crystallochemical peculiarities and the prevalent chemical bond.

Minerals of coordination and frame structures are basically of isometric shape, while chain oxides, as a rule, are represented by elongated-and-prismatic crystals. Minerals of the ribbon and layered structures form bladed-and-tabular crystals, or foliated-and-scale aggregates, often with a clear-cut cleavage in one direction.

A considerable part of oxides is either colourless or faintly coloured. This is characteristic of ionic compounds. Their colouring is connected with the impurity of elements—chromophores, as is the case with  $Cr^{3+}$  in bright-red ruby. The other part of oxides, in which the species-forming elements are the ions of Fe and Mn, as well as Ti, Nb and Ta is of black or dark-brown colour. As compared with colourless dielectrics, they function as semiconductors with metallic or metalline lustre. Maximum hardness is shared by oxides of coordination structure (corundum, spinel), the same can be said of simple oxides of frame (quartz) and chain structures (cassiterite). With most of the other

oxides the hardness is medium (from 5 to 6), and only with layered hydroxides of hydrogen bonds it is markedly lower.

Oxides and hydroxides belong to minerals that are widely spread. They constitute approximately 17% of the whole Earth's crust. More than 150 species of minerals pertaining to this class are known at present.

The origin of oxides is connected with various processes, viz. magmatic, pegmatitic, skarn, hydrothermal, hypergene, and metamorphic. Oxides are the most significant ores of Fe, Cr, Mn, Ti, Al, Nb, Ta, U, Th, TR, and other metals, as well as non-metallic mineral resources.

## Systematization

### Oxides of Coordination Structure

#### Simple

<i>The group of ice</i>	ice H <sub>2</sub> O (hexagonal).
<i>The group of cuprite</i>	CUPRITE Cu <sub>2</sub> O (cubic).
<i>The group of periclase</i>	periclase MgO (cubic).
<i>The group of uraninite</i>	URANINITE UO <sub>2</sub> (cubic), torianite ThO <sub>2</sub> (cubic), baddeleyite ZrO <sub>2</sub> (monoclinic).
<i>The group of corundum</i> (hexagonal-R)	CORUNDUM Al <sub>2</sub> O <sub>3</sub> , HEMATITE Fe <sub>2</sub> O <sub>3</sub> .

#### Complex

<i>The group of ilmenite</i> (hexagonal-R)	ILMENITE FeTiO <sub>3</sub> ; geikielite MgTiO <sub>3</sub> , etc.
<i>The family of spinelides</i> (cubic)	SPINEL MgAl <sub>2</sub> O <sub>4</sub> , CHROMITE FeCr <sub>2</sub> O <sub>4</sub> , MAGNETITE FeFe <sub>2</sub> O <sub>4</sub> , hercynite FeAl <sub>2</sub> O <sub>3</sub> , franklinite (Fe, Zn, Mn)(Fe, Mn)O <sub>4</sub> , gahnite ZnAl <sub>2</sub> O <sub>4</sub> , magnesioferrite MgFe <sub>2</sub> O <sub>4</sub> , ulvite Fe <sub>2</sub> TiO <sub>4</sub> .

### Oxides of Chain Structure

#### Simple

<i>The family of rutile</i>	RUTILE TiO <sub>2</sub> (tetragonal), anatase TiO <sub>2</sub> (tetragonal), brookite TiO <sub>2</sub> (orthorhombic), CASSITERITE SnO <sub>2</sub> (tetragonal).
<i>The family of oxides and hydroxides Mn</i>	PYROLUSITE MnO <sub>2</sub> (tetragonal), MANGANITE MnO(OH) (monoclinic), PSILOMELANE BaMn <sup>2+</sup> Mn <sub>3</sub> <sup>3+</sup> O <sub>20</sub> ·3H <sub>2</sub> O (orthorhombic).

**Complex**

*The family of oxides*  
Ta, Nb, and Ti

COLUMBITE (Fe, Mn)Nb<sub>2</sub>O<sub>6</sub> (orthorhombic),  
TANTALITE (Fe, Mn)Ta<sub>2</sub>O<sub>6</sub> (orthorhombic),  
samarskite Y(Fe, U)(Ta, Nb)<sub>2</sub>O<sub>8</sub> (monoclinic),  
fersmite CaNb<sub>2</sub>O<sub>6</sub> (orthorhombic).

*The group of wolframite* (monoclinic)

HUEBNERITE MnWO<sub>4</sub>,

*The group of ilmenorutile*

FERBERITE FeWO<sub>4</sub>,  
ilmenorutile FeTiNbO<sub>6</sub> (tetragonal).

**Hydroxides of Belt and Layered Structures****Simple**

*The group of brucite*  
*The family of hydroxides* Al

BRUCITE Mg(OH)<sub>2</sub> (hexagonal-R),  
HYDRARGILLITE Al(OH)<sub>3</sub> (monoclinic),  
DIASPORE AlOOH (orthorhombic),  
BOEHMITE AlO(OH) (orthorhombic).

*The family of hydroxides* Fe

GOETHITE FeOOH (orthorhombic),  
LEPIDOCROCITE FeO(OH) (orthorhombic)  
hydrogoethite FeOOH · nH<sub>2</sub>O (amorphous).

**Oxides of Frame Structure****Simple**

*The family of silica*

low-temperature QUARTZ SiO<sub>2</sub> (hexagonal-R),  
high-temperature QUARTZ SiO<sub>2</sub> (hexagonal),  
tridymite SiO<sub>2</sub> (hexagonal),  
cristobalite SiO<sub>2</sub> (cubic),  
coesite SiO<sub>2</sub> (monoclinic),  
stishovite SiO<sub>2</sub> (tetragonal),  
OPAL SiO<sub>2</sub> · nH<sub>2</sub>O.

**Complex**

*The group of perovskite* (cubic)  
*The group of aeschynite*

PEROVSKITE Ca[TiO<sub>3</sub>],  
loparite (Ce, Na, Ca) [(Ti, Nb)O<sub>3</sub>] and others.  
aeschynite Ce[TiNbO<sub>6</sub>] (orthorhombic).

*The group of pyrochlore* (cubic):

PYROCHLORE NaCa[Nb<sub>2</sub>O<sub>6</sub>(OH, F)],  
MICROLITE NaCa[Ta<sub>2</sub>O<sub>6</sub>(OH, F)],  
betafite (Na, U) [TiNbO<sub>6</sub>F].

**Oxides of Coordination Structure****Simple**

CUPRITE Cu<sub>2</sub>O (88.8% of Cu)

The crystalline structure represents a volume-centered cubic cell of oxygen ions, in which Cu<sup>+</sup> ions (coordination number is 2) are in the centre of four octants; the O<sup>2-</sup> ions are in a tetrahedral coordination of Cu<sup>+</sup> ions (coordination number is 4) (Fig. 74).

The system is cubic. The crystals are small, of octahedral shape,

more seldom cubic. Cuprite is found mainly in the form of block granular masses. Powdery and earthy accumulations of cuprite are sometimes mixed with iron hydroxides. They are called red copper ore.

The colour is red of various shades. The streak is black. The crystalline-granular varieties of cuprite have an adamantine lustre. Hardness equals 3.5-4 and the density is 6.

*Origin.* The origin is exogenetic. The mineral is often formed in the oxidation zone of deposits at the expense of copper sulphides. It occurs together with native copper, malachite, azurite, iron hydroxides, and other secondary minerals. When cuprite is being decomposed, it is mainly transformed into malachite, which forms pseudomorphs after it.

*Deposits.* Cuprite is found in a large number of places, though substantial accumulations are rare. In the USSR it is known to occur in the pyrite deposits in the Urals.

*Practical use.* Cuprite is used in melting together with other copper minerals.

#### URANINITE $\text{UO}_2$ (50-65% of U)

Uraninite contains Th, Ra, Pb, He. Its crystalline structure is similar to that of fluorite,  $\text{U}^{4+}$  is located in the position of  $\text{Ca}^{2+}$  (coordination number is 8);  $\text{O}^{2-}$  is in the position of  $\text{F}^-$ .

The system is cubic. It is rarely found in crystals of cubic habit, and usually forms sintered, nodular-like solid masses.

The colour is black, brownish-grey. The streak is brown-black. The lustre is submetallic and resinous. Hardness equals 5.6-6. The density is 8-10. The mineral is highly radioactive.

*Varieties.* Pitchblende forms collomorphic and cryptocrystalline extractions, while the group of uranium oxide minerals forms earthy aggregates. Pitchblende differs from uraninites also by the presence of  $\text{U}^{6+}$ , the redundant charge of which is compensated by the fact that additional ions  $\text{O}^{2-}$  with the formation of the uranyl ion  $(\text{UO}_2)^{2+}$  enter into the structure.

*Origin.* 1. Uraninite of pegmatite origin is found in pegmatitic veins in association with feldspar, orthite, zircon, and monazite. Such deposits are of no great importance. 2. The hydrothermal origin is related to sulphides and arsenides of cobalt, nickel, native bismuth and silver, pyrite, molybdenite, chalcopyrite, galena, barite, fluorite and carbonates. The hydrothermal deposits are highly significant as far as their practical implementation is concerned. 3. The sedimentary origin is associated with bituminous rocks. In the oxidation zone the mineral is unstable and is transformed into earthy varieties and numerous secondary minerals (uran-micas, etc.).

*Deposits.* In the USSR there are uraninite deposits in the Ukraine and Central Asia. In other countries, the following deposits should be mentioned: the deposits of Great Bear Lake and many other districts in Canada, the Katanga district in Zaire, Poland (hydrothermal) and Hamar (sedimentary, in cretaceous sediments) in Czechoslovakia. There is also a huge mining enterprise in Namibia, and other large deposits of uraninite in Northern Brazil.

*Practical use.* Uraninite is the most important ore of uranium and radium.



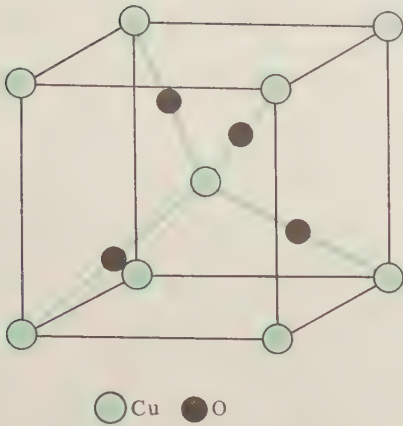


Fig. 74. Cuprite structure

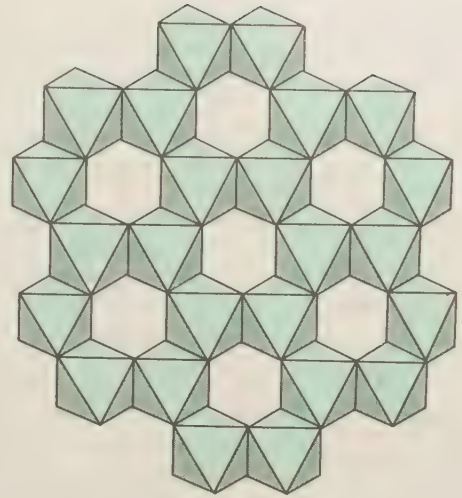


Fig. 75. The corundum motif of the closest hexagonal packing:  $Al^{3+}$  occupies  $2/3$  of octahedral voids

**CORUNDUM  $Al_2O_3$**

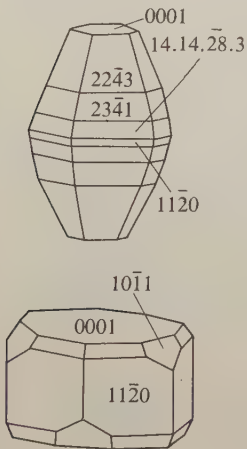
Corundum, sometimes, contains the impurities of Fe and Cr. The crystalline structure represents a closest hexagonal packing of  $O^{2-}$  ions, in which the  $Al^{3+}$  ions occupy  $2/3$  of octahedral voids (Fig. 75).

The system is hexagonal-R. The crystals are columnar, barrel-shaped, and sometimes bladed. They represent combinations of a ditrigonal prism and a number of ditrigonal dipyramids, a rhombohedron, and a pinacoid (Fig. 76). The mineral is also found in block granular aggregates.

The colour is blue, greyish-blue, grey, or pink. The lustre is glassy to adamantine. There is no cleavage, though there is a well developed jointing parallel to pinacoid  $\{0001\}$ , at the surface of which a slanted striation due to repeated twinning becomes apparent. The fracture is uneven. Hardness is high, equals to 9 and the density equals 4. *Varieties.* The transparent blue corundum is called *sapphire*. The blood-red variety of corundum is known as *ruby* (its colour is conditioned by the impurity of  $Cr_2O_3$ ).

*Emery* is a block granular corundum rock of the greyish-black colour resulting from a slight impurity of hematite, magnetite, spinel, and other minerals.

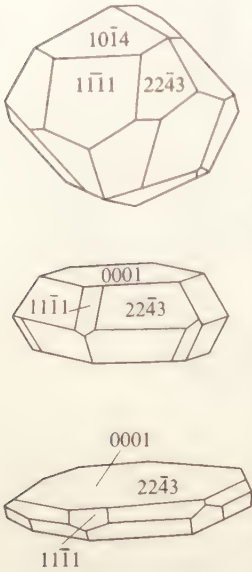
Fig. 76. Corundum crystals



*Origin.* 1. The magmatic and pegmatite origins are connected with syenites. 2. The contact-metamorphic origin is associated with the mineral being formed at the expense of the transformation of high-alumina rocks.

*Deposits.* In the USSR corundum is found in the Semizbugu deposit in north-east Kazakhstan, corundum-feldspar veins are discovered along the Borzovka River in the Kyshtym district, and in the pegmatites of the Ilmen Mountains in the Urals, in the chlorite schist of the Kosoi Brod deposit in the Sverdlovsk Region there is emery. The solid granular red corundum occurs in the contact deposits of Yakutia. It also exists in the ultra-basic rocks of the Raiz mass (the Polar Urals). In other countries, the deposits of ruby and sapphire of world renown, are located in South-East Asia. Rubies of the best quality are mined in Burma (the Mogok mines and others); their deposits are concentrated in the soil and in the alluvium of the Irawadi River. Placers in Sri

Fig. 77. Hematite crystals



Lanka are the main suppliers of sapphire. Ruby and sapphire are also mined in Thailand and India. There are large deposits of emery in Chester (USA) and on the islands of Naxos and Samos in the Aegean Sea (Greece).

*Practical use.* Corundum and emery are used as abrasive material. Ruby and sapphire are precious stones.

#### HEMATITE (iron red ore) $\text{Fe}_2\text{O}_3$ (70.0% of Fe)

The crystalline structure is of the type shared by corundum.

The system is hexagonal-R. Colour is red, dark-red to black. The streak is cherry-red (a characteristic diagnostic feature). The mineral is not susceptible to magnetization. The lustre is submetallic. Hardness equals 5-6, and the density is 5.2. The mineral is a semiconductor. *Varieties.* By the form of its segregation and shape the following varieties of hematite are distinguished: *iron glance*, or fine-scaled formation of the black colour; the crystals of hematite also belong here (Fig. 77) as well as various clear crystalline aggregates: e.g. hematite, specularite; iron red ore, which includes solid aggregates of the red colour and sinter formations with a smooth surface, viz. red glassy head, earthy, ochre masses and oölites; *martite* which comprises the pseudomorph of hematite by magnetite.

*Origin.* 1. Contact-metasomatic. 2. Hydrothermal (iron glance) in veins; beautiful crystals and aggregates. 3. Sedimentary. 4. Metamorphic, during the metamorphism of sedimentary iron ores (brown iron ores). In the oxidation zone the mineral loses its stability, and is transformed into various iron hydroxides.

*Deposits.* The largest deposits of hematite are related to the sedimentary-metamorphic type. In the USSR this type is represented by the deposits in Krivoi Rog and Kursk Magnetic Anomaly (Yakovlev, Gostishchev, Lebedinsk, Mikhailovskoye and others). There are deposits in the ferruginous quartzites of Precambrian age. A large ferruginous quartzite deposit is located in Karelia (Kostomush). In countries outside the USSR, hematite ores in Precambrian metamorphic rocks are known in the region of Lake Superior in the USA, notable deposits also occur in Brazil and India. In Algeria the stratiform deposit is associated with the cretaceous limestone.

*Practical use.* Hematite is the most important mineral of iron ores.

#### Complex

ILMENITE (titanium iron ore)  $\text{FeTiO}_3$  (36.8% of Fe, 31.6% of Ti) Impurities of Mg, Nb, Cr, V, etc. are common. The crystalline structure is similar to the structure of corundum, in which 1/3 of octahedral voids is occupied by  $\text{Fe}^{2+}$  ions, while the  $\text{Ti}^{4+}$  ions occupy the other third.

The system is hexagonal-R. The crystals are thick tabular, lamellar. It is commonly found in the form of irregular disseminations.

The colour is black. The streak is black too. The lustre is either metallic, or submetallic. The fracture is shelly. Hardness equals 5.5. The density is 4.7. Sometimes, the mineral is weakly magnetic. Ilmenite is a semiconductor.

*Origin.* The magmatic origin is connected with the basic igneous rocks, in which it forms schlieren and disseminations. It is often found in

alkaline pegmatites together with sphene, feldspars, biotite, and other minerals, as well as in kimberlites and carbonatites. In the weathering zone, the mineral is stable and is accumulated in placers.

*Deposits.* In the USSR ilmenite is known in the pegmatites of the Ilmen Mountains. Large industrial deposits of ilmenite are associated with placers (the Pravoberezhny deposit in the Dnepropetrovsk Region, the placers in the basin of the Zeya River). In other countries there are the following deposits: magmatic, in anorthosites in Canada; the coastal placers of Western Australia, India, and Sierra-Leone.

*Practical use.* Ilmenite is the most important ore of titanium. It is used in the production of metallic titanium, ferrotitanium, special kinds of steel and white titanium paint.

### The Family of Spinel

#### SPINEL $MgAl_2O_4$

The usual impurities are those of  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ ,  $Ti^{4+}$ . The crystalline structure represents a closest cubic packing of oxygen ions, in which Mg occupy 1/4 of tetrahedral voids, while 1/2 of them is occupied by Al (Fig. 78).

The system is cubic. It is found in the form of crystals and grains disseminated in the rock. The crystals are of octahedral habit. Twins formed by the 'spinel law' are common (see Fig. 24).

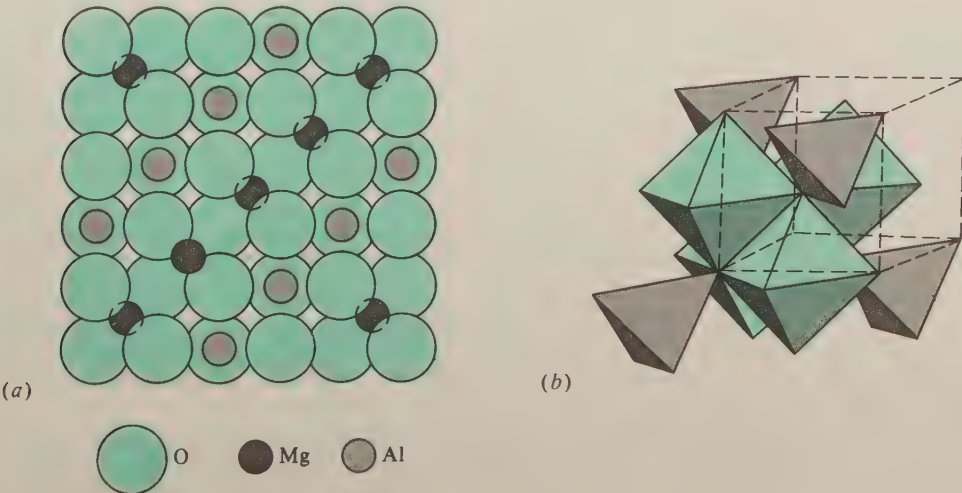
The colour is light-blue, blue, pink, red, green, brown to black. The lustre is glassy. Hardness equals 8, and the density is 3.6.

*Varieties.* The noble spinel (lhal) of the pink or red-purple colour, conditioned by the impurity of  $Cr^{3+}$ .

*Origin.* The contact-metamorphic origin is usually associated with marmorized limestone and is commonly found in dolomites, magnesian skarns together with phlogopite, pyroxene, and scapolite. It is also related to crystalline schists and gneisses, and infrequently to ultrabasic rocks.

*Deposits.* In the USSR there are deposits in Shishim and Nazyam Mountains in the southern Urals. Spinel is mined in the phlogopite deposit of Slyudyanka in the southern Baikal region (blue spinel), in the Aldan phlogopite deposits (black spinel), and noble spinel is

Fig. 78. Fragments of spinel structure in globular (a) and polyhedral (b) models



known in the Pamirs. In other countries the largest deposits of red and pink spinel are located in Burma, where it is mined together with ruby. Spinel is also found in the placers of Sri Lanka, Thailand, as well as in Afghanistan.

*Practical use.* Transparent and beautifully coloured crystals of noble spinel are of no minor practical importance. They are used as precious stones.

**CHROMITE** (chromic iron)  $\text{FeCr}_2\text{O}_4$  (32% of FeO; 68.0% of  $\text{Cr}_2\text{O}_3$ ) It usually contains the isomorphous impurities of Mg,  $\text{Fe}^{3+}$ , Al. The crystalline structure is similar to the structure of spinel.

The system is cubic. The mineral is usually massive, in the form of disseminations and granular aggregates.

The colour is black. The streak is brown, which is significant for diagnostic purposes. The lustre is submetallic. Hardness equals 5.5, and the density is 4.5-4.8. Sometimes, the mineral is weakly magnetic. This is accounted for by the magnetite inclusions, or the product of disintegration of solid solutions.

*Origin.* The origin is exclusively magmatic, and is connected with ultrabasic rocks. The minerals form dissemination, schlieren secretions or deposits in dunites, peridotites and serpentinites together with serpentine, olivine, magnetite, uvarovite, platinum, kaemmererite, and kotschubeite.

*Deposits.* In the USSR there are chromite deposits in the northern Urals (Saranovsk); in the southern Urals: the group of the Aktyubinsk Region deposits: the Almaz Zhemchuzhina, Millionnoye, the 40th Anniversary of the Kazakh SSR, and others. In other countries, chromite is mined in South Africa, Turkey, India, and the Philippines.

*Practical use.* Chromite is the only ore of chromium. In metallurgy chromium is used as an addition to various kinds of steel, which make the steel viscous, enhances its hardness and anticorrosive properties. Chromium ores of low quality are used by metallurgy as a refractory material.

**MAGNETITE** (magnetic iron ore)  $\text{FeFe}_2\text{O}_4$  (72.4% of Fe)

The isomorphous impurities of Mg, Ti, Mn are common. The crystalline structure is analogous to that of spinel, in which the tetrahedral voids are occupied by half of  $\text{Fe}^{3+}$  ions, while the other half of  $\text{Fe}^{2+}$  ions and all the  $\text{Fe}^{2+}$  ions (the inverse structure) function similarly in respect to the tetrahedral voids.

The system is cubic. The crystals are found in the form of octahedrons, and more seldom as rhombododecahedrons (Fig. 79). They usually form solid, granular and mixed masses, or dissemination.

The colour is black. The streak is also black. The lustre is either metallic or submetallic. Hardness is 5.5-6, and density is 5.0-5.2. The mineral is excessive ferromagnetic. It is also a semiconductor. *Varieties.* *Titanomagnetite*, or magnetite with up to several per cent of  $\text{TiO}_2$  content; it also contains vanadium; *magnomagnetite* ( $\text{Fe, Mg}$ ) $\text{Fe}_2\text{O}_4$ .

*Origin.* 1. The magnetite is solely connected with basic and rare acid rocks. 2. Skarn. 3. Hydrothermal. 4. The metamorphic origin is associated with the metamorphism of primary sedimentary ores

Fig. 79. Magnetite crystals

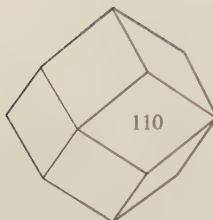
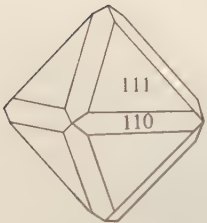
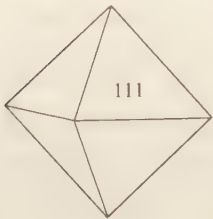
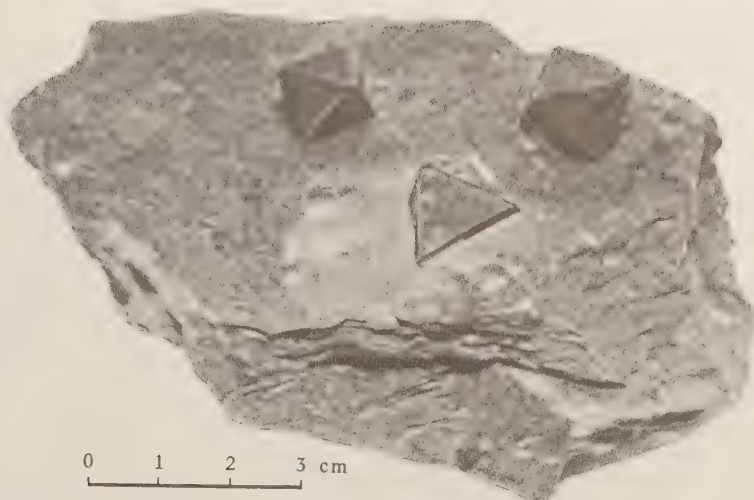


Fig. 80. Octahedral crystals of magnetite on a talc-chlorite schist. The Shabra talc deposit in the Urals



(brown iron ore). The mineral is also found in chlorite and talc schists (Fig. 80). In the process of oxidation magnetite is transformed first into martite (pseudomorphs of hematite after magnetite), then into various ferric oxides. Magnetite is often found in placers. *Deposits.* The magmatic origin is shared by Kachkanar (magnetite), Kusun, Nizhni Tagil and Pervouralsk titanomagnetite deposits (Urals), as well as by those in Sweden (Kiruna and Gellivare).

Great importance is attributed to the following skarn deposits of magnetite: the Magnitnaya Mountain (Magnitogorsk), Dashkesan (Azerbaijan), Tashtagol, Sheregesh, Teisk (the Mountain Shoriya), Sokolovsk, Sarbai, Kurzunkul and Kachar (Kazakhstan), Irbinsk (the South of Krasnoyarskii Krai), Tayozhnoye and Sivagli (Southern Yakutia) and others.

The hydrothermal deposits, connected with traps, include the Korshunov, Rudnogorsk and others, thus forming the group of the Angaro-Ilim deposits in the Irkutsk Region. These ores are represented by the magnetite which often has an oölitic structures.

Metamorphic deposits can be exemplified by those in Krivoi Rog and the Kursk Magnetic Anomaly. Similar deposits though smaller in size, are known in the USA and India.

*Practical use.* Magnetite has the same practical application as hematite, and is used as the most important mineral of iron ores. Titanomagnetite also serves as an ore of titanium and vanadium.

## Oxides of Chain Structure

### Simple

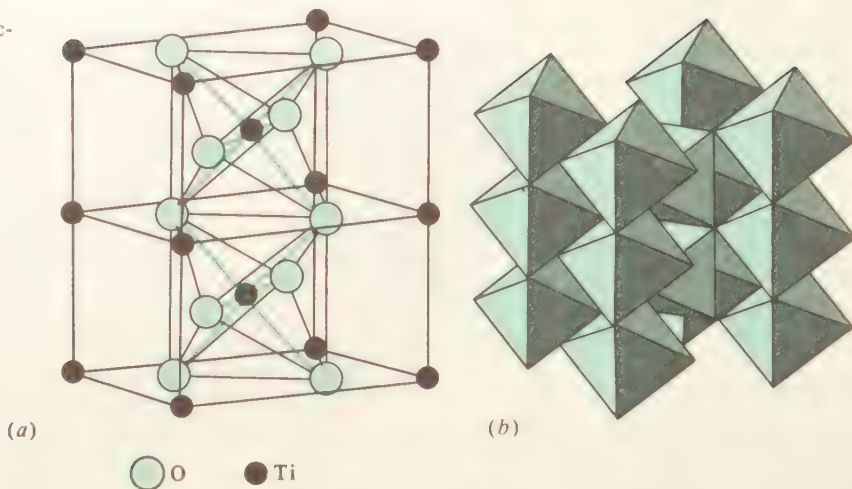
#### The Family of Rutile-Cassiterite

#### RUTILE $TiO_2$

Rutile often contains the impurities of Fe, Nb, Sn, V and others. The crystalline structure of rutile is a closest hexagonal packing of oxygen ions, in which 1/2 of the octahedral voids occupied by titanium forms chains along the axis of the second order (Fig. 81).

The system is tetragonal. The crystals are prismatic, longitudinally

Fig. 81. Rutile structure in globular (a) and polyhedral (b) models



striated, often acicular. Gemiculated and polysynthetic twins and trillings are found to be characteristic (see Fig. 27).

The colour is brownish-red, dark-red to dark-brown and black. Sometimes the colour is bluish. The streak is light brown, yellow. The lustre is either submetallic or adamantine. The cleavage is clear along the line of elongation. The fracture is shelly. Hardness equals 6-6.5, and the density is 4.2.

*Varieties.* *Sagenite*, or an acicular rutile, is in latticed aggregates or in the form of intergrowths in other minerals. The fibrous crystals of rutile are particularly common in quartz.

*Origin.* 1. The magmatic origin is found in basic and alkaline igneous rocks. 2. The metamorphic origin is related to gneisses and schists. 3. The hydrothermal origin is connected with quartz veins and particularly with the veins of the alpine type, where rutile forms separate crystals and druses. 4. The minerals is also found in placers.

*Deposits.* In the USSR rutile and sagenite are mined in the Urals, in the placers along the Kamenka River in the Sisertsky district of the Sverdlovsk Region. Other countries remarkable for the deposits of rutile are: Norway, the Suisse Alps, and Madagascar.

*Practical use.* When densely accumulated, rutile serves as an important ore of titanium.

#### CASSITERITE (tinstone) $\text{SnO}_2$ (78.8% of Sn)

Cassiterite contains the impurities of Fe, Nb, Ta, and W. The crystalline structure is similar to the structure of rutile.

The system is tetragonal. The crystals are prismatic, dipyrmidal, and isometric. Twins are common (see Fig. 27). Usually the crystals are small, but occasionally they are of up to several centimetres. They are also found in the form of disseminated grains of irregular form, nodular and spherulite aggregates.

The colour is dark-brown, brown to black. The streak is light-brown. The lustre is either submetallic or adamantine. The hardness equals 6.5-7 and the density is 6.8-7.0.

*Varieties.* Cassiterite of the brown colour having compact sintered and shelly forms, resembling wood, is called *wood tin*.

*Origin.* The origin of cassiterite is connected with the following rocks: (1) pegmatites, where cassiterite is found together with muscovite, albite, quartz, columbite, etc.; (2) the albitized granites and greisens, often together with muscovite, topaz, and quartz; (3) the skarns, usually together with tin-containing garnet, scheelite, and others; (4) the hydrothermal veins of quartz-cassiterite, tourmaline-cassiterite and sulphide-cassiterite formations, in which cassiterite is found together with wolframite, molybdenite, tourmaline, chlorite, pyrrhotite, arsenopyrite, and chalcopyrite.

*Deposits.* In the USSR cassiterite is concentrated in the eastern parts of the country where there are primary as well as placer deposits. In the North-East, the deposits of cassiterite are known in the Central Yan district of Yakutia, the Magadan Region and Chukotka Autonomous Region: Ege Khaya, Valkumei, etc. (the cassiterite-silicate-sulphide formations). Iultin and Kester (the cassiterite-quartz formations), in the Primorski Krai: Dalnee, Khrustalnoye, etc. (the cassiterite-quartz formations), and the Khabarovsk Krai: Solnechnoye, Perevalnoye, etc. (the quartz-cassiterite formation). Cassiterite is found in the Transbaikal region (Ononsk, Khapcheranga, Etyka), along the Ladoga Lake (Kitelya) and Tadzhikistan (Maikhura), where cassiterite is of the skarn type with scheelite.

In other countries large primary deposits of cassiterite are found in Bolivia (sulphide veins); alluvial and eluvial placer deposits of world renown are known in Malaysia, as well as in Thailand, Burma and Indonesia (the islands of Bangka and Billiton).

*Practical use.* Cassiterite is the most important ore of tin. Tin is used on easily fusible alloys with Cu, Zn, and Pb for tinplating, and its production, as a solder in electrical engineering industry.

#### The Family of Oxides and Hydroxides Mn

##### PYROLUSITE $MnO_2$ (63.2% of Mn)

The crystalline structure is similar to that of rutile.

The system is tetragonal. It is usually found in black crystalline or cryptocrystalline earthy masses, and sometimes in the form of radially fibrous acicular aggregates as well as oörites.

Both the colour and the streak are black. The lustre is either metallic or submetallic. The hardness varies from 2 with friable and earthy varieties to 5-6 with the crystalline varieties. The density is 4.7-5.0.

*Origin.* 1. Pyrolusite is formed in the crust of the weathering zone at the expense of various minerals and rocks, containing manganese. 2. The sedimentary origin of pyrolusite is associated with that of manganite, psilomelane, wad, rhodochrosite, etc.

*Deposits.* In the USSR there are sedimentary deposits in Chiatura (Georgia), and in Nikopol in the Ukraine. In other countries, the deposits are located in India, Africa (Ghana) and Brazil.

*Practical use.* Pyrolusite is the most important ore of manganese. In metallurgy manganese is used as an additive to steel, and makes it hard, viscous and malleable.

##### MANGANITE $MnO(OH)$

The crystalline structure represents a distorted hexagonal packing in which the chains of  $MnO_2$ -octahedrons are elongated along the C axis.

The system is monoclinic. The crystals are columnar, roughly longi-

tudinally striated, and often in druses. The mineral is usually found in solid, earthy and sinter forms.

The colour is black. The streak is brown, and the lustre is submetallic. Hardness equals 4, and the density is 4.3.

*Origin.* 1. Low-temperature hydrothermal (in veins with barite, calcite, and siderite). 2. Sedimentary (in manganese deposits together with pyrolusite).

*Practical use.* Manganite is the most important ore of manganese.

#### PSILOMELANE

The formula is  $\text{BaMn}^{2+}\text{Mn}^{4+}_3\text{O}_{20}\cdot 3\text{H}_2\text{O}$ . However, there are other means of expressing it too. Psilomelane contains the impurities of Fe, Al, Si, W, etc. The crystalline structure is composed of pipe-like chains of double and triple  $\text{MnO}_6$ -octahedral ribbons. In the large voids there are  $\text{Ba}^{2+}$  ions,  $\text{H}_2\text{O}$  molecules and impurities.

The system is orthorhombic. Psilomelane is found in the form of botryoidal and reniform sinter, as well as in solid compact masses as dendrites and oölites.

The colour is from steel-grey to black. The streak is brown-black to black, shiny. The lustre is either submetallic or dull. The fracture is uneven. Hardness is up to 6, and the density is 4.0-4.7.

*Varieties.* *Wad* is the friable earthy mixture of psilomelane and other hydroxides of manganese. Its hardness is usually about 1-2. The colour and the streak, as in the case with psilomelane, are black. The density is 2.8-4.4. *Asbolan* contains the impurity of cobalt, while *tungomelane* contains the impurity of tungsten.

*Origin.* The origin is exogenetic. Both psilomelane and wad are formed under the oxidation of various minerals of manganese, and by means of sedimentation. Besides, tungomelane is also known to originate in mineral springs. Asbolan is characteristic of the crust of the weathering of ultrabasites. Psilomelane and wad are widely spread in the manganese deposits, where they are associated with the following minerals: pyrolusite, manganite, rhodochrosite, calcite, dolomite, and barite.

*Deposits.* In the USSR the deposits are: Chiatura, in Georgia; Nikopol in the Ukraine; Dzhezdy, in Kazakhstan; Sapal, near Nizhni Tagil, in the Urals.

*Practical use.* Psilomelane and wad are ores of manganese, asbolan is an ore of cobalt, and tungomelane is an ore of tungsten.

#### Complex

#### The Family of Ta, Nb, and Ti Oxides

COLUMBITE  $(\text{Fe}, \text{Mn})\text{Nb}_2\text{O}_6$  and TANTALITE  $(\text{Fe}, \text{Mn})\text{Ta}_2\text{O}_6$  are the extreme members of the isomorphic series.

The content of Mn and Fe is also variable, though Mn is usually prevalent. The crystalline structure represents a closest hexagonal packing of oxygen ions, in one layer of which 1/2 of the octahedral voids is occupied by  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  ions, while the other half contains  $\text{Ta}^{5+}$  and  $\text{Nb}^{5+}$  ions, thus forming zigzag chains.

The system is orthorhombic. The crystals are bladed, ranging from thickly-tabular to foliated.

The colour is black to dark-brown. The streak is dark-red to black. The lustre is metallic. The cleavage is medium. The fracture is uneven.



The minerals are brittle. Their hardness equals 6, and the density is 5.3-8.0.

*Origin.* The pegmatitic origin is found in rare-metal replacement pegmatites and albitized granites together with tabular and saccharoidal albite, microcline, lepidolite, quartz, muscovite, spodumene, black and polychrome tourmaline, beryl, cassiterite, and phosphates of manganese and iron.

*Deposits.* The following deposits serve as examples: Nazareno in Brazil: tantalum-niobium pegmatoid granites; Abu Dobbab (ARE) in apogranites; large deposits of columbite, associated with granitoids, are known in Nigeria.

*Practical use.* Both columbite and tantalite are significant ores of tantalum and niobium.

#### HUEBNERITE $MnWO_4$ and FERBERITE $FeWO_4$

are the extreme members of the isomorphic series of wolframite  $(Mn, Fe)WO_4$  (76.5% of  $WO_3$ ).

Sometimes they contain the isomorphic impurities of  $Nb^{5+}$ ,  $Ta^{5+}$ , and  $Sc^{3+}$ . The crystalline structure of the chain-layered type represents a distorted closest cubic packing of oxygen ions. The octahedrons

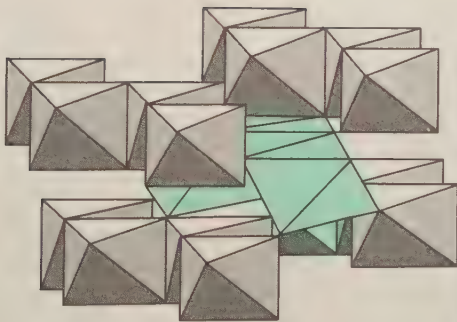


Fig. 82. Wolframite structure in polyhedral models: different colours show sinuous chains of  $(Fe, Mn)O_6$  (grey) and  $WO_6$  octahedra (green)

Fig. 83. Wolframite in a quartz vein



occupied by  $Mn^{2+}$  and  $Fe^{2+}$  ions are joined by their edges into zigzag chains along the  $C$  axis, which are connected by common apexes with analogous chains of  $WO_6$ -octahedrons (Fig. 82).

The system is monoclinic. The crystals are flattened and elongated, tabular, scaly, and occasionally acicular with a characteristic striation along the  $C$  axis. They form radiating aggregates and compact crystalline secretions (Fig. 83).

The colour is from black with ferberite, dark-brown with wolframite, to reddish-brown and yellowish-brown with huebnerite. The streak is, respectively, from black, dark-brown to light-brown. The cleavage is perfect in one direction of elongation across the flattening parallel to  $\{010\}$ . The fracture is uneven. The lustre on faces and particularly on cleavage planes is from submetallic to adamantine. At an uneven surface it is dull or resinous-greasy. Huebnerite is semi-transparent, brittle, its hardness is 4-4.5, and the density is approximately 7.5. It differs from the granular aggregates of sphalerite, to which it resembles, in density, in that it has one direction of cleavage, greater degree of hardness and a negative reaction to  $H_2S$ . As compared with the smaller grains of ilmenite, columbite, cassiterite (in heavy concentrates), huebnerite becomes luminescent on undergoing  $CaCl_2$  processing and the subsequent wash off.

*Origin.* The mineral is formed mainly in greisen and high-temperature hydrothermal quartz veins together with muscovite, topaz, molubdenum, scheelite, infrequently replacing it together with pyrite and fluorite; it is also found in tin ore hydrothermal deposits near the surface, as well as in the low-temperature veins with antimonite, cinnabar, and scheelite. It forms large placers. In the oxidation zone it is replaced by ferritungstite or tungstite.

*Deposits.* In the USSR, greisen and vein deposits are situated in the Transbaikal region (Bukuka, the Sherlov mountain, and Dzhida), in Kazakhstan (Akchatau, Kara-Oba), there are low-temperature veins in Georgia (Zopkhito, Racha, etc.). In other countries, there are large deposits in China, Burma, Mongolia, Portugal.

*Practical use.* It is the most important mineral of tungsten ores.

## Hydroxides of Belt and Layered Structures

### Simple

#### BRUCITE $Mg(OH)_2$

It is not infrequently that this mineral contains the isomorphic impurities of  $Fe^{2+}$  and  $Mn^{2+}$ . The crystalline structure consists of layers of closest hexagonal packing of  $(OH)^-$  ions, in which  $Mg^{2+}$  ions occupy all the octahedral voids; between the layers there is a weak hydrogen bond.

The system is hexagonal-R. It is usually found in the form of small scaly and tabular, less often parallel-fibrous aggregates (*nemalite*). Thick tabular crystals are not common. The mineral also forms pseudomorphs by periclase  $MgO$ .

The colour is white or greyish-green. The streak is white. The lustre is glassy to dull, purple or silky. The cleavage is perfect and parallel to pinacoid  $\{0001\}$ . Brucite is brittle, its hardness equals 2.5 and the density is 2.4.

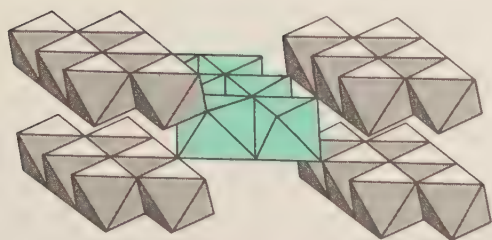


Fig. 84. Diaspore structure in a polyhedral model

### The Family of Al Hydroxides

in Kazakhstan; in the magnesian skarns of Yakutia. In other countries there is the Asbestos deposit in Canada, as well as in KPDR, Italy, and elsewhere.

*Practical use.* Brucite is a valuable raw material in the production of metallic magnesium and refractory material for metallurgy.

### HYDRARGILLITE (gibbsite) $\text{Al}(\text{OH})_3$

The crystalline structure is similar to that of brucite, in which Al occupies  $2/3$  of octahedral voids in accordance with the corundum law.

The system is monoclinic. The crystals are small, tabular form. They are usually found in compact, earthy, and often sinter masses.

The colour is white, greyish-white. The cleavage is perfect. The lustre on the planes of cleavage is purple. The hardness equals 2.5-3.5, and the density is 2.35. The mineral differs from diaspore, to which it resembles, in that its hardness is lower.

*Origin.* The exogenetic origin is associated with the weathering of aluminosilicates. Hydrargillite is a component of bauxites.

### DIASPORE $\text{AlOOH}$

This mineral often contains the isomorphic impurities of  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Ga}^{3+}$ . The crystalline structure is a closest hexagonal packing of oxygen and hydroxyl ions, in which  $\text{Al}^{3+}$  occupies the half of the distorted octahedral voids in such a way that the bands of paired  $\text{Al}(\text{O}, \text{OH})_6$ -octahedral chains form a layered pattern (Fig. 84).

The system is orthorhombic. The crystals are tabular, elongated; the aggregates—foliated and scaly.

The colour is brown, greyish-white. The cleavage is perfect. The lustre is adamantine. On the cleavage faces it is purple. The hardness equals 6.5-7, and the density is 3.4. Diaspore is a brittle mineral.

*Origin.* 1. In most cases it is exogenetic, and is found in bauxite deposits. 2. In contact deposits it often occurs together with corundum.

*Deposits.* In the USSR the contact-metasomatic diaspore in large foliated crystals is known in the emery deposit of Kosoi Brod in Urals.

### BOEHMITE $\text{AlO}(\text{OH})$

The crystalline structure is derived from the closest cubic packing, in which  $\text{AlO}_3(\text{OH})_3$ -octahedrons, connected in pairs by common edges, form corrugated packings.

The system is rhombic. The mineral forms cryptocrystalline, small scaly and porcelain-like aggregates.

The colour is white, yellowish, or there is absence of colour altogether. The lustre is glassy, purple, and silky. It is semitransparent. The cleavage is perfect. The fracture in block aggregates is uneven to

shelly. The hardness equals 3.5-4, and the density is 3.1.  
*Origin.* The exogenetic origin is related to bauxite deposits.

### BAUXITE

represents a blend comprising hydrargillite, diaspore, and boehmite, as well as kaolin, silica and oxides of iron. These are clay-like, occasionally compact, and often of oölitic composition rocks. The formation of bauxites is connected with the weathering of aluminosilicate rocks in a hot climate. The bauxite deposits are of the following types: residual, platform, and sedimentary.

*Deposits.* In the USSR the sedimentary deposits include the Tikhvin in the Leningrad Region and those of the North-Ural bauxite district. In other countries there are deposits in France and in Jamaica. Residual deposits are known in Australia, the USA, Sirunam, Guyana, Guinea, India, and elsewhere.

*Practical use.* Bauxite is an ore of aluminium.

### The Family of Fe Hydroxides

#### GOETHITE $\text{FeOOH}$ (62.9% of Fe)

The crystalline structure is similar to that of diaspore.

The system is orthorhombic. The crystals are small, tabular and acicular. The mineral is earthy, and has the form of spherulite crusts.

The colour is dark-brown to yellow-brown. The streak is brown-yellow of various shades. The lustre of the crystals is adamantine; with fibrous varieties it is silky, and usually dull. The hardness equals 5.5, and the density is 3.3-4.3.

*Origin.* The sedimentary origin is either a biogenic or chemical sediment. The minerals is often found in the crust of weathering as a disintegration product of pyrite, siderite, magnetite and silicates, containing iron. It enters into the composition of limonite (brown iron ore).

#### LEPIDOCROCITE $\text{FeO}(\text{OH})$

The crystalline structure is similar to that of boehmite.

The system is orthorhombic. It is difficult to distinguish this mineral

Fig. 85. The sintered form of limonite.  
 Natural size



from goethite. Lepidocrocite is found in the form of scaly aggregates, earthy or massive masses.

The colour is red, brown to yellow. The streak is orange. The hardness equals 5, and the density is 4.

*Origin.* As far as the conditions of its formation are concerned, lepidocrocite is analogous to goethite. It is a composite part of limonite.

#### LIMONITE (brown iron ore)

is a blend of various hydroxides of iron of the brown, and brown-yellow colour, goethite, hydrogoethite, lepidocrocite and hydrolepidocrocite, as well as the mechanical impurities, e.g. clay matter, quartz, etc.

Limonite forms crusts, powder, various sinter forms (Fig. 85), and spherulite crusts with a black string surface (*the black glass head*), earthy and ochre masses; it is also found in the form of concretions and oölites. The limonites of the oölitic composition are often called *bean ore*. Pseudomorphs of limonite after pyrite, siderite, marcasite and other minerals are of common occurrence.

There is a marked fluctuation in the physical properties of limonite depending on its composition and structure. The hardness is from 1 with friable and earthy varieties rich in water, up to 5 with compact varieties in which the content of water is inconsiderable. The density is 2.7-4.3.

Limonite emerges as a result of the oxidation of ferriferous minerals (sulphides, oxides, silicates). It often makes the so-called gossans in the oxidation zones of copper ores, in the crusts of the weathering of ultrabasic and carbonate rocks, as well as chemical and biochemical sediments, forms at the bottom of lakes, marches, and along the coastal line of seas.

*Deposits.* In the USSR large deposits of oölitic brown iron ore are located in the Crimea (Kerch), and in the Northern Caucasus (Malkin). Limonites of the lake-bog origin are known in the European part of the country (Lipetsk, Tula, Khoper, etc.), in the Urals (Baikal—a gossan after siderite, Komarovo-Zagizin, etc.), in Kazakhstan (Ayat, and Lisakov). In countries outside the USSR there are deposits in France and Luxemburg.

*Practical use.* Limonite is an important ore of iron.

## Oxides of the Frame Structure

### Simple

#### The Family of Silica

#### QUARTZ $\text{SiO}_2$

The crystalline structure of quartz resembles a three-dimensional frame, composed of silica-oxygenous tetrahedrons, each of which has apexes common with four neighbouring ones. There are several modifications of  $\text{SiO}_2$  in the composition of the silica family. They differ in the orientation of  $\text{SiO}_4$ -tetrahedrons (Fig. 86). Each of them is characterized by particular limits of the temperature stability (Table 3). At high pressures more compact modifications of  $\text{SiO}_2$  have artificially been received; for example, coesite (density 2.93) and

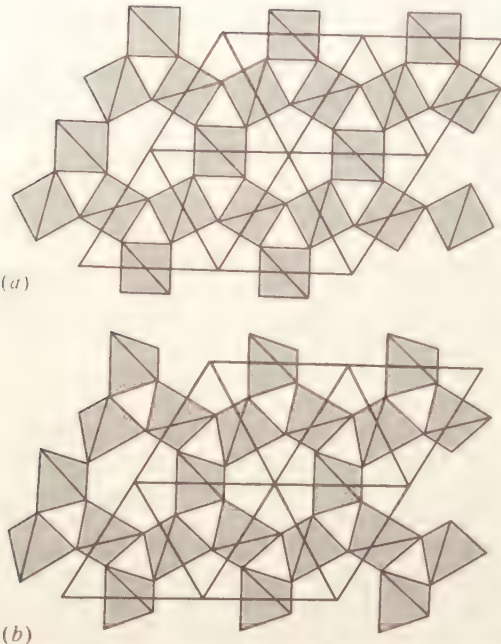


Fig. 86. The structure of high-temperature quartz (a) and low-temperature quartz (b) in a polyhedral model (projection parallel to {0001})

rutile-like stishovite (density 4.35). They have also been found in the impactites of large meteorite craters.

The system of the low-temperature ( $\beta$ -quartz) is hexagonal-R while that of the high-temperature ( $\alpha$ -quartz) is hexagonal. High-temperature quartz is usually found in the form of isometric hexagonal dipyramidal crystals ranging from 3-5 to 20 mm in the discharged acid rocks, viz, liparites. In granites and pegmatites quartz is usually represented by the paramorphs of  $\beta$ -quartz after  $\alpha$ -quartz.

Low-temperature quartz is mainly massive and forms granular aggregates. It is often found in perfectly faced crystals forming druses (Fig. 87). As a rule, crystals are of the elongated-and-prismatic habit. As far as simple forms are concerned, it may be said that faces of the prism of negative and positive rhombohedrons, trigonal dipyramid and trigonal trapezohedrons are common. Horizontal striation in prism faces is characteristic. It is often the case that earlier long-prismatic crystals

grow on the short-prismatic dipyramidal crystals of later quartz. This leads to the formation of scepter-like crystals (see Fig. 22).

According to the position of trapezohedrons the right- and the left-handed varieties of quartz crystals are distinguished (Fig. 88). They often form twins of the Dauphine, Brazil and Japanese types (see Fig. 28).

The colour of quartz is white, grey, and pink. The lustre is glassy on faces and greasy on spallings. Cleavage is usually absent, though sometimes it is distinct after rhombohedron and prism. The fracture is shelly. Its hardness equals 7, and the density is 2.65. Quartz possesses piezoelectric properties. The left- and the right-handed varieties of quartz differ in the direction in which the planes of the light polarization

TABLE 3 The Temperature Stability of Polymorphic Modifications of Silica

Polymorphic modifications	Temperature stability, °C	System
Low-temperature quartz ( $\beta$ -quartz)	below 575	hexagonal-R
High-temperature quartz ( $\alpha$ -quartz)	575-870	hexagonal
trimyditite	870-1470	hexagonal
crystalite	1470-1710	cubic
The melting point—above 1710°—(liquid SiO <sub>2</sub> )		

Fig. 87. A druse of quartz crystals.  
Natural size



rotate. The transparent varieties are good conductors of ultraviolet and infrared light.

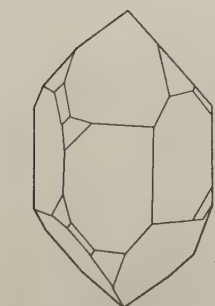
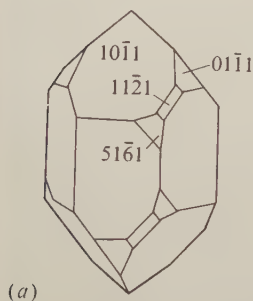
*Varieties.* According to its colour the following varieties of quartz are distinguished: *rock crystal*, which is aquatic-transparent, usually forms perfect crystals, and is found in the low-temperature veins of the alpine type and some pegmatites; *amethyst*, of purple colour, low-temperature and hydrothermal origin; *rose quartz*, of pale-pink colour, and characteristic of the central parts of some of the pegmatite veins; *smoky quartz* of smoky, brownish colour, transparent, and is formed in the low-temperature hydrothermal veins; *morion*—a black variety of quartz, which is found in the pegmatite veins and greisens together with orthoclase, albite, topaz, and beryl; the green quartz or *prase*, whose colour is connected with the mechanical impurity of actinolite or chlorite; owing to the ingrowths of mica and hematite *aventurine* has a characteristic golden-red or red-brown colour and submetallic iridescent light (tinge).

The cryptocrystalline variety of quartz is called *chalcedony*. It forms nodular aggregates (Fig. 89), concretions, crusts, fulfilling the secretions, amygdules, and other voids. Chalcedony is nontransparent, but is usually translucent. The lustre is waxy and dull. The more widely spread variety of chalcedony is that of grey or bluish-grey colour.

Numerous varieties of chalcedony are distinguished in colour, pattern, and composition. Among the transparent or translucent coloured varieties mention can be made of *carnelian* of the red and orange colours. The banded varieties of chalcedony are called *agates*. The compact impure chalcedony rock with a considerable amount of impurities of other minerals and mineral pigments is called *jasper*. Jasper is of various colour. Chalcedony with the admixtures of sand and clay are called *flint*.

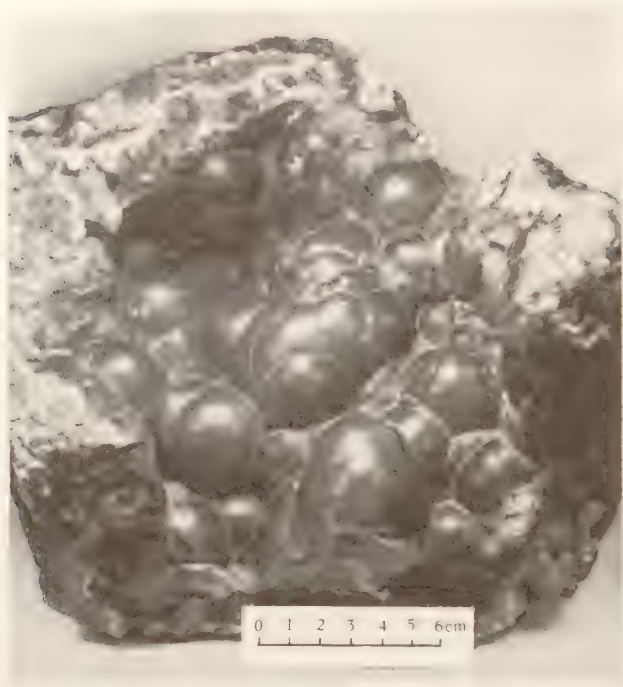
*Origin.* Quartz is of various origin. The quartz of magmatic origin is singled out in the form of irregular grains, as is the case with granites.

Fig. 88. The right- (a)  
and the left-handed (b)  
quartz crystals



(b)

Fig. 89. The nodular-shaped aggregates of chalcedony. The Transcaucasus



In granites and pegmatites together with feldspars it is the main rock-forming mineral. Under hydrothermal mineral formation quartz is the most widely spread veined mineral.

Quartz is a weathering-resistant mineral, and does not lend itself to chemical disintegration. The mechanical decomposition of quartz-containing rocks leads to its accumulation in placers and the formation of quartz sands. When metamorphic processes take place, the later are transformed into solid rocks, viz. quartzites.

Quartz is found together with a large number of other minerals. It does not associate only with nepheline, olivine, chromite and several other minerals poor in the silicic acid of magmatic rocks.

The formation of chalcedony is connected with the low-temperature hydrothermal process, accompanying the igneous activity. Chalcedony and its varieties, agates, carnelians and others, are extracted in the fissures and voids of solidified lava, and are found in the form of amygdules in many effusive rocks, e.g. in Siberian traps. Chalcedony of exogenetic origin is represented by secretions and concretions of flint in sedimentary masses.

*Deposits.* In the USSR rock crystal is found in pegmatites in Volyn, in the Urals, the Pamirs and the Aldan River; amethyst is recovered in the Northern Urals, in the Angaro-Ilim and Angaro-Katsk districts in the south of the Siberian platform; carnelian and other varieties of chalcedony are occurred in the pebbles of the Vilyui and the Lower Tunguska river basins; the deposits of industrial agate are located in Georgia (Akhaltzykh) and Yakutia; the best jasper in the world is found on the Southern Urals (the Orsk jasper is particularly valued for its beautiful pattern) and Altai; pure quartz sands are notable in the Moscow (Lubertsy), Vladimir (Gus-Khrustalny) and other regions. In



other countries there are rock crystal deposits in the Swiss Alps, Brazil, and Madagascar. Amethyst is found in Uruguay.

*Practical use.* Rock crystal (piezoquartz) is employed in radio engineering and optics. Amethyst, smoky quartz, chalcedony, agate, and jasper are used in jewellery as precious and semiprecious stones. Agate is also used in fine mechanics. Pure quartz sands are made use of in glass industry; sandstone and quartzite function as building materials.

#### OPAL $\text{SiO}_2 \cdot n\text{H}_2\text{O}$

Opal has a globular inner structure

This mineral has an ordered structure. It is found in sintered glass-like formations with shelly fracture.

The colour is white, grey; sometimes it displays a beautiful change of colour (opalescence). The transparent or semitransparent opalescent varieties with regular structure are called noble opals and have different shades of blue or, more rarely, red. The lustre is glassy, dull. Its hardness equals 5.5, and the density is 1.9-2.3.

*Origin.* Opal is a typical mineral of the weathering crust, but it can also be of hydrothermal origin. It is formed in the amygdules of effusive rocks and in connection with the activity of geysers and hot springs, depositing siliceous sinters (geyserites). Large masses of opal matter have a biogenic origin as a result of the living activity of organisms that have a siliceous skeleton (diatomite, tripoli).

*Deposits.* The best deposits of noble opal are found in Australia, Hungary, and Czechoslovakia. There are diatomite deposits in Georgia, and those of tripoli in the Volga River district, the Kaluga and Kursk regions.

*Practical use.* Noble opal is a precious stone. Diatomite and tripoli are used in construction, and in abrasive industry for heat insulation and other purposes.

#### Complex

##### PEROVSKITE $\text{Ca}[\text{TiO}_3]$ (58.9% of $\text{TiO}_2$ )

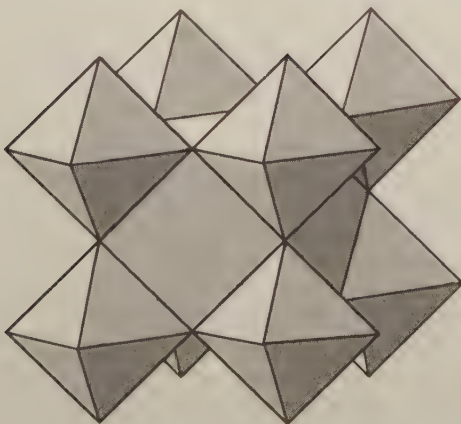
This mineral contains the impurities of Nb, Th, Fe, Ta, and TR. Its crystalline structure represents a framework comprising  $\text{TiO}_6$ -octahedrons with common apexes; the  $\text{Ti}^{4+}$  ions are located in the nodes of the primitive cubic cell, in the centre of which there is the  $\text{Ca}^{2+}$  ion with coordination number 12 (Fig. 90).

The system is cubic. It is usually found in the form of crystals of cubic habit, more seldom in massive masses.

The colour is black, reddish-brown to yellowish-orange. The streak is grey. The lustre is adamantine to submetallic, and sometimes dull. The cleavage is imperfect; the fracture is uneven. Perovskite is brittle, its hardness equals 5.5-6, and the density is approximately 4.

*Varieties.* *Dysanalyte* contains up to 26%

Fig. 90. Perovskite structure



of  $\text{Nb}_2\text{O}_5$ . There are up to 8% of  $\text{TR}_2\text{O}_3$  in *knopite*. The composition of perovskite is close to that of *loparite* ( $\text{Ca}$ ,  $\text{Na}$ ,  $\text{Ce}$ )  $(\text{Ti}, \text{Nb})_2\text{O}_6$  which is often found in the form of penetration twins according to the fluorite law.

*Origin*. 1. The magmatic origin is exemplified by the accessory mineral of ultrabasic and alkaline rocks, which is characteristic of carbonatites and alkaline pegmatites. 2. The contact-metasomatic origin is associated with garnet, pyroxene, vesuvianite, chlorite, sphene, etc. *Deposits*. In the USSR, the mineral is deposited in the skarns of the Shishim and Nazyam Mountains in the Urals, in the carbonatites of Vuoriyarvi (the Northern Karelia); the deposits of loparite are situated in the alkaline rocks and pegmatites of the Kola peninsula.

*Practical use*. In large accumulation perovskite is a valuable raw material of  $\text{Ti}$ ,  $\text{Nb}$ ,  $\text{Ta}$ ,  $\text{TR}$ ,  $\text{Th}$ , etc.

**PYROCHLORE**  $\text{NaCa}[\text{Nb}_2\text{O}_6(\text{OH},\text{F})]$  and **MICROLITE**  $\text{NaCa}[\text{Ta}_2\text{O}_6(\text{OH},\text{F})]$

are the extreme members of the continuous isomorphic series. Their composition is markedly inconsistent. Besides the elements given in the formulae, they contain  $\text{TiO}_2$  (up to 13%),  $\text{UO}_2$  (up to 11%),  $\text{UO}_3$  (up to 15%), rare earths (up to 13%), etc. The crystalline structure is analogous to the structure of fluorite, in which one part of the smallest cubes is occupied by  $\text{Na}$  and  $\text{Ca}$  ions and the other part is filled with the octahedrons with  $\text{Nb}$  and  $\text{Ta}$ , thus forming the frame pattern.

The system is cubic. The crystals are of octahedral shape, and are also found in the form of disseminated grains.

The colour of pyrochlore ranges from reddish-brown to black. It is found in light-yellow to brown for microlite. The lustre is glassy to adamantine. The hardness is 5-5.5, and the density is 4.2-4.6. Microlite is found in octahedral crystals that are small in size (hence, the origin of the name). It is of rarer occurrence than pyrochlore.

*Origin*. Pyrochlore is found in alkaline pegmatites and carbonatites in association with microcline, zircon, ilmenite, aegirine, titanite, magnetite, and other minerals. Microlite is common in granite pegmatites together with albite, spodumene, rubellite, and lepidolite.

*Practical use*. When their accumulations are considerable, the two minerals have a practical significance as an important ore of niobium, tantalum and uranium.

## Silicates and Alumosilicates

Silicates, alumosilicates and their analogues constitute the most copious class of minerals. They represent compounds of silicates, alumosilicates and other anion radicals with cations, among which the species-forming are:  $\text{Al}$ ,  $\text{Fe}$ ,  $\text{Mg}$ ,  $\text{Mn}$ ,  $\text{Ca}$ ,  $\text{Na}$ ,  $\text{K}$ , as well as  $\text{Li}$ ,  $\text{B}$ ,  $\text{Be}$ ,  $\text{Ti}$ ,  $\text{Zr}$ ,  $\text{TR}$ ,  $\text{Cs}$ ,  $\text{Sr}$ ,  $\text{Y}$ ,  $\text{Zn}$ ,  $\text{Cu}$ , etc. The composition of anion radicals includes besides  $\text{Si}$  and  $\text{Al}$  also  $\text{Ti}$ ,  $\text{Zr}$ ,  $\text{Be}$ ,  $\text{B}$ ,  $\text{Fe}^{3+}$ . The function of additional anions is undertaken by the groups  $(\text{OH})^-$ ,  $\text{F}^-$ ,  $\text{O}^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{Cl}^-$ ,  $[\text{BO}_3]^{3-}$ , as well as  $[\text{CO}_3]^{2-}$ ,  $[\text{SO}_4]^{2-}$ , etc. Besides the composition of some minerals pertaining to the class of silicates includes crystallized, zeolite, interlayered and adsorbent water.

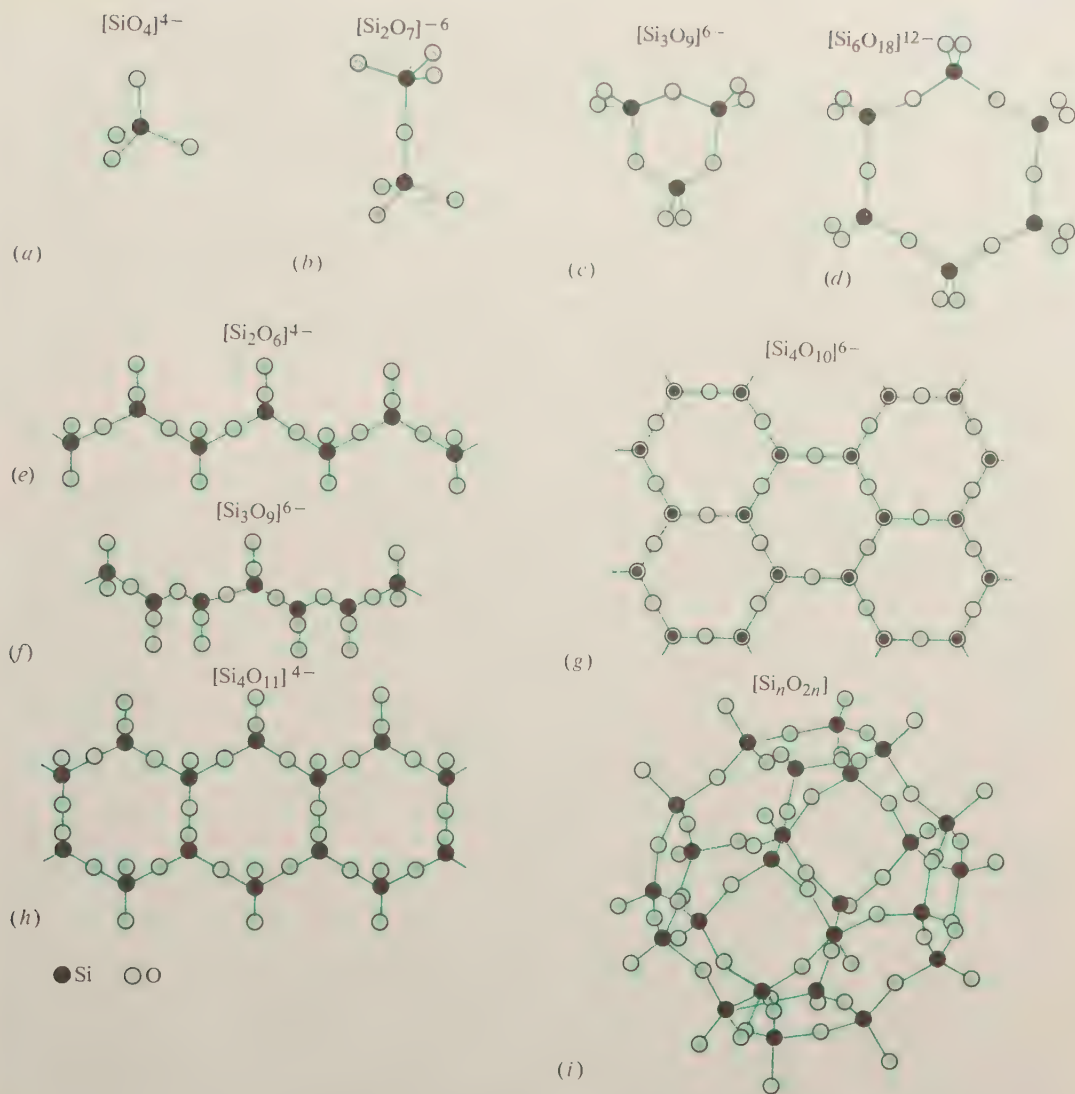


Fig. 91. Types of jointing of silicon-oxygen tetrahedrons in silicates: *a*—single tetrahedron; *b*—paired tetrahedra; *c*—threefold and *d*—sixfold tetrahedral rings; *e*—binary and *f*—ternary single chains of tetrahedrons; *g*—paired chain (ribbon) of tetrahedrons; *h*—hexagonal net (layer) of tetrahedrons; *i*—volumetric framework of tetrahedrons

Silicates are distinguished by a complex chemical composition and wide isomorphous replacements of isovalent as well as heterovalent type in both the cation and the anion parts. Isovalent isomorphous replacements in silicates can be exemplified by the pair  $\text{Mg}^{2+}-\text{Fe}^{2+}$  in olivine,  $\text{Al}^{3+}-\text{Fe}^{3+}$  in garnet,  $\text{Ca}^{2+}-\text{Mn}^{2+}$  in wollastonite. The heterovalent isomorphism among cations is usually accompanied by analogous replacements among anions, as is the case with plagioclases. Wide isovalent replacements among additional  $(\text{OH})^-$  and  $\text{F}^-$  anions are characteristic, for example, of topaz, a large number of micas, etc.

In silicates and their analogues the prevalent bonds are those of  $Sp^3$  within the limits of anion radicals  $[\text{SiO}_4]^{4-}$  and, substantially, the ionic bonds between cations and anions. In minerals, containing  $(\text{OH}^-)$  and  $\text{H}_2\text{O}$  groups, the hydrogen type of bond is also present.

The following structural classification of silicates, and aluminosilicates is based on the kind of combination that exists between silica- and aluminosilicates tetrahedrons (Fig. 91).

1. *Silicates of island structure* (nesosilicates) with isolated tetrahedrons and isolated groups of tetrahedrons. Among them the following are distinguished:

(a) nesosilicates have silica-oxygenous tetrahedrons  $[\text{SiO}_4]^{4-}$  (Fig. 91a), in which each of four atoms of oxygen has one free charge; among themselves the tetrahedrons are directly not connected. The association takes place through cations;

(b) sorosilicates have paired tetrahedrons  $[\text{Si}_2\text{O}_7]^{6-}$  (Fig. 91b); they have one common atom of oxygen; the others are connected with cations;

(c) cyclosilicates, consisting of three, four, six silica-oxygenous tetrahedrons  $[\text{Si}_3\text{O}_9]^{6-}$ ,  $[\text{Si}_4\text{O}_{12}]^{8-}$ ,  $[\text{Si}_6\text{O}_{18}]^{12-}$  (Fig. 91c and d).

2. *Silicates of chain structure* (inosilicates) consisting of simple chains of silica-oxygenous tetrahedrons  $[\text{Si}_2\text{O}_6]^{4-}$ ,  $[\text{Si}_3\text{O}_9]^{6-}$  and others, with a different cycle of recurrence (Fig. 91e and f), and paired chains, or ribbons, comprising silica-oxygenous tetrahedrons of the type  $[\text{Si}_4\text{O}_{11}]^{6-}$  (Fig. 91g). In some minerals  $\text{Si}^{4+}$  is replaced by  $\text{Al}^{3+}$  which leads to the formation of aluminosilicate radicals of the type  $[(\text{Si}, \text{Al})_4\text{O}_{11}]^{6-}$ .

3. *Silicates and aluminosilicates of layered structure* (phyllosilicate) have silica-oxygenous and aluminosilicate layers  $[\text{Si}_4\text{O}_{10}]^{4-}$  and  $[\text{Si}_{4-p}\text{Al}_p\text{O}_{10}]^{(4+p)-}$ , in which the tetrahedrons are connected by three common apexes (Fig. 91h).

4. *Aluminosilicates of frame structure* (tectosilicates) with continuous three-dimensional frame of aluminosilicate and silica-oxygenous tetrahedrons  $[\text{AlO}_4]^{5-}$  and  $[\text{SiO}_4]^{4-}$ , in which all oxygen atoms are common (Fig. 91i). In aluminosilicates with frame structure the sum of  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  ions is always twice smaller than the number of oxygen ions, while the number of aluminosilicate tetrahedrons cannot exceed half of the silica-oxygenous tetrahedrons. Thus conditioned, the formula of aluminosilicate-oxygenous radicals finds the expression:  $[\text{Si}_{n-p}\text{Al}_p\text{O}_{2n}]^{p-}$ . When  $p=0$ , we have the electrostatically neutral silica-oxygenous framework  $[\text{Si}_n\text{O}_{2n}]$ , which corresponds only to silicon oxides, as is the case with quartz. When  $p > 0$ , there emerge excessive negative charges in the framework, which are compensated at the expense of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and other large cations, occupying the cavities in the frame structure.

The inner structure and the chemical composition of silicates are reflected in their form and physical properties. Thus, silicates, the structure of which is represented by isolated silica-oxygenous tetrahedrons, often have an isometric form (garnets). The structure of hexagonal-prismatic beryl is characterized by the six-fold rings of  $[\text{Si}_6\text{O}_{18}]^{12-}$ . In the structure of pyroxenes, which often form elongated-prismatic crystals, the chains of silica-oxygenous radicals  $[\text{Si}_2\text{O}_6]^{4-}$  are connected by zigzag octahedral chains (Fig. 92a). For other silicates, e.g. epidote, vesuvianite and others, the elongated-and-prismatic form of crystals is accounted for by the leading structural role played by large cations of calcite, forming continuous polyhedral columns, to which the dimensionally corresponding paired

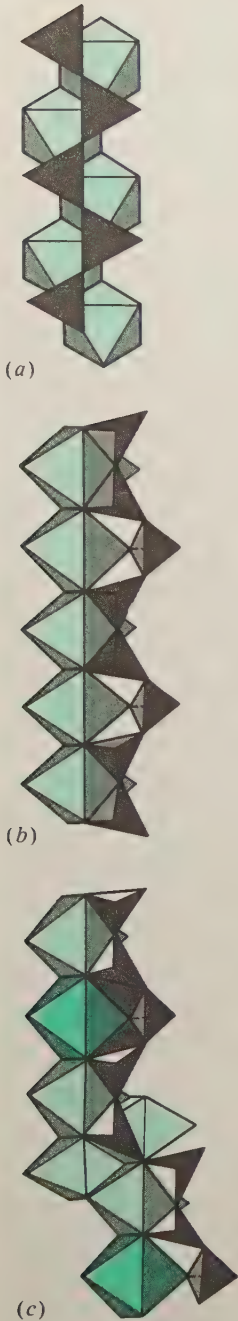


Fig. 92. Types of tetrahedral silicon-oxygen chains and the character of their jointing with

cation polyhedrons in pyroxenes (a), wollastonite (b), and rhodonite (c)

silica-oxygenous radicals  $[\text{Si}_2\text{O}_7]^{6-}$  are only 'being accustomed'. According to N.V. Belov, the structural function performed by large cations opens the second chapter of crystallochemistry of silicates, thus making it possible to explain, for example, the periodicity of silica-oxygenous chains in wollastonite  $\text{Ca}_3[\text{Si}_3\text{O}_9]$  (Fig. 92b), rhodonite  $\text{Ca}_4\text{Mn}[\text{Si}_5\text{O}_{15}]$  (Fig. 92c) and other pyroxenoids.

In phyllosilicates (micas, talc, chlorites) the interatomic bonds within the limits of the layers of silica-oxygenous tetrahedrons are extremely stable, which cannot be said of the bonds between the layers. This is the reason why it is easy to split and destroy these minerals along the longitude of the layers, the fact which is conditioned by their characteristic perfect cleavage. Phyllosilicates are distinguished by the lowest degree of hardness, which decreases regularly beginning with aluminosilicates with the ionic type of chemical bond (micas) up to silicates with van-der-Waals and hydrogen bonds (chlorites, talc, clays).

The colour of silicates is basically of chromophore nature. Prevalence is allotted here to the ions of iron and manganese, while those of chromium, nickel and copper play the least part. The colour of some silicates is conditioned by the defective centres of colouring. The allochromatic colouring is, in most cases, connected with the inclusions of dark-coloured minerals. The density of silicates depends on the density of packing (the island silicates are heavier than those with the frame structure), as well as on the atomic mass of cations and the content of water.

The origin of most of the silicates is endogenic, mainly magmatic (olivine, pyroxenes, feldspars). They are also characteristic of pegmatites (micas, tourmaline, beryl, etc.), skarns (garnets, wollastonite and others), greisens and hydrothermal veins (micas, topaz, feldspars). Silicates are widely spread in metamorphic rocks, e.g. in schists and gneisses (garnets, disthene, chlorite, etc.). Silicates of the exogenetic origin usually represent the products of weathering or the change of primary (initial) (endogenic) minerals (kaolinite, glauconite) and compose huge masses of sedimentary rocks.

Silicates are important nonmetallic mineral resources (ceramic and refractory raw materials, construction, thermal and insulating materials). Silicates are also ores of beryllium, lithium, caesium, zirconium, nickel, zinc, and rare earths. Besides, they include a large number of precious and semi-precious stones (emerald, aquamarine, topaz, nephrite, rhodonite, etc.)

The number of mineral species of silicates is approximately 800. As far as their distribution is concerned, silicates constitute 75% of all the minerals of the lithosphere. This is accounted for by the fact that silicates and aluminosilicates are the most important species-forming minerals, of which the bulk of rocks is composed (feldspars, quartz, micas, hornblende, pyroxenes, olivine, etc.). Among them feldspars are the most widely spread in nature.

## Systematization

### Silicates of Island Structure

Silicates with Isolated Tetrahedrons  $[\text{SiO}_4]^{4-}$   
(Orthosilicates or Nesosilicates)

#### Simple

*The group of phenacite*  
(hexagonal-R)  
*The group of olivine*  
(orthorhombic)  
*The group of zircon*  
(tetragonal)

phenacite  $\text{Be}_2[\text{SiO}_4]$ ,  
willemite  $\text{Zn}_2[\text{SiO}_4]$ .  
FORSTERITE  $\text{Mg}_2[\text{SiO}_4]$ ,  
FAYALITE  $\text{Fe}_2[\text{SiO}_4]$ .  
ZIRCON  $\text{Zr}[\text{SiO}_4]$ ,  
THORITE  $\text{Th}[\text{SiO}_4]$ .

#### Complex

*The family of garnets*  
(cubic)

ugrandites  
GROSSULAR  $\text{Ca}_3\text{Al}_2[\text{SiO}_4]_3$ ,  
ANDRADITE  $\text{Ca}_3\text{Fe}_2[\text{SiO}_4]_3$ ,  
UVAROVITE  $\text{Ca}_3\text{Cr}_2[\text{SiO}_4]_3$ ,  
pyralspites  
ALMANDINE  $\text{Fe}_3\text{Al}_2[\text{SiO}_4]_3$ ,  
SPESSARTINE  $\text{Mn}_3\text{Al}_2[\text{SiO}_4]_3$ ,  
PYROPE  $\text{Mg}_3\text{Al}_2[\text{SiO}_4]_3$ .

#### With Additional Anions

*The group of titanite*

TITANITE  $\text{CaTi}[\text{SiO}_4]\text{O}$  (monoclinic),  
malayite  $\text{CaSn}[\text{SiO}_4]\text{O}$  (monoclinic).

*The group of topaz*

TOPAZ  $\text{Al}_2[\text{SiO}_4](\text{F}, \text{OH})_2$  (orthorhombic),  
euclase  $\text{BeAl}[\text{SiO}_4](\text{OH})_2$  (monoclinic).

*The family of disthene-andalusite*

DISTHENE  $\text{Al}_2[\text{SiO}_4]\text{O}$  (triclinic),  
ANDALUSITE  $\text{AlAl}[\text{SiO}_4]\text{O}$  (orthorhombic),  
SILLIMANITE  $\text{Al}[\text{SiAlO}_5]$  (orthorhombic),

*The group of chloritoid*

STAUROLITE  $\text{FeAl}_4[\text{SiO}_4]_2\text{O}_2(\text{OH})_2$  (orthorhombic).  
chloritoid  $(\text{Fe}, \text{Mg})_2(\text{Al}, \text{Fe}^{3+})\text{Al}_3[\text{SiO}_4]\text{O}_2(\text{OH})_4$  (monoclinic).

*The group of dumortierite*

dumortierite  $(\text{Al}, \text{Fe})_7[\text{SiO}_4]_3[\text{BO}_3](\text{O}, \text{OH})_3$  (orthorhombic).

*The group of chondrodite*

chondrodite  $\text{Mg}_5[\text{SiO}_4]_2\text{F}_2$  (monoclinic),  
humite  $\text{Mg}_7[\text{SiO}_4]_3\text{F}_2$  (orthorhombic).

Silicates with Double Tetrahedrons  $[\text{Si}_2\text{O}_7]^{6-}$   
(Diorthosilicates or Sorosilicates)

#### With Additional Anions

*The group of bertrandite*

bertrandite  $\text{Be}_4[\text{Si}_2\text{O}_7](\text{OH})_2$  (orthorhombic).

*The group of ilvaite*

ilvaite  $\text{CaFe}_2^+\text{Fe}^{3+}[\text{Si}_2\text{O}_7]\text{O}(\text{OH})$  (orthorhombic).

#### Aquatic

*The group of hemimorphite*

HEMIMORPHITE  $\text{Zn}_4[\text{Si}_2\text{O}_7](\text{OH}_2) \cdot \text{H}_2\text{O}$  (orthorhombic).

Silicates with Isolated and Double Tetrahedrons  
 $[\text{SiO}_4]^{4-} + [\text{Si}_2\text{O}_7]^{6-}$  (Ortho-Diorthosilicates)

**With Additional Anions**

<i>The group of idocrase</i>	IDOCRASE $\text{Ca}_{10}(\text{Mg}, \text{Fe})_2\text{Al}_4[\text{SiO}_4]_5[\text{Si}_2\text{O}_7]_2(\text{OH})_4$ (tetragonal).
<i>The group of epidote</i>	EPIDOTE $\text{Ca}_2(\text{Fe}, \text{Al})\text{Al}_2[\text{SiO}_4][\text{Si}_2\text{O}_7]\text{O}(\text{OH})$ (monoclinic), ZOISITE $\text{Ca}_2\text{Al}_3[\text{SiO}_4][\text{Si}_2\text{O}_7]\text{O}(\text{OH})$ (orthorhombic), ORTHITE $\text{Ca}(\text{Ca}, \text{Ce})(\text{Al}, \text{Fe})\text{Al}_2[\text{SiO}_4][\text{Si}_2\text{O}_7]\text{O}(\text{OH})$ (monoclinic), piemontite $\text{Ca}_2\text{Mn}_2\text{Al}[\text{SiO}_4][\text{Si}_2\text{O}_7]\text{O}(\text{OH})$ (monoclinic).
<i>The group of lamprophyllite</i>	lamprophyllite $\text{SrNa}_3\text{Ti}_3[\text{Si}_2\text{O}_7]_2\text{O}_2\text{F}$ (monoclinic), rinkolite (lovchorrite) $\text{Na}_2\text{Ca}_4\text{CeTi}[\text{Si}_2\text{O}_7]_2\text{F}_3$ (monoclinic).

Silicates with Isolated Rings of Tetrahedrons  
 $[\text{Si}_6\text{O}_{18}]^{12-}$ ,  $[\text{Si}_8\text{B}_2\text{O}_{30}(\text{OH})_2]^{24-}$ , etc. (Cyclosilicates)

**Complex**

<i>The group of beryl</i>	BERYL $\text{Be}_3\text{Al}_2[\text{Si}_6\text{O}_{18}]$ (hexagonal), CORDIERITE $(\text{Mg}, \text{Fe})_2\text{Al}_3[\text{Si}_5\text{AlO}_{18}]$ (orthorhombic), indialite $(\text{Mg}, \text{Fe})_2\text{Al}_3[(\text{Si}, \text{Al})_6\text{O}_{18}]$ (hexagonal).
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**With Additional Anions**

<i>The group of tourmaline</i> (hexagonal-R)	SHORL $(\text{Na}, \text{Ca})\text{Fe}_3(\text{Al}, \text{Fe})_6[\text{Si}_6\text{O}_{18}][\text{BO}_3]_3(\text{OH}, \text{F})_4$ , DRAVITE $\text{NaMg}_3(\text{Al}, \text{Fe})_6[\text{Si}_6\text{O}_{18}][\text{BO}_3]_3(\text{OH}, \text{F})_4$ , ELBAITE $\text{Na}(\text{Li}, \text{Al})_3\text{Al}_6[\text{Si}_6\text{O}_{18}][\text{BO}_3]_3(\text{OH}, \text{F})$ .
<i>The group of axinite</i>	axinite $\text{Ca}_4(\text{Fe}, \text{Mn})_2\text{Al}_4[\text{Si}_8\text{B}_2\text{O}_{30}(\text{OH})_2]$ (triclinic).

**Aquatic**

<i>The group of diopside</i>	DIOPTASE $\text{Cu}_6[\text{Si}_6\text{O}_{18}] \cdot 6\text{H}_2\text{O}$ (hexagonal-R).
<i>The group of eudialyte</i>	eudialyte $(\text{Na}, \text{Ca})_9(\text{Zr}, \text{Ti}, \text{Mn})[\text{Si}_3][\text{Si}_9\text{O}_{24}](\text{OH})_3$ (hexagonal-R).

**Silicates of Chain Structure (Inosilicates)**

Silicates with Single Chains of Tetrahedrons  $[\text{Si}_2\text{O}_6]^{4-}$   
 (Pyroxenes)

**Simple (orthopyroxenes)**

<i>The group of enstatite</i> (pseudoorthorhombic)	ENSTATITE $\text{Mg}_2[\text{Si}_2\text{O}_6]$ , HYPERSTHENE $(\text{Mg}, \text{Fe})_2[\text{Si}_2\text{O}_6]$ , ferrosilite $\text{Fe}_2[\text{Si}_2\text{O}_6]$ .
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**Complex (clinopyroxenes)**

<i>The group of diopside</i> (monoclinic)	DIOPSIDE $\text{CaMg}[\text{Si}_2\text{O}_6]$ , HEDENBERGITE $\text{CaFe}[\text{Si}_2\text{O}_6]$ , johannsenite $\text{CaMn}[\text{Si}_2\text{O}_6]$ , AUGITE $(\text{Ca}, \text{Na})(\text{Mg}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al})[(\text{Si}, \text{Al})_2\text{O}_6]$ .
<i>The group of aegirine</i> (monoclinic)	AEIRINE $\text{NaFe}^{3+}[\text{Si}_2\text{O}_6]$ , jadeite $\text{NaAl}[\text{Si}_2\text{O}_6]$ , SPODUMENE $\text{LiAl}[\text{Si}_2\text{O}_6]$ .

Silicates with Single Chains of Tetrahedrons  
 $[\text{Si}_3\text{O}_9]^{6-}$ ,  $[\text{Si}_5\text{O}_{15}]^{10-}$ , etc. (Pyroxenoids)

*The group of  
wollastonite  
The group of  
rhodonite*

WOLLASTONITE  $\text{Ca}_3[\text{Si}_3\text{O}_9]$  (triclinic).

RHODONITE  $\text{CaMn}_4[\text{Si}_5\text{O}_{15}]$  (triclinic).

Silicates with Double Chains of Tetrahedrons  
 $[\text{Si}_4\text{O}_{11}]^{6-}$  (Amphiboles)

**With Additional Anions**

*The group of  
anthophyllite  
(orthorhombic)*

anthophyllite  $\text{Mg}_7[\text{Si}_4\text{O}_{11}]_2(\text{OH})_2$ ,  
 gedrite  $(\text{Mg, Fe, Al})[(\text{Si, Al})_4\text{O}_{11}]_2(\text{OH, F})_2$ .

*The group of  
actinolite  
(monoclinic)*

TREMOLITE  $\text{Ca}_2\text{Mg}_5[\text{Si}_4\text{O}_{11}]_2(\text{OH})_2$ ,  
 ACTINOLITE  $\text{Ca}_2\text{Fe}_5[\text{Si}_4\text{O}_{11}]_2(\text{OH})_2$ .

*The group of horn-  
blende (monoclinic)*

HORNBLLENDE  $(\text{Ca, Na})(\text{Mg, Fe})_4(\text{Al, Fe})[(\text{Si, Al})_4\text{O}_{11}]_2(\text{OH})_2$ ,  
 ferrohastingsite  $\text{NaCa}_2\text{Fe}_2^+(\text{Al, Fe}^{3+})[\text{Si}_3\text{AlO}_{11}]_2(\text{OH, F})_2$ .

*The group of  
alkaline amphiboles  
(monoclinic)*

ARFVEDSONITE  $\text{Na}(\text{Ca, Na})(\text{Fe, Mg, Fe, Al})[(\text{Al, Si})_4\text{O}_{11}]_2(\text{OH, F})_2$ ,  
 GLAUCOPHANE  $\text{NaNaMg}_3\text{Al}_2[\text{Si}_4\text{O}_{11}]_2(\text{OH, F})_2$ ,  
 RIEBECKITE  $\text{NaNaFe}_3^+\text{Fe}_2^+[\text{Si}_4\text{O}_{11}]_2(\text{OH, F})_2$ .

Silicates with Complicated Chains of Tetrahedrons  
 $[\text{Si}_4\text{O}_{12}]^{8-}$ ,  $[\text{Si}_8\text{O}_{20}]^{8-}$ ,  $[\text{Si}_{12}\text{O}_{30}]^{12-}$

**With Additional Anions**

*The group of  
astrophyllite*

astrophyllite  $\text{K}_3(\text{Fe, Mn})_7\text{Ti}_2[\text{Si}_4\text{O}_{12}]\text{O}_2(\text{OH})_5$ .

**Aquatic**

*The group of  
palygorskite  
(monoclinic)*

palygorskite  $\text{Mg}_2\text{Al}_2[\text{Si}_8\text{O}_{20}](\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ,  
 sepiolite  $\text{Mg}_8[\text{Si}_{12}\text{O}_{30}](\text{OH})_4 \cdot 12\text{H}_2\text{O}$ ,  
 charoite  $\text{K}_2\text{NaCa}_5[\text{Si}_{12}\text{O}_{30}](\text{OH, F}) \cdot 3\text{H}_2\text{O}$ .

**Silicates and Aluminosilicates of the Layered Structure (Phyllosilicates)**

Silicates with Two-Layered Packages

**With Additional Anions**

*The group of  
serpentine  
(monoclinic)*

SERPENTINE  $\text{Mg}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$ .

*The family of  
kaolinite  
(monoclinic)*

KAOLINITE  $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$ ,  
 dickite  $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$ ,  
 nacrite  $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$ ,

**Aquatic**

*The group of  
halloysite*

HALLOYSITE  $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8 \cdot 4\text{H}_2\text{O}$  (monoclinic).  
 Allophane  $m\text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot p\text{H}_2\text{O}$  (amorphous).



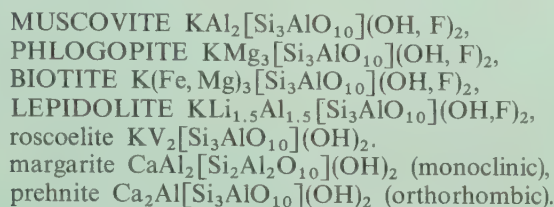
## Silicates and Aluminosilicates with Three-Layered Packages

**With Additional Anions**

*The group of talc-pyrophyllite*  
(monoclinic)



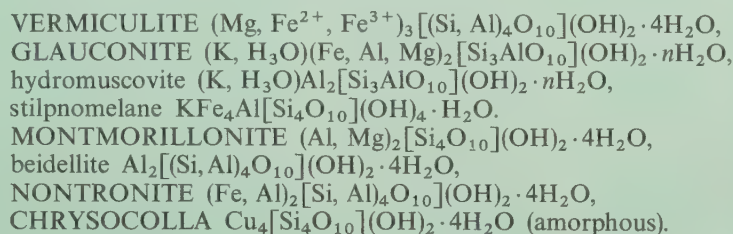
*The family of micas*  
(monoclinic)



*The group of margarite*

**Aquatic**

*The family of hydro-micas* (monoclinic)

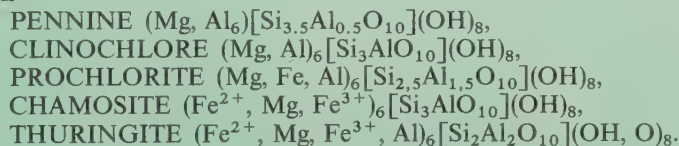


*The family of montmorillonite*  
(monoclinic)

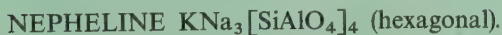
## Silicates and Aluminosilicates with Multilayered Packages

**With Additional Anions**

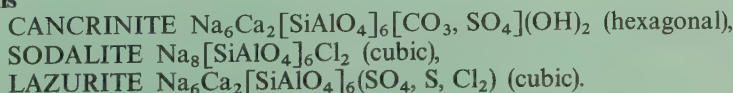
*The family of chlorites*  
(monoclinic)

**Aluminosilicates and Their Analogues of the Frame Structure (Tectosilicates)**Aluminosilicates with Radicals  $[SiAlO_4]^-$  (Feldspathoids)**Complex**

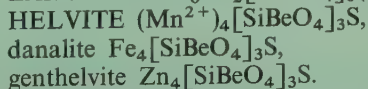
*The group of nepheline*

**With Additional Anions**

*The family of cancrinite*



*The group of helvite*  
(cubic)



	Alumosilicates with Radicals $[\text{Si}_2\text{AlO}_6]^-$
<b>Simple</b>	
<i>The group of leucite</i>	LEUCITE $\text{K}[\text{Si}_2\text{AlO}_6]$ (pseudocubic).
<b>Aquatic</b>	
<i>The group of analcite</i> (pseudocubic)	ANALCITE $\text{Na}[\text{Si}_2\text{AlO}_6] \cdot \text{H}_2\text{O}$ , POLLUCITE $\text{Cs}_{1-n}\text{Na}_n[\text{Si}_2\text{AlO}_6] \cdot n\text{H}_2\text{O}$ .

	Alumosilicates with Radicals $[\text{Si}_3\text{AlO}_8]^-$ , $[\text{Si}_2\text{Al}_2\text{O}_8]^{2-}$ , $[\text{Si}_2\text{B}_2\text{O}_8]^{2-}$ , etc.
<b>Simple (feldspars)</b>	
<i>The group of K-Na-feldspars</i>	SANIDINE (K, Na) $[\text{Si}_3\text{AlO}_8]$ (monoclinic), ORTHOCLASE (K, Na) $[\text{Si}_3\text{AlO}_8]$ (monoclinic), MICROCLINE (K, Na) $[\text{Si}_3\text{AlO}_8]$ (triclinic).
<i>The group of plagioclase</i> (triclinic)	ALBITE $\text{Na}[\text{Si}_3\text{AlO}_8]$ , ANORTHITE $\text{Ca}[\text{Si}_2\text{Al}_2\text{O}_8]$ , CELSIAN $\text{Ba}[\text{Si}_2\text{Al}_2\text{O}_8]$ .
<i>The group of danburite</i>	danburite $\text{Ca}[\text{Si}_2\text{B}_2\text{O}_8]$ (orthorhombic), datolite $\text{Ca}_2[\text{Si}_2\text{B}_2\text{O}_8(\text{OH})_2]$ (monoclinic).
<b>With Additional Anions (scapolites)</b>	
<i>The group of scapolite</i> (tetragonal)	MARIALITE $\text{Na}_4[\text{Si}_3\text{AlO}_8]_3\text{Cl}$ , MEIONITE $\text{Ca}_4[\text{Si}_2\text{Al}_2\text{O}_8]_3(\text{Cl}, \text{CO}_3, \text{SO}_4)$ .

	Alumosilicates with Radicals $[\text{Si}_3\text{Al}_2\text{O}_{10}]^{2-}$ , $[\text{Si}_4\text{Al}_2\text{O}_{12}]^{2-}$ , etc.
<b>Aquatic (zeolites)</b>	
<i>The group of natrolite</i> (orthorhombic)	NATROLITE $\text{Na}_2[\text{Si}_3\text{Al}_2\text{O}_{10}] \cdot 2\text{H}_2\text{O}$ , SCOLECITE $\text{Ca}[\text{Si}_3\text{Al}_2\text{O}_{10}] \cdot 3\text{H}_2\text{O}$ , mesolite $\text{Na}_2\text{Ca}_2[\text{Si}_3\text{Al}_2\text{O}_{10}]_3 \cdot 8\text{H}_2\text{O}$ .
<i>The group of laumontite</i>	laumontite $\text{Ca}[\text{Si}_4\text{Al}_2\text{O}_{12}] \cdot 4\text{H}_2\text{O}$ (monoclinic).
<i>The group of chabasite</i>	chabasite $(\text{Ca}, \text{Na}_2)[\text{Si}_4\text{Al}_2\text{O}_{12}] \cdot 6\text{H}_2\text{O}$ (hexagonal-R), gmelinite $(\text{Na}, \text{Ca})[\text{Si}_4\text{Al}_2\text{O}_{12}] \cdot 6\text{H}_2\text{O}$ (hexagonal).
<i>The group of heulandite</i> (monoclinic)	heulandite (clinoptilolite) $\text{Ca}[\text{Si}_7\text{Al}_2\text{O}_{18}] \cdot 6\text{H}_2\text{O}$ , desmine (stilbite) $(\text{Ca}, \text{Na}_2)[\text{Si}_7\text{Al}_2\text{O}_{18}] \cdot 7\text{H}_2\text{O}$ .
<i>The group of mordenite</i>	mordenite (ptilolite) $(\text{Na}_2, \text{Ca})[\text{Si}_{10}\text{Al}_2\text{O}_{24}] \cdot 7\text{H}_2\text{O}$ (orthorhombic).

## Silicates of Island Structure

Silicates with Isolated Tetrahedrons  $[\text{SiO}_4]^{4-}$   
(Orthosilicates or Nesosilicates)

### Simple

FORSTERITE  $\text{Mg}_2[\text{SiO}_4]$  and FAYALITE  $\text{Fe}_2[\text{SiO}_4]$  are the extreme members of the isomorphic series of *olivine* ( $\text{Mg}, \text{Fe}$ ) $[\text{SiO}_4]$ . They contain the impurities of Co, Ni, and others. The

crystalline structure resembles a closest hexagonal packing, in which the octahedral polyhedron of the two types  $M_1$  and  $M_2$  with Mg and Fe cations are distributed in the form of zigzag chains, bounded by isolated tetrahedrons  $[\text{SiO}_4]^{4-}$  (Fig. 93).

The system is orthorhombic. They are distributed in the form of granular masses and associated crystals.

The colour is yellow-green, olive-green (which accounts for the name of the mineral), however, the content can cause a change in the colour from light-yellow to dark-green and black. The black colour of olivine is conditioned by the development of serpentine along numerous microfissures. The lustre is glassy. Hardness equals 6.5-7. The cleavage is medium. The fracture is conchoidal. The density is 3.2-3.5 (depending on the composition). Olivine is easily decomposed in acids, even that of vinegar, with the segregation of jellied silica.

*Varieties.* The yellowish-green transparent olivine is called *chrysolite*.\* *Origin.* The origin is magmatic. The mineral is formed when the ultrabasic magma, poor in silica and alumina, is crystallized. It is one of the most important minerals of the ultrabasic rocks: dunitites are almost completely composed of olivine, in peridotites it is found together with pyroxene, chromite, magnetite, platinum, and also in gabbro, basalts, and kimberlites together with pyroxene, the basic plagioclases. It is presumed that olivine in the mantle is not stable, and is represented by a more dense spinel-like modification.

Forsterite is formed in magnesite skarns together with other magnesian minerals: spinel, periclase, phlogopite, tremolite, etc. It is usual for olivine to be replaced by serpentine, and at its expense talc and chrysotile-asbestos are formed. When olivine rocks are decomposed, there is a development of magnesian layered silicates enriched with nickel, iron hydroxides containing cobalt, magnesite, opal within the crusts of the weathering.

Rocks, containing olivine, are widely spread. In the USSR, they are known in the Urals, Karelia, the Eastern Sayan, in Kamchatka, and elsewhere.

*Practical use.* The olivine rocks with a small amount of iron, can be of practical significance as a refractory raw material. Chrysolite is used as a precious stone.

#### ZIRCON $\text{Zr}[\text{SiO}_4]$

In the form of isomorphic impurities it contains Hf, Th, and TR. In the crystalline structure the isolated  $[\text{SiO}_4]$  tetrahedrons are connected by common edges with the octoapicals, in the centre of which the  $\text{Zr}^{4+}$  ions are situated.

The system is tetragonal. The mineral is usually found in the form of properly developed crystals. Tetragonal prisms and dipyrramids are the most developed of the simple forms.

The colour is golden, yellow, brown, and grey. The lustre is adamantine. A high degree of hardness (7.5-8) and a considerable density (4.7) are found to be characteristic of this mineral. The cleavage here is absent.

\* This green mineral, recovered from the placers in the Urals is actually none other than demantoid, or garnet.

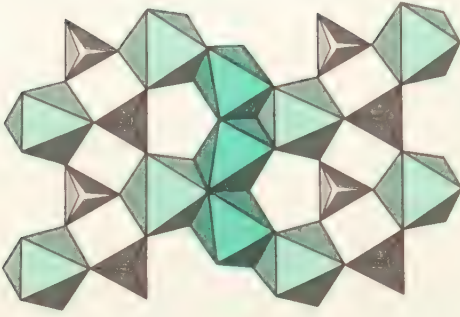


Fig. 93. The crystalline structure of olivine in polyhedral representation in projection to  $\{100\}$ ; green colour here shows cations in the octahedral position of  $M_1$ , while light green is used to indicate the cations in position  $M_2$



Fig. 94. Zircon crystals of dipyramidal form comprising alkaline pegmatites (the Urals). Twice the natural size

*Varieties.* The transparent variety of zircon is called *hyacinth*. The metamict variety is known as *malacon*.

*Origin.* The origin is magmatic and pegmatitic. As an accessory (secondary) mineral, it is spread in igneous rocks, granites and syenites. Dipyramidal crystals of 1 cm and more are characteristic of alkaline pegmatites (Fig. 94). It is found together with feldspars, apatite, sphene, nepheline, black mica (lepidomelane), the minerals of rare earths, tantalum, niobium and thorium. As a mechanically resilient material zircon is accumulated in placers, wherefrom it is recovered (occasionally together with monazite).

*Deposits.* In the USSR, zircon is found in the alkaline pegmatites in the Urals. In other countries, there are deposits in Brazil, in the USA (Florida), in the island of Sri Lanka, in the pegmatites of Norway and Madagascar.

*Practical use.* Zircon is an ore of the zirconium metal which is used in the production of high-speed steels and armour plates. Zirconium oxide is employed as a highly refractory and acid-resisting material. One of the by-products of zircon is hafnium. Hyacinth is known as a precious stone.

### Complex

#### The Family of Garnets

Garnets comprise complex in their composition orthosilicates of two- or three-valent cations, the general formula of which has the following expression:  $R_3^{2+}R_2^{3+}[\text{SiO}_4]_3$ , where  $R^{2+} = \text{Ca, Mg, Mn, Fe}$ , while  $R^{3+} = \text{Al, Fe, Cr}$ . Two subgroups are singled out among garnets. They are: *ugrandites* with  $R^{2+} = \text{Ca}^{2+}$ , and  $R^{3+} = (\text{Al, Fe}^{3+}, \text{Cr}^{3+})$ , and *pyralspites*, with  $R^{3+} = \text{Al}$  and  $R^{2+} = (\text{Mg, Fe}^{2+}, \text{Mn}^{2+})$ . In the crystalline structure of garnet the isolated  $[\text{SiO}_4]^{4-}$  tetrahedrons are connected by their apexes with the octahedrons of  $R^{3+}$ -cations and by their edges with the  $R^{2+}$ -polyhedrons with eight summits, thus forming a frame motif.

The system is cubic. They are usually found in perfect crystals, e.g. rhombododecahedrons and tetragon-trioctahedrons or the combinations of these forms (Fig. 95). Besides, they form block granular and interflowing masses.

The colour is various (see below). The lustre is glassy. A high degree

of hardness (7-8) and the absence of cleavage are found to be characteristic. The density changes in respect to the composition from 3.4 to 4.3.

*Ugrandites (Calcium Garnets)*

**GROSSULAR**  $\text{Ca}_3\text{Al}_2[\text{SiO}_4]_3$

The colour is light-green, reddish or greenish-brown. It is characteristic of limestone (skarns).

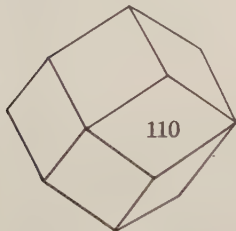
**ANDRADITE**  $\text{Ca}_3\text{Fe}_2[\text{SiO}_4]_3$

The colour is brown to black, red, greenish-brown. The mineral is also found in skarns, more seldom in schists and other rocks. *Demantoid garnet* is a transparent variety of andradite of the green colour (1.5% of  $\text{Cr}_2\text{O}_3$ ). It is precious stone, and is found in the placers of the Nizhni Tagil district in the Urals. *Melanite* is the black variety of andradite, enriched with titanium.

**UVAROVITE**  $\text{Ca}_3\text{Cr}_2[\text{SiO}_4]_3$

The colour is emerald-green. It forms small crystalline crusts on chromite. The mineral is rare. Interesting specimens have been recovered from the Saranovsk deposit of chromite in the Northern Urals.

Fig. 95. Garnet crystals



*Pyrospites (Aluminium Garnets)*

**ALMANDINE**  $\text{Fe}_3\text{Al}_2[\text{SiO}_4]_3$

The colour is red, brown, and purple. It is the most widespread of garnets. It is usually found in crystalline schists and gneisses.

**SPESSARTINE**  $\text{Mn}_3\text{Al}_2[\text{SiO}_4]_3$

The colour is pink, red, and yellowish-brown. The mineral is found in pegmatites and crystalline schists (Eastern Siberia, Karelia).

**PYROPE**  $\text{Mg}_3\text{Al}_2[\text{SiO}_4]_3$

The colour is dark-red. Pyrope occurs in ultrabasic rocks, rich in magnesium and the products of their disintegration. The mineral is characteristic of their diamond-bearing rocks (kimberlites) of Yakutia and SAR.

*Origin.* 1. Metamorphic. Garnets are widely spread and particularly characteristic of metamorphic rocks, such as crystalline schists and gneisses. In crystalline schists garnets, mainly almandine and spessartine, are rock-forming minerals together with micas, disthene and others (micaceous-garnet and other schists). These rocks are known in Eastern Siberia, Karelia, as well as in the Urals.

2. Contact-metasomatic. Contacts with limestones are mainly achieved by grossular and andradite. In skarns garnet is found together with sahlite, hedenbergite, vesuvianite, epidote, scheelite, magnetite, sulphides of iron, copper, lead, and zinc. Skarns, in which garnet is the leading rock-forming mineral are known in Central Asia, in the Northern Caucasus, in Khakasia, the Eastern Sayan, and elsewhere.

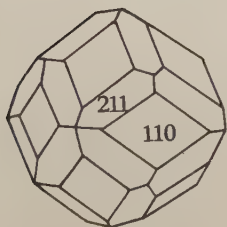


Fig. 96. Titanite crystals



3. Magmatic. In kimberlites garnet is represented by pyrope. Garnets are also found in granites and pegmatitic veins. Under weathering garnets, as chemically resilient minerals, are transformed into placers. *Practical use.* In industry garnets find their application as abrasive material. Transparent red and green crystals of garnet (almandine, pyrope, and andradite) are valued as gems.

#### With Additional Anions

#### TITANITE (sphene) $\text{CaTi}[\text{SiO}_4]\text{O}$

It is sometimes found with the impurities of  $\text{TR}^{3+}$  and Sn. The crystalline structure of sphene has a layered motif, spliced of the columns of  $\text{Ca}^{2+}$ -heptaapicals with common edges and chains of  $\text{Ti}^{4+}$ -octahedrons, interconnected by silicon-oxygen tetrahedrons.

The system is monoclinic. The crystals are wedge-shaped of tabular form, and plane (Fig. 96). Isolated crystals ingrown in feldspar are typical; in cross-section all of them have the form of a flattened rhomb.

The colour is brown, golden, sometimes yellowish, etc. The lustre is adamantine, greasy in the fracture. The cleavage is distinct. The hardness is 5.5, and the density equals 3.5.

*Origin.* Titanite can be of various origin. As an accessory mineral in igneous rocks it has a magmatic origin. Large crystals of titanite (up to several centimetres) are found in pegmatitic veins, particularly of alkaline composition. It associates here with feldspar, hornblende, ilmenite, zircon, and other minerals. It is usual for contacts with limestones (with diopside, apatite, scapolite) and for the metamorphic rocks. In veins of the alpine type it forms beautiful crystals in association with calcite, adular, and chlorite.

*Deposits.* In the USSR, titanite is found in the pegmatites of the Ilmen Mountains in the Urals, in the contact rocks of Slyudyanka (the Baikal Region), and in the alkaline rocks of the Khibiny Mountains. *Practical use.* Considerable accumulations of titanite can have practical significance as an ore of titanium.

#### TOPAZ $\text{Al}_2[\text{SiO}_4](\text{F}, \text{OH})_2$

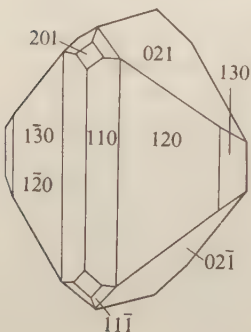
The crystalline structure of topaz has a four-layered hexagonal closest packing, in which each ion of  $\text{Al}^{3+}$  is in octahedral environment of four  $\text{O}^{2-}$  ions, belonging to  $[\text{SiO}_4]^{2-}$  tetrahedrons, and two ions of  $\text{F}^-$  that are situated by layers.

The system is orthorhombic. The crystals are prismatic and well-formed, also rich in faces, e.g. rhombic prisms, dipyrramids, and pinacoids (Fig. 97). The mineral is found in the form of beautiful druses and fine-grained masses (topaz greisen). Rough striation along the vertical axis of crystals is common. The size of crystals can be very large. A topaz crystal weighing 117 kg and 82 cm high was found in the Ukraine in 1966.

The colour is yellow, smoky, light-blue, pink, and often colourless. The lustre is vitreous. Perfect  $\{001\}$  cleavage is a characteristic feature. The hardness is high (8), and the density is also considerable (3.5). These features, in conjunction with vertical striation, distinguish topaz from quartz.

*Origin.* The mineral originates in pegmatitic veins, especially in their

Fig. 97. Topaz crystals



cavities ('bags') and is paragenetic with quartz, orthoclase, albite, and mica. In greisens (pneumatolitic origin) it associates with quartz, aquamarine, fluorite, cassiterite, and wolframite.

*Deposits.* In the USSR, the mineral is mined in the pegmatites of the Urals, in Volyn (large smoky topaz), in Eastern Siberia, in the placers along the rivers Sanarka and Kamenka in the Urals (pink topaz). In other countries there are deposits in Brazil and Madagaskar.

*Practical use.* The transparent and coloured varieties are used as precious stones.

#### The Family of Disthene-Andalusite

Disthene, andalusite, and sillimanite, though of one and the same chemical composition, are different as far as their structure is concerned, and are formed within the process of highly-aluminous rock metamorphism at different temperature and pressure.

#### DISTHENE (cyanite) $\text{Al}_2[\text{SiO}_4]\text{O}$

(from the Greek 'di', meaning two, and 'sthenos', meaning force). In the crystalline structure of disthene, andalusite, and sillimanite half of  $\text{Al}^{3+}$ -octahedrons forms elongated along the *C* axis columns with common edges. In disthene, as compared with other modifications, these columns are connected with the other half of analogous octahedral columns into corrugated layers, which are interconnected by silicon-oxygen tetrahedrons  $[\text{SiO}_4]^{4-}$  in such a way that the base of each tetrahedron belongs to one layer, while the apex to the neighbouring one.

The system is triclinic. The crystals are elongated, tabular, and sometimes curved.

The colour is blue, light-blue, more seldom white, or grey. The lustre is vitreous. The cleavage {010} is perfect. The hardness on the cleavage plane is 4.5 (vertically), and 6 (when measured horizontally). The density equals 3.6.

*Origin.* Metamorphic: disthene is a typical mineral of crystalline schists (disthene-garnet, mica-disthene and other schists). The mineral associates of disthene are: micas, garnet, corundum, andalusite, etc.

*Deposits.* The crystalline schists with disthene are widely spread in the Sayan-Baikal mountain region, in the Kola Peninsula, in Karelia, and in the Urals.

*Practical use.* Rocks containing disthene can be utilized as highly-aluminiferous raw material and in the production of refractory materials.

#### ANDALUSITE $\text{AlAl}[\text{SiO}_4]\text{O}$

In the crystalline structure of andalusite, as distinct from disthene, the second half of  $\text{Al}^{3+}$  ions is in an unusual environment of five oxygen ions.

The system is orthorhombic. The crystals are prismatic, tabular; their cross-section closely resembles that of a square, which is a characteristic feature.

The colour is pink, grey. The lustre is vitreous. The cleavage {010} is perfect. The mineral has a high hardness (7.5). Its density is 3.2. *Varieties.* Andalusite, containing regularly symmetrical inclusions of carbonaceous substance, is called *chiastolite*. It is usual for these inclusions in cross-section to have the form of a black cross.

*Origin.* The metamorphic origin is characteristic of micaceous and clay-carbonaceous schists. It is often formed at contacts between igneous rocks and schists. In clay schists large prismatic crystals are often found. The mineral associates are micas, garnet, and sometimes corundum.

*Deposits.* Schists with andalusite are known in Kazakhstan, Turkestan Range, Eastern Sayan, and elsewhere. Andalusite with corundum is found in the deposits of Semizbugu (North Kazakhstan).

*Practical use.* Andalusite is used in porcelain industry as a highly-aluminiferous raw material.

#### SILLIMANITE $\text{Al}[\text{SiAlO}_5]$

The crystalline structure of sillimanite differs from that of disthen and andalusite in that the second half of  $\text{Al}^{3+}$  ions is in a tetrahedral coordination and forms with the ions of silicon continuous  $[\text{AlSiO}_5]^{3-}$  chains, elongated along the *C* axis.

The system is orthorhombic. It is usually found in the form of fibrous masses (*fibrolite*). The crystals are acicular.

The colour is grey with a brownish or greenish tinge. The cleavage is perfect. The lustre is vitreous. The hardness equals 6.5-7.

*Origin.* The metamorphic origin is characteristic of deep metamorphosed rocks, rich in alumina (gneisses, crystalline schists). It is found together with cordierite, biotite, and quartz.

*Deposits.* In the USSR, sillimanite gneisses are located in a large number of places of Eastern Siberia. Rocks rich in sillimanite are found near Kyakhta in Buryatia. Sillimanite gneisses together with other types of rock enter into the basis of the East-European platform. Large deposits of sillimanite are known in India.

*Practical use.* Sillimanite is an important ceramic raw material.

#### STAUROLITE $\text{FeAl}_4[\text{SiO}_4]_2\text{O}_2(\text{OH})_2$

(the term comes from the Greek '*stavros*', meaning 'to cross'. The mineral is characterized by cruciform twins; see Fig. 29). The crystalline structure of staurolite represents layers of the cyanite type, alternating with the layers comprising Fe-tetrahedrons and  $\text{Al}^{3+}$ -octahedrons, which are bound apically.

The system is orthorhombic. The crystals are of prismatic form.

The colour is brown. The lustre is vitreous. The cleavage is medium, and the hardness equals 7-7.5.

*Origin.* The mineral is formed as a result of regional metamorphism. It is typical of crystalline schists. Staurolite is found together with andalusite, disthen, micas, and garnet.

### Silicates with Double Tetrahedrons $[\text{Si}_2\text{O}_7]^{6-}$ (Diorthosilicates or Sorosilicates)

#### Aquatic

#### HEMIMORPHITE (Calamine) $\text{Zn}_4[\text{Si}_2\text{O}_7](\text{OH})_2 \cdot \text{H}_2\text{O}$ .

In the crystalline structure of hemimorphite group the  $[\text{Si}_2\text{O}_7]^{6-}$  groups are connected with the paired  $\text{Zn}_2(\text{O}, \text{OH})_7$  tetrahedrons by commonly related apexes. The molecules of water are distributed in the intertetrahedral voids.



The system is orthorhombic. The crystals are small, and have a tabular or prismatic form. They usually form druses, fine-crystalline crusts (in the voids); reniform and sintered forms are also found.

The mineral is either colourless or lightly coloured (white, light-yellow, pale-blue). The lustre is vitreous. The hardness is 5, and the density is 3.5.

*Origin.* The exogenetic origin is restricted to the oxidation zone of polymetallic deposits, the mineral is formed at the expense of the disintegration of sphalerite. In the oxidation zone hemimorphite associates with smithsonite, cerussite, limonite, calcite, dolomite, sulphides of lead and zinc.

*Deposits.* In the USSR, hemimorphite is recovered from the polymetallic deposits of the Eastern Transbaikal region, e.g. Klichka, Taininka, etc. (Chita Region).

*Practical use.* When there are large accumulations of hemimorphite with smithsonite, it becomes an important ore of zinc (galmei ores).

## Silicates with Isolated and Paired Tetrahedrons $[\text{SiO}_4]^{4-} + [\text{Si}_2\text{O}_7]^{6-}$ (Ortho-Diorthosilicates)

### With Additional Anions

**IDOCRASE (Vesuvianite)**  $\text{Ca}_{10}(\text{Mg}, \text{Fe})_2\text{Al}_4[\text{SiO}_4]_5[\text{Si}_2\text{O}_7]_2(\text{OH})_4$   
Sometimes the mineral contains Be, TR, B, F, etc. In the crystalline structure of vesuvianite the columns of  $\text{Ca}^{2+}$  ions (coordination number is 8) and  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  ions (coordination number is 6) are connected by isolated and paired tetrahedrons  $[\text{SiO}_4]^{4-}$  and  $[\text{Si}_2\text{O}_7]^{6-}$ .

The system is tetragonal. The crystals are properly faced, and are usually prismatic (lath-like or short prismatic); occasionally they are pyramidal. The aggregates have a rod-like structure, and form solid granular masses.

The colour is green of various shades, from grey-green and yellowish-green to greenish-brown. The lustre is vitreous. The mineral is brittle. The cleavage is usually absent; sometimes it is very indistinct to  $\{110\}$ ,  $\{100\}$ . The fracture is uneven. The hardness equals 6.5, and the density is 3.4. In block masses the mineral resembles epidote and garnet.

*Varieties.* Properly formed crystals of vesuvianite are found together with grossular in contact rocks along the Akhtarande River, a tributary of the Vilyui River (Yakutsk ASSR) and are called *wiluite*.

*Origin.* Vesuvianite is a characteristic mineral of skarns; it is spread in contacts with limestone, and found together with calcite, diopside, garnet, epidote, wollastonite, chlorite, and others.

The mineral is common to the skarns in Central Asia, metamorphic rocks in the Urals, and a number of other regions in the USSR.

*Practical use.* Vesuvianite containing beryllium (up to 9.2% of BeO) can serve as an ore of beryllium (occurs rarely).

**EPIDOTE**  $\text{Ca}_2(\text{Fe}, \text{Al})\text{Al}_2[\text{SiO}_4][\text{Si}_2\text{O}_7]\text{O}(\text{OH})$

The  $\text{Mn}^{2+}$  and  $\text{TR}^{3+}$  impurities are common. In the crystalline struc-

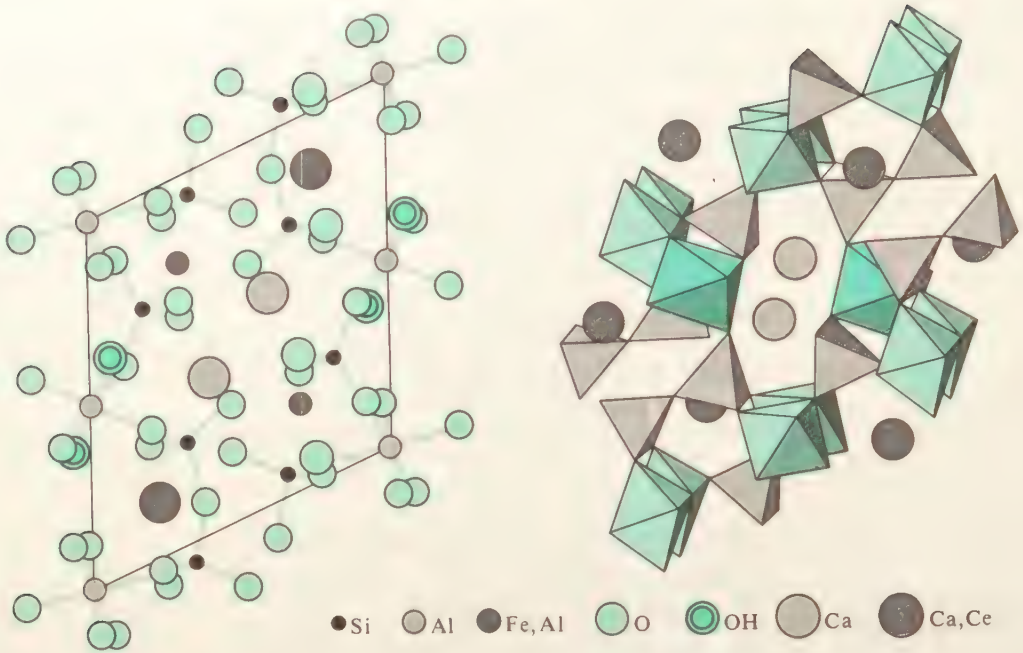


Fig. 98. Epidote structure in globular (a) and polyhedral (b) models

ture the chain motif is brought out by the columns of Al-octahedrons, fixed by isolated and paired  $[\text{SiO}_4]^{4-}$  and  $[\text{Si}_2\text{O}_7]^{6-}$ -tetrahedrons, between which we find isolated  $(\text{Fe}^{3+}, \text{Al})$ -octahedrons,  $\text{Ca}^{2+}$  with seven summits and  $\text{Ca}^{2+}$ ,  $\text{Ce}^{3+}$  with nine summits (in orthite) (Fig. 98).

The system is monoclinic. The crystals are elongated-prismatic, rod-like, sometimes bladed, and occasionally twinned. Rough striation along the elongation of crystals is found to be characteristic. The mineral often forms solid, granular, and rod-like aggregates.

The colour is yellow-green and of other tinges of green. The lustre is vitreous. The hardness equals 6.5, and the density is 3.5.

*Origin.* Epidote of the skarn origin is found in contacts with garnet, calcite, quartz, and diopside. It is characteristic of epidote to occur in basic effusive rocks and in metamorphic rocks with chlorite and amphibole (green schists). Properly formed crystals are found in the veins of the Alpine type.

The mineral is widespread. The Akhmatovskaya Mine in the Nazyam Mountains (Urals) is renowned for its perfectly faced crystals. Radiated aggregates of epidote with andradite from the Dashkesan deposit of iron ores in Azerbaidzhan are very beautiful.

#### ZOISITE $\text{Ca}_2\text{Al}_3[\text{SiO}_4][\text{Si}_2\text{O}_7]\text{O}(\text{OH})$

The mineral sometimes contains the impurities of iron and manganese. The crystalline structure is approximately the same as the structure of epidote.

The system is orthorhombic. The mineral forms prismatic, deeply striated crystals and granular masses.

The colour is grey, green. The lustre is vitreous. The hardness equals 6. Zoisite can be properly discerned only under the microscope.

*Varieties.* *Saussurite* is a fine-granular zoisite in a mixture with albite or sericite, the product of the decomposition of plagioclase, observed only under the microscope. *Thulite* is a variety containing the impurity of Mn.

*Origin.* Zoisite of metamorphic origin is formed during the hydrothermal processing of the rocks, containing basic plagioclases. It usually associates with amphiboles, and is a widespread mineral of metamorphic schists, amphiboles and igneous rocks.

#### ORTHITE $\text{Ca}(\text{Ca}, \text{Ce})(\text{Al}, \text{Fe})\text{Al}_2[\text{SiO}_4][\text{Si}_2\text{O}_7]\text{O}(\text{OH})$

Besides Ce, the mineral contains La, Y and other rare earths, as well as Th. The crystalline structure is analogous to that of epidote.

The system is monoclinic. The tabular or platy form of crystals is a characteristic feature. The orthite crystals have straight even faces (the term comes from the Greek '*orthit*', meaning 'straight').

The colour is resinous-black, dark-brown. The lustre is resinous, greasy. The hardness is 6, and the density is 4.1. The mineral is radioactive.

*Origin.* Orthite of the magmatic origin is found as an accessory mineral in acid intrusive rocks. Pegmatitic origin is found to be more characteristic. Here the mineral sometimes forms large crystals with up to 10 cm in length.

*Deposits.* The mineral is known in the pegmatites of the Ilmen Mountains in the Urals, Slyudyanka (the Baikal Region), and elsewhere.

*Practical use.* Orthite may well be a source of rare earths and thorium.

### Silicates with Isolated Rings of Tetrahedrons $[\text{Si}_6\text{O}_{18}]^{12-}$ , etc. (Cyclosilicates)

#### Complex

##### BERYL $\text{Be}_3\text{Al}_2[\text{Si}_6\text{O}_{18}]$ (5.1% of Be)

The mineral often contains  $\text{H}_2\text{O}$ , alkaline metals Li, Na, K, Rb, Cs and also  $\text{Cr}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . In the crystalline structure of beryl the hexagonal rings  $[\text{Si}_6\text{O}_{18}]^{12-}$  (Fig. 99) are interconnected by ions  $\text{Be}^{2+}$  (coordination number is 4) and  $\text{Al}^{3+}$  (coordination number is 6), thus forming void hexagonal columns, the channels of which contain alkaline ions and  $\text{H}_2\text{O}$  molecules.

The system is hexagonal. The crystals are of columnar type. They usually represent a combination of a hexagonal prism and a pinacoid. Sometimes the head of the crystals is made more complex by dipyrramids (Fig. 100). Vertical striation may well be considered a characteristic feature. The mineral is usually found in the form of crystals, that are often large, weighing as much as several scores of kilogrammes.

The colour is green, yellow-green, light-blue, white, pink. The lustre is vitreous. The fracture is uneven. The hardness equals 7.5-8, and the density is 2.7.

*Varieties.* A variety of beryl that is transparent and green is called *emerald* (the colour is conditioned by the impurity of chromium). Transparent, light-bluish green crystals are called *aquamarine* (from the Latin '*aqua*', meaning 'water', and '*marinus*', meaning 'sea').

Fig. 99. Beryl structure as projected on the pinacoid (a) and prism (b); the  $\text{SiO}_4$ -tetrahedrons are shown by green. Large black circles indicate Al, small ones show Be

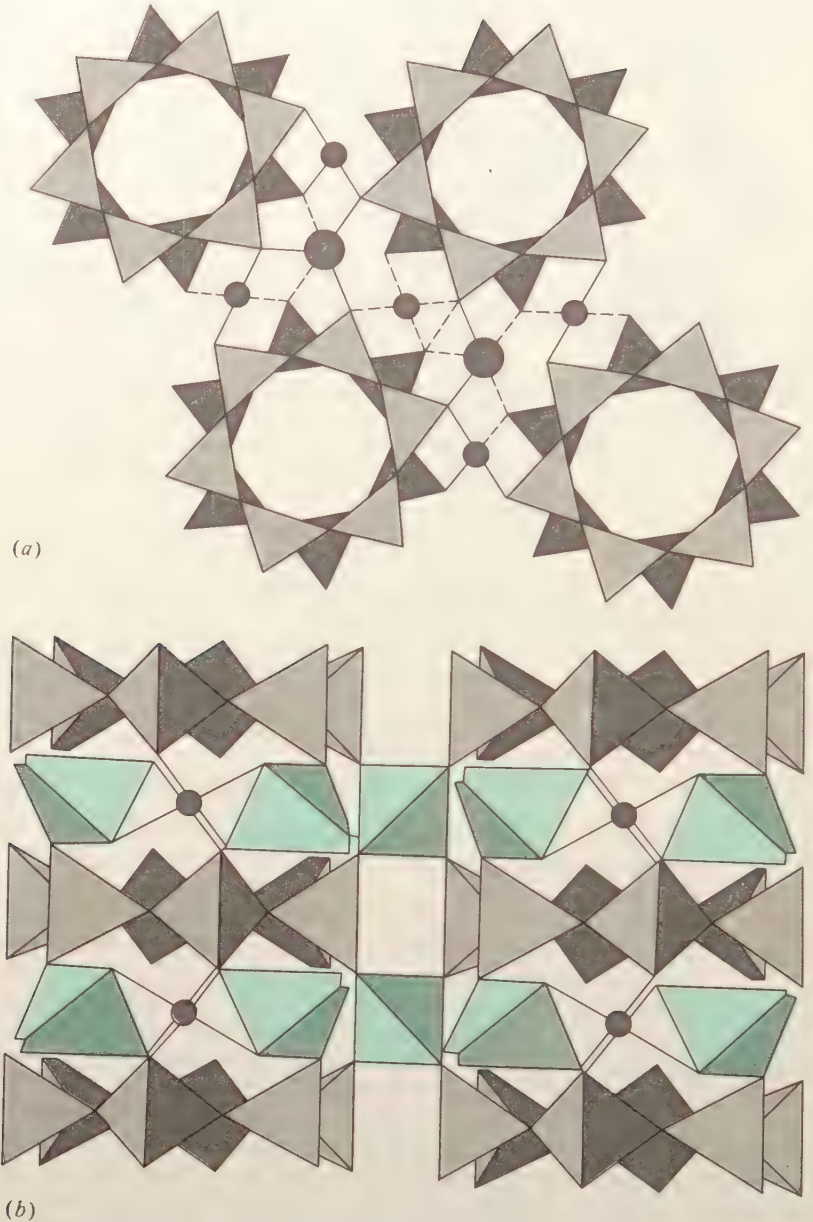
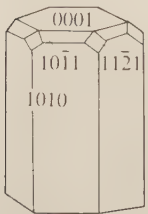


Fig. 100. Beryl crystal



The yellow varieties are known under the term *heliodor* (from the Greek 'helios', which means 'the sun'). *Vorobyevite* is a pale-pink alkaline variety of beryl.

*Origin.* Beryl of pegmatite origin is found in association with feldspar, quartz, muscovite, tourmaline and other minerals of the pegmatite veins, the said origin is characteristic of albitites, greisens and high-temperature hydrothermal veins; in them beryl associates with topaz, wolframite, cassiterite, and molybdenite.

*Deposits.* In the USSR beryl is known in a large number of

pegmatite veins. Emerald is mined in the Urals, whereas aquamarine is recovered from the pegmatites in the Urals and from the greisens in the Transbaikal region and Kazakhstan. In other countries the mineral is found in the pegmatites in the USA (the states of Maine and New Hampshire), SAR, Madagascar, and Afghanistan. Large deposits of emerald are located in Columbia. The mineral is also found in the bituminous limestones and schists with pegmatites. Deposits of aquamarine are related to the pegmatites of Brazil (Minas Gerais).

*Practical use.* Beryl is used as an ore of beryllium, which is used in the production of light alloys with magnesium, aluminium and copper. Beryl salts are utilized in various branches of industry. Emerald is a precious stone of the highest class. Aquamarine is also a gem stone.

#### CORDIERITE $(\text{Mg}, \text{Fe})_2 \text{Al}_3 [\text{Si}_5 \text{AlO}_{18}]$

It sometimes contains Be. The crystalline structure is similar to the structure of beryl.

The system is orthorhombic. The crystals are prismatic and pseudo-hexagonal. It is more often found in block masses and irregular disseminations.

The colour is grey, often dichroic blue of various shades; more seldom the colour is purple, or colourless. The cleavage is imperfect. The hardness equals 7-7.5, the lustre is vitreous.

*Origin.* Cordierite is a typical mineral of metamorphic rocks, i.e. gneisses and crystalline schists. It is found together with plagioclases, hornblende, sillimanite, andalusite, and biotite. Sometimes the mineral is of magmatic origin, and is found in effusive rocks (trachytes, andesites). When decomposed, it is transformed into mica- and talc-like products.

*Deposits.* In the USSR the metamorphic rocks with cordierite are known in the Urals, in Eastern Sayan, on the Patom upland, and in the Transbaikal region.

*Practical use.* Transparent dichroic cordierite is a jewelry stone.

#### With Additional Anions

SHORL  $(\text{Na}, \text{Ca}) \text{Fe}_3 (\text{Al}, \text{Fe})_6 [\text{Si}_6 \text{O}_{18}] [\text{BO}_3]_3 (\text{OH}, \text{F})_4$ , DRAVITE  $\text{NaMg}_3 (\text{Al}, \text{Fe})_6 [\text{Si}_6 \text{O}_{18}] [\text{BO}_3]_3 (\text{OH}, \text{F})_4$ , ELBAITE  $\text{Na} (\text{Li}, \text{Al})_3 \text{Al}_6 [\text{Si}_6 \text{O}_{18}] [\text{BO}_3]_3 (\text{OH}, \text{F})$

are, as far as their composition is concerned, complex ring borate-silicates and extreme members of the TOURMALINE group.

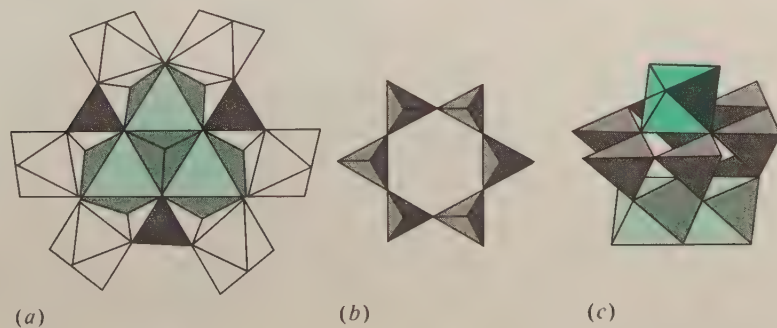


Fig. 101. Tourmaline structure  
*a*—layers of  $[\text{BO}_3]^{3-}$ -radicals (black),  $(\text{Mg}, \text{Fe})\text{O}_6$ -octahedrons—light-green and  $\text{AlO}_6$ -octahedrons (colourless);  
*b*—hexagonal silicon-oxygen ring of the following layer; *c*—the position of  $(\text{Ca}, \text{Na})\text{O}_6$ -octahedrons (dark-green)

Fig. 102. Tourmaline crystal

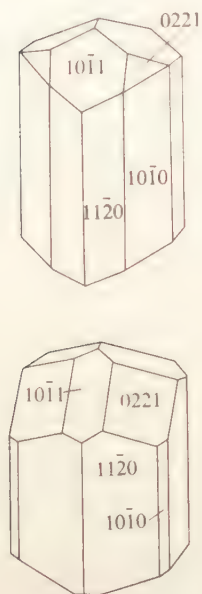


Fig. 103. Radiating aggregates of tourmaline (the 'Tourmaline Sun') in talc schist (the Urals). Three times reduced in size

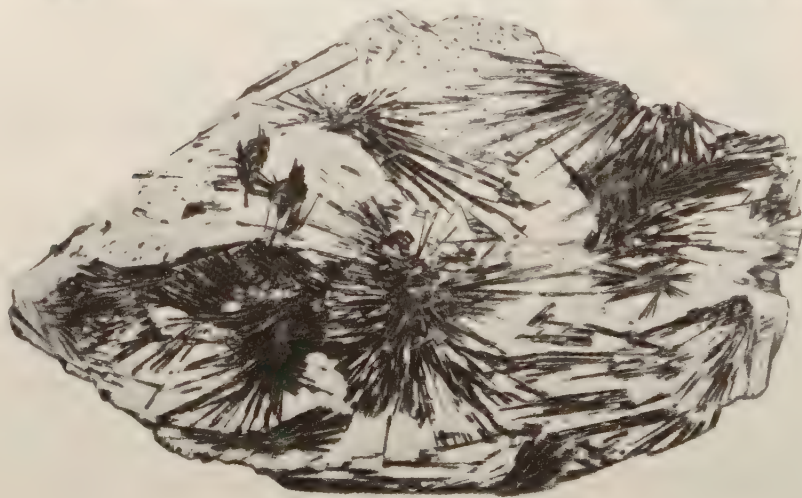
Complete isomorphic miscibility has been established between shorl and elbaite, and between shorl and dravite. Besides, the  $Mg_3^{2+}$ ,  $Fe_3^{2+}$  or  $(Li^+, Al^{3+})_3$  positions are usually partially replaced by  $Mn^{2+}$  ions. Tourmaline occasionally contains the impurity of  $Cr^{3+}$ ,  $V^{3+}$ ,  $Ti^{4+}$ , and other elements. In the crystalline structure the hexagonal (or ditrigonal) ring of silicon-oxygen tetrahedrons (Fig. 101) is linked by common apexes with three  $(Mg^{2+}, Fe^{2+})$  octahedrons, surrounded by the three radicals of  $[BO_3]^{3-}$  and three pairs of  $Al^{3+}$ -octahedrons, connected the rings between them. Among the neighbouring sequential double-layered rings the  $Na^+$  and  $(OH)^-$  ions are located.

The system is hexagonal. The crystals are elongated, columnar, and elongated along the  $C$  axis. The simple forms are mostly characterized by trigonal and ditrigonal prisms and pyramids, though sometimes a monohedron also occurs (Fig. 102). The striation of crystals along the vertical axis and the form of spherical triangle in cross-section is found to be a characteristic feature. There are crystals the size of which reaches 30-40 cm, but, as a rule, they are small. Radially fibrous aggregates are called the *tourmaline sun* (Fig. 103). Acicular and granular aggregates are not uncommon.

The colour is various. Shorl is dark-blue, black; dravite is brown; elbaite is pink, green or white. The cleavage is absent. Cross-sectional jointing is characteristic. The mineral is brittle. The lustre is vitreous. Its hardness equals 7.5-8, and the density is 2.9-3.2. Tourmaline possesses pyro- and piezoelectric properties.

*Varieties.* *Rubellite* (the Siberian ruby) is a pink lithium-manganese variety of elbaite. *Achroite* is a colourless, white, alkaline elbaite. Besides, there is green tourmaline, or *verdelite*, blue tourmaline, or *indigolite* and *polychrome* (multicoloured) crystals of tourmaline that are either zonal or striated; the usual zones of pink colour merge into colourless and green zones. Black tourmaline crystals (shorls) are predominant. The coloured varieties of tourmaline are comparatively rare and are usually found in pegmatites with such minerals as lithium, caesium, beryl, tantalum, and niobium.

*Origin.* The mineral is predominantly of pegmatite origin. Its largest crystals (shorls) are sometimes found in considerable quantities in



pegmatite veins with feldspar, quartz, muscovite, and biotite. The coloured varieties of tourmaline are common for rare-metal pegmatites with albite, lepidolite, beryl, spodumene, and columbite. The varieties are also found in greisens with topaz and cassiterite (pneumatolytic origin), in ore veins (hydrothermal) and some of the metamorphic and contact rocks.

*Deposits.* In the USSR, it is found in the Turkestan Range (Central Asia), in the Urals, Karelia, Eastern Siberia in pegmatite veins with feldspar, quartz, muscovite, and biotite; in Kazakhstan, Central Asia and the Transbaikal region, the coloured varieties of tourmaline are found in the rare-metal pegmatites.

*Practical use.* Owing to its pyro- and piezoelectric properties tourmaline is used in radio engineering. Rubellite is a gem stone. When the accumulations of magnesite tourmaline are substantial, the mineral can serve as a raw material in the production of boron (from 8 to 12% of  $B_2O_3$ ).

### Aquatic

DIOPTASE (ascharite)  $Cu_6[Si_6O_{18}] \cdot 6H_2O$

In the crystalline structure of dioptase the hexagonal rings of  $[Si_6O_{18}]^{12-}$  are interconnected by  $Cu^{2+}$  ions.

The system is hexagonal. The crystals are of emerald-green colour and form crusts and druses. The cleavage is perfect. The hardness is 5.5. The streak is green, and the lustre is vitreous. The mineral is transparent or translucent. The density is 3.5.

*Origin.* The mineral is formed in the oxidation zone of copper deposits, and associates with chrysocolla, malachite and other minerals characteristic of the zone. Dioptase is a fairly rare mineral. Its beautiful druses and crystals are known from the deposits of Altyn-Tyube in Kazakhstan and in Zaire.

## Silicates of Chain Structure (Inosilicates)

### Silicates with Single Chains of Tetrahedrons $[Si_2O_6]^{4-}$ (Pyroxenes)

According to their chemical composition these are the silicates of Ca, Mg, Fe, Mn, in which Al and alkali (Na, Li) are present. Pyroxenes are characterized by a wide isomorphic replacement of some of the elements by others.

In the crystalline structure of pyroxenes (Fig. 104) the anion chain radicals  $[Si_2O_6]^{4-}$  are interconnected by means of cations located in two dissimilar positions: the more regular octahedrons, that have common edges with silicon-oxygen tetrahedrons and in distorted 6- and 8-coordination polyhedrons, each of which is apically connected with the neighbouring pair of tetrahedrons. In pyroxenes the composition of which is complex large ions of  $Ca^{2+}$ ,  $Na^+$ , or  $Li^+$  are distributed in distorted polyhedrons, while  $Mg^{2+}$  and  $Fe^{2+}$  find their place in octahedrons (monoclinic pyroxenes). In magnesium-ferriferous pyroxenes the cations are usually equally distributed as far as positions common to them are concerned (pseudorhombic pyroxenes). In

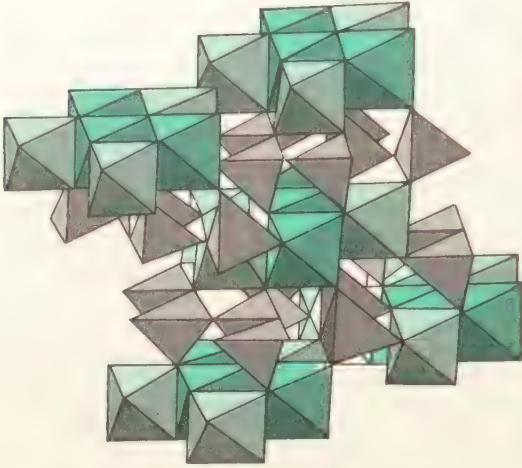


Fig. 104. Structure of pyroxenes in a polyhedral model. Ca ions are in the octahedral position  $M_1$  (light green), Mg and  $Fe^{2+}$  ions are in position  $M_2$  (dark green)

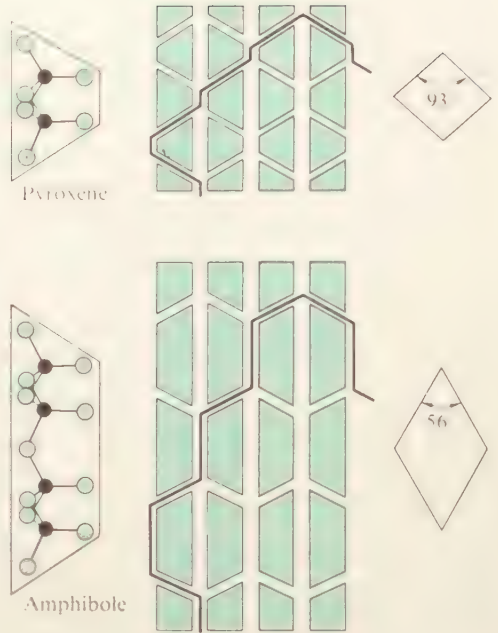


Fig. 105. Fragments of structure and the direction of cleavage in pyroxene and amphibole crystals

accordance with the crystalline structure pyroxenes are characterized by medium cleavage at an angle which is approximately the same as the right angle (87 and 93°) (Fig. 105).

### Simple (orthopyroxenes)

ENSTATITE  $Mg_2[Si_2O_6]$  and HYPERSTHENE  $(Mg, Fe)_2[Si_2O_6]$  are representatives of a continuous isomorphous series with enstatite at one end and ferrosilite  $Fe_2[Si_2O_6]$  at the other. The mineral of an intermediate composition between enstatite and hypersthene is called *bronzite*, which is quite congruous with its bronze lustre.

The system is not orthorhombic (as can be exemplified by the morphology of the crystals), but pseudorhombic as a result of fine twinning, which is actually pertinent to monoclinic minerals. The minerals are rarely found in the form of perfect crystals. They usually form irregular grains and granular aggregates.

The colour is light-grey, yellowish or greenish-grey with enstatite to dark-grey, dark-brown or brownish-green with hypersthene. When the content of iron increases from enstatite to hypersthene, the colour becomes darker. The density and other properties undergo changes as well. (The density with enstatite is 3.1-3.2 to 3.4-3.5 with hypersthene). The hardness of these minerals is 5.5-6. The lustre is purple, vitreous with enstatite to bronze with bronzite and to metalline with more ferrous representatives of the series.

*Origin.* Enstatite, bronzite and hypersthene (of magmatic origin) are rock-forming minerals of some of the ultrabasic rocks. Their mineral associates are olivine, serpentine, magnetite and the basic plagioclases. Under the action of the hydrothermal solutions they are easily



changed and are transformed into serpentine (bastite) and talc. The minerals are found in crystalline schists, gneisses, as well as in meteorites.

### Complex (clinopyroxenes)

DIOPSIDE  $\text{CaMg}[\text{Si}_2\text{O}_6]$  and HEDENBERGITE  $\text{CaFe}[\text{Si}_2\text{O}_6]$  form a continuous isomorphic series and often contain  $\text{Mn}^{2+}$ .

The system is monoclinic. The crystals have the form of short prisms, and are sometimes large, up to 40 cm. Hedenbergite is often found in radiated aggregates. There are cases when it is fibrous. Block granular masses are also found to be widespread.

The white, grey, light-green colour is characteristic of diopside. Hedenbergite is distinguished by its green, dark-green almost black colouring and greenish streak. The lustre is vitreous. The cleavage  $\{110\}$  is medium at an angle of  $87^\circ$ . The hardness is 5.5-6. The density is from 3.27 (diopside) to 3.55 (hedenbergite).

*Varieties.* *Baikalite* is a variety characterized by large, perfect prismatic crystals of diopside, which are sometimes transparent and green (the Slyudyanka deposit, the Baikal region). *Lavrovite* (of the same deposit) is a bright-green variety of diopside (the colour is conditioned by the vanadium impurity). *Blue diopside* is known from the Dovyren massif in the Northern part of Baikal region. *Chrome-diopside* contains up to 3% of  $\text{Cr}_2\text{O}_3$ . It is emerald-green and is found exclusively among the ultrabasic rocks and in the kimberlites of Yakutia. *Manganhedenbergite* is a variety of hedenbergite containing up to 10% of MnO. It is characteristic of the skarns in Central Asia, the Northern Caucasus, and the Primorski Krai.

*Origin.* Minerals of the diopside-hedenbergite series are typical of contacts of igneous rocks with lime-stone (skarns). The usual mineral associates in skarns are calcite, garnet, vesuvian, tremolite, scapolite, phlogopite, and apatite (for diopside), epidote, wollastonite. Ore minerals found in pyroxene-garnet skarns are the following: scheelite, molybdenite, sulphides of Cu, Pb, Zn and magnetite. Secondary changes consist in the development of the pyroxenes of uralite (hornblende, first discovered in the Urals), chlorite and nontronite. Diopside also has a magmatic origin, being a rock-forming mineral of basic and ultrabasic rocks.

*Deposits.* There are skarn deposits in Central Asia, the Urals, the Northern Caucasus, the Baikal region, the Primorski Krai, and elsewhere.

*Practical use.* Chrome-diopside is known as a jewel.

AUGITE  $(\text{Ca}, \text{Na})(\text{Mg}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al})[(\text{Si}, \text{Al})_2\text{O}_6]$

Sometimes this mineral contains Mn, Ti, and Cr. The crystals are short and stout prismatic, and tabular. The aggregates are solid and granular.

The colour is black, brown-black, dark-green. The lustre is vitreous. The cleavage  $\{110\}$ , as with all pyroxenes, is medium at an angle of  $87^\circ$ . The hardness is 5-5.6, and the density is 3.2-3.6.

*Varieties.* *Diallage* (foliated augite) is a variety of augite, distinguished by a perfect jointing parallel to  $\{110\}$ . Common augite is dark-green. *Basaltic augite* is black, and contains Ti and Mn.

*Origin.* Augite of magmatic origin is a characteristic rock-forming mineral in basic intrusive and effusive rocks. In gabbro and diabases there are dark-green (common) augites; the well formed crystals of black (basaltic) augite are found in basalts, andesites, tuffs, and volcanic ash. The mineral is also known in contacts with limestone.

The products of the secondary alteration of augite are uralite and chlorite.

#### AEGIRINE $\text{NaFe}^{3+}[\text{Si}_2\text{O}_6]$

Sometimes this mineral contains impurities of Al.

The crystals are long-prismatic, tabular, and occasionally acicular; the aggregates are radiate, rod-like.

The colour is greenish-black, dark-green or green. The streak is light-green. The lustre is vitreous. The hardness is 6-6.5 and the density is 3.5.

*Varieties.* *Aemite* is distinguished from aegirine by tapered crystals; it contains Ti and Al.

*Origin.* The mineral is found in alkaline igneous rocks, and is a component of nepheline syenites and the pegmatites connected with them. The mineral associates of aegirine are nepheline, microcline, alkaline amphiboles, etc.

*Deposits.* Large crystals of aegirine with nepheline and feldspar are known in the Vishneve Mountains in the Urals, as well as in the alkaline rocks of the Khibiny Mountains.

#### SPODUMENE $\text{LiAl}[\text{Si}_2\text{O}_6]$ (up to 8.1% of $\text{Li}_2\text{O}$ )

The crystals are lath-like, often flattened and prismatic, tabular and large.

The colour is white, grey, pink, and greenish. The cleavage {110} is perfect. The lustre is vitreous. The hardness equals 6-7, and the density is 3.2. The mineral is often found to be luminescent. Spodumene resembles feldspar, but differs from the latter in that its crystals are flattened, and its fracture is hackly.

*Varieties.* *Kunzite* is either transparent or of pink, purple colour. *Hiddenite* is green.

*Origin.* The pegmatite origin covers quartz, feldspar, cleavelandite, muscovite, lepidolite, polychromes, pink tourmalines, beryl, cassiterite, and tantalite.

*Deposits.* In the USSR there are deposits in Central Asia, Kazakhstan and Eastern Siberia. Some of the deposits are remarkable in that their spodumene crystals are as long as 1 m. In other countries spodumene is found in the USA (South Dakota), in Canada, in Madagaskar, Afghanistan, and Brazil.

*Practical use.* Spodumene is a very important ore of lithium. The addition of lithium to aluminium and lead gives them a greater degree of hardness and makes the two minerals resilient to corrosion. Lithium is also used in alloys and in the form of various preparations in medicine and photography. Kunzite and hiddenite are jewels.

## Silicates with Single Chains of Tetrahedrons $[\text{Si}_3\text{O}_9]^{6-}$ , $[\text{Si}_5\text{O}_{11}]^{10-}$ , etc. (Pyroxenoids)

Minerals pertaining to this group are also characterized by a chain structure, though these chains are of a particular type. As compared with pyroxenes, where the radical is  $[\text{Si}_2\text{O}_6]^{4-}$ , pyroxenoids include minerals with more complex radicals, e.g.  $[\text{Si}_3\text{O}_9]^{6-}$ ,  $[\text{Si}_5\text{O}_{15}]^{10-}$  etc.

### WOLLASTONITE (table spar) $\text{Ca}_3[\text{Si}_3\text{O}_9]$

The mineral often contains the impurities of  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$ . In the crystalline structure of wollastonite the silicon-oxygen anion chain is distinguished by a three-member periodicity (see Figs. 91f, 92b). The  $\text{Ca}^{2+}$  cations occupy the octahedrons that are bound by common edges into columns.

The system is triclinic (pseudomonoclinic). The crystals are tabular with perfect cleavage in one direction; the aggregates are rod-like and radiate.

The colour is white. The lustre is vitreous. The cleavage {100} is perfect and that parallel to {001} is medium. The hardness is 4.5-5. The mineral is brittle. Its density equals 2.9. Wollastonite is remarkable for not infrequent yellow or orange luminescence.

*Origin.* The mineral is characteristic of contacts of igneous rocks and quartz veins with limestone. Moreover, it is found directly at the contact itself. It is deposited in the outer-contact zones of skarns together with quartz, garnet, calcite, epidote and hedenbergite. It differs from tremolite, which resembles it, in the character of cleavage and a lower degree of hardness.

*Deposits.* The mineral is fairly widespread, and is known from the deposits in the Far East, Khakassiya, the Urals and Central Asia.

*Practical use.* Wollastonite is a valuable ceramic raw material.

### RHODONITE $\text{CaMn}_4[\text{Si}_5\text{O}_{15}]$

The term is derived from the Greek '*rhodon*', which means 'rose'. In the crystalline structure there is a five-member silicon-oxygen chain jointing with meandering chains of Ca- and Mn-octahedrons, connected by common edges (Fig. 92c).

The system is triclinic. The crystals are exceptionally rare. The mineral is found in solid compact masses.

Rhodonite is easily recognized by its pink colour in solid granular masses. The presence of black veinlets and spots resulting from manganese hydroxides is a characteristic feature. The hardness is 6, and the density is 3.6.

*Origin.* 1. Contact. 2. Metamorphic; under the metamorphism of sedimentary rocks of the manganese deposits. The mineral associates of rhodonite are: rhodochrosite, psilomelane, and garnet.

*Deposits.* The mineral is found near Sverdlovsk (the Urals).

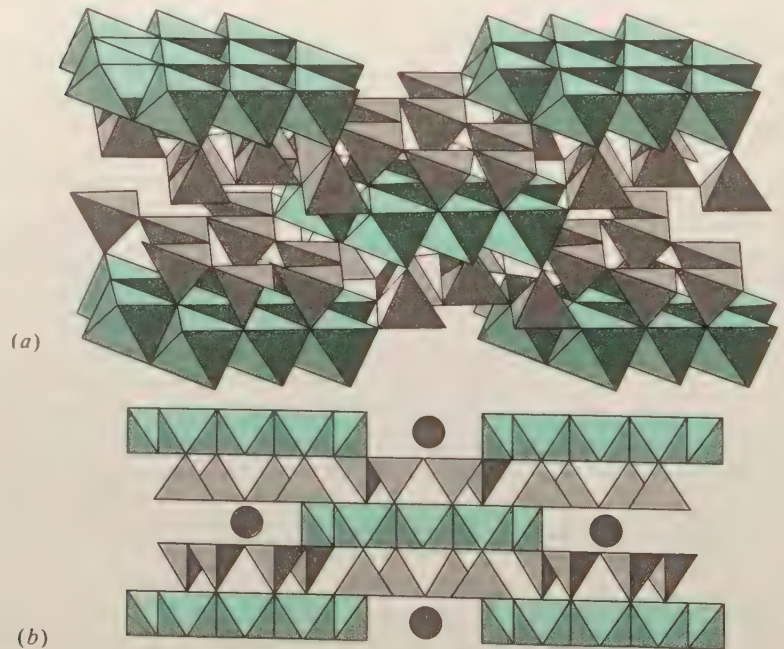
*Practical use.* Rhodonite has the quality of lending itself to being well polished, and thus becomes a valuable semiprecious stone. Together with other minerals it can serve as an ore of manganese.

## Silicates with Double Chains of Tetrahedrons [Si<sub>4</sub>O<sub>11</sub>]<sup>6-</sup> (Amphiboles)

Amphiboles include minerals the composition of which is approximately the same as that of pyroxenes. However, they differ from the latter in that they contain the anions of (OH)<sup>-</sup> as well as of F<sup>-</sup>, and more seldom, of Cl<sup>-</sup>. Paired chains or ribbon anion radicals [Si<sub>4</sub>O<sub>11</sub>]<sup>6-</sup> in amphiboles are interconnected by cation, among which prevalence is attributed to Fe<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>, Na<sup>+</sup>; those that are of rarer occurrence are: Mn<sup>2+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Ti<sup>4+</sup>. Cations in the structure of amphiboles (Fig. 106) occupy nonequivalent positions, thus forming bands, connected by common edges of polyhedrons, elongated along the paired chains. In rhombic Mg-Fe-amphiboles, that are comparatively simple in their composition, the cations are equally distributed in all octahedral positions. In monoclinic amphiboles, the composition of which is more complex, the large ions of Ca<sup>2+</sup> and Na<sup>+</sup> occupy outer polyhedrons (coordination number is 8) of cation bands, while in those, rich in alkaline, they occupy large voids with coordination number 10. Amphiboles are characterized by wide isomorphic replacements, and in particular by the isovalent miscibility between Mg<sup>2+</sup> and Fe<sup>2+</sup> occupying the octahedral positions in the structure between the additional anions of (OH)<sup>-</sup> and F<sup>-</sup>. The heterovalent replacements of silica atoms by aluminium in tetrahedral coordination are accompanied either by the entering of alkaline cations into large voids, or by the entering into octahedral positions of Fe<sup>3+</sup> or Al<sup>3+</sup> ions.

In accordance with the crystalline structure amphiboles are characterized by an elongated-and-prismatic habit with good {110} cleavage, intersecting at an angle of 56° and 124° (see Fig. 105).

Fig. 106. The structure of amphiboles in polyhedral models (a) and in the projection of {001} (b). Octahedral bands comprise ions of Ca, Mg, Fe and Al; the position of Na ions (circles) is shown in the projection parallel to {001}



**With Additional Anions**

**TREMOLITE**  $\text{Ca}_2\text{Mg}_5[\text{Si}_4\text{O}_{11}]_2(\text{OH})_2$  and **ACTINOLITE**  $\text{Ca}_2\text{Fe}_5[\text{Si}_4\text{O}_{11}]_2(\text{OH})_2$

form a continuous isomorphic series. Besides, they often contain  $\text{Na}^+$ ,  $\text{Al}^{3+}$ , sometimes  $\text{Cr}^{3+}$  and  $\text{F}^-$ . In the crystalline structure the  $\text{Ca}^{2+}$  ions occupy the polyhedrons with coordination number 8, edging the bands of octahedrons, occupied by  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  ions.

The system is monoclinic. The crystals are elongated-and-prismatic, acicular; the aggregates are radiate, rod-like (Fig. 107), and sometimes fibrous.

The colour of the mineral is white, light-grey, light-green and green of various shades of colour with actinolite. The lustre is vitreous; it is silky with radiant and fibrous aggregates. The mineral is exceptionally brittle, its fracture is hackly. The hardness equals 5.5-6, and the density is 2.9-3.3.

*Varieties.* Finely fibrous soft aggregates are called *actinolite-asbestos*. Compact, cryptocrystalline masses, consisting of interwoven microscopic fibrous crystals are known as *nephrite*. Tremolite varieties of asbestos and nephrite are of rarer occurrence.

*Origin.* Skarn origin is related to contact, with limestones, while the metamorphic origin is associated with crystalline schists. Actinolite is more often found, particularly in talc and chlorite schists. Sometimes it functions as the main rock-forming mineral (actinolite schists). Nephrite is formed at contacts of serpentinites with aluminosilicate rocks.

*Deposits.* In the USSR there are nephrite deposits in the Eastern Sayan along the Onot and Kitoi Rivers. New deposits have recently been found here, e.g. Ulan-Khodinsk, Ospinsk, and Botogol. Nephrite of various colour has been discovered: bright-green, dark-green, lettuce-green, etc. In other countries there are deposits and placers in the west spurs of the Kunlun Shan in China, as well as in Burma.

*Practical use.* By being exceptionally viscous, nephrite lends itself to be

Fig. 107. Radiating aggregates of tremolite with diopside. Slyudyanka (the Near-Baikal region)

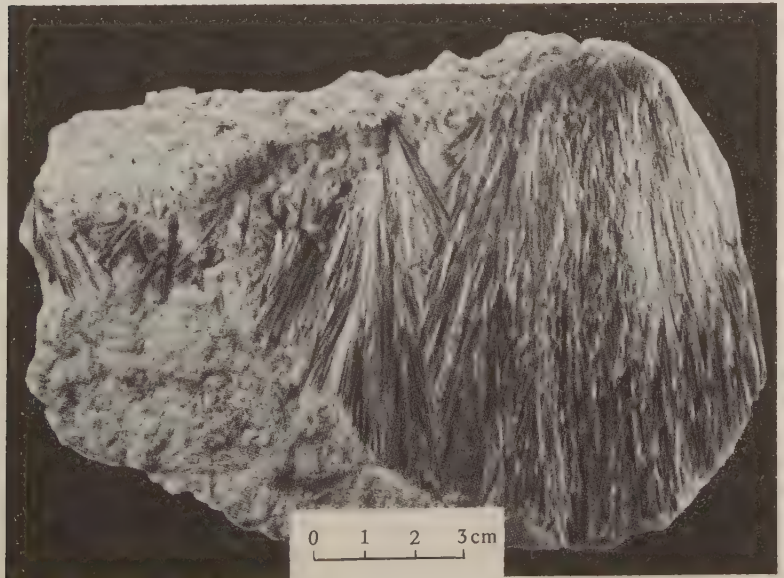


Fig. 108. Structural types of layered silicates and aluminosilicates (diagram)



talc  
(pyrophyllite)



muscovite  
(biotite)



chlorite

▽ Si, Al ● AlMgFe ● K

○ OH ○ H<sub>2</sub>O

polished to perfection, thus serving as a beautiful semiprecious stone. Actinolite-asbestos is used as a heat insulating material.

**HORNBLLENDE**  $(Ca, Na)(Mg, Fe)_4(Al, Fe)[(Si, Al)_4O_{11}]_2(OH)_2$   
The mineral contains the impurities of  $Ti^{4+}$ ,  $F^-$  or  $Cl^-$ , as well as  $O^{2-}$ . Its crystalline structure is the same as that of tremolite. Hornblende is distinguished by a wide heterovalent isomorphism, including  $Si^{4+}$  by  $Al^{3+}$ ,  $Ca^{2+}$  by  $Na^+Mg^{2+}$ , and  $Fe^{2+}$  by  $Fe^{3+}$  and  $Al^{3+}$ ; besides  $Na^+$  can occupy the voids with coordination number 10.

The system is monoclinic. The crystals are prismatic, elongated, not infrequently elongated and flattened, deformed; the aggregates are fibrous or of acicular structure.

The colour is green, of various shades, from brown-green to black. The hardness is 5.5-6, and the density is 3.0-3.5.

*Varieties.* *Common hornblende* of a dark-green colour is found in the intrusive and metamorphic rocks and in zones of contact. *Basalt hornblende* of a brown or black colour is related to basalts and tuffs. The secondary hornblende formed as a result of change of pyroxenes and particularly of augite, under the action of hydrothermal solutions, is called *uralite*. The process involving the transformation of pyroxene into uralite hornblende is referred to as *uralitization*.

*Origin* 1. The magmatic origin pertains to middle and alkaline intrusive rocks (e. g. in diorites) where hornblende is one of the nonferrous metals. 2. When hornblende is of metamorphic origin, it becomes rock-forming mineral of hornblende schists, gneisses, and amphiboles. Hornblende is less typical of the contact process and of less widely-spread pegmatites of the basic magma, where it is sometimes found in the form of large crystals.

**ARFVEDSONITE**  $Na(Ca, Na)(Fe, Mg, Fe, Al)[(Al, Si)_4O_{11}]_2(OH, F)_2$   
This mineral sometimes contains the impurity of  $Mn^{2+}$  and  $K^+$ . In the crystalline structure of arfvedsonite the  $Na^{2+}$  ions can replace half of the  $Ca^{2+}$  ions with coordination number 8, and wholly occupy the voids with coordination number 10. In all other respects the structure is similar to hornblende structure.

The system is monoclinic. It is found in the form of prismatic crystals, occasionally markedly elongated, and forms elongated-granular, radiate and rod-like aggregates.

The colour of the mineral is black. Its lustre is vitreous. Arfvedsonite is opaque, and its cleavage  $\{110\}$  is good. The fracture is step-like, uneven, to shelly. The mineral is brittle. The hardness equals 5.5-6. The streak is greenish-grey or bluish-grey. The density is 3.5.

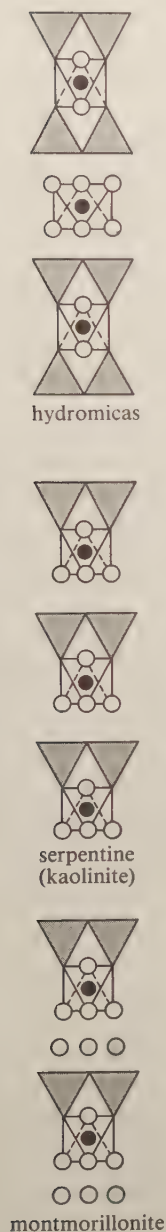
*Origin.* The magmatic origin is associated with alkaline rocks and pegmatites together with aegirine, albite, nepheline, eudialyte, to alkaline granites, and carbonatites.

*Deposits.* In the USSR there are deposits in the Kola peninsula (Khibiny and Lovozero massifs), in the Ukraine (the Mariupol massif), in Eastern Siberia (the Ozerny massif) and elsewhere.

**GLAUCOPHANE**  $NaNaMg_3Al_2[Si_4O_{11}]_2(OH, F)_2$  and **RIEBECKITE**  $NaNFe_3^+Fe_2^{3+}[Si_4O_{11}]_2(OH, F)_2$

form solid solutions; their representatives, intermediate in composition,

Fig. 108 (contin.)



are called *crossite*. The crystalline structure is approximately the same as the structure of arfvedsonite. Half of the  $\text{Na}^+$  ions are located in the voids with coordination number 10, while the other half occupy the polyhedrons with coordination number 8. Two- and trivalent cations occupy the unequal octahedral positions.

The system is monoclinic. Prismatic, acicular crystals are rare, while rod-like, fibrous, and asbestos-like aggregates are common.

The colour is from light-blue of various shades with glaucophane to dark-blue and black (in crystals) with riebeckite. The lustre is vitreous to silky. The cleavage  $\{110\}$  is good. Fibrously-acicular aggregates are easily split into fibres. In crystal form the mineral is brittle. The fracture is uneven and hackly. The hardness equals 5-6.5; in fibrous varieties the hardness is low. The streak is from light-bluish-grey to dark blue. The density is 3-3.4.

*Varieties.* *Rhodusite* is a fibrous variety of glaucophane. *Crocidolite* is a fibrous riebeckite.

*Origin.* Riebeckite of magnetic origin is found as an accessory mineral in granites, syenites, and carbonatites, it also enters into the composition of trachytes and rhyolites. Sometimes it is formed in granitic pegmatites, as well as in hydrothermal veins. Metamorphic origin is typical of glaucophane; the formation of glaucophane schists takes place at low temperatures and high pressures. The formation of some of the crocidolite deposits is connected with the metamorphic ferri-ferous quartzites.

*Deposits.* In the USSR glaucophane schists are found in the Altai, the Urals, and in Kazakhstan. The deposits of rhodusite are known in Khazakhstan and crocidolite—in Karelia. In other countries there are large crocidolite deposits in South Africa.

*Practical use.* Fibrous varieties are used as filters, resilient in corrosive chemical media, as well as heat-resistant material. Crocidolite, changed and silicified, becomes a valuable semiprecious stone (the tiger's eye).

## Silicates and Aluminosilicates of the Layered Structure (Phyllosilicates)

Silicates and aluminosilicates of the layered structure comprise a group of minerals, the composition of which includes, besides silica and aluminium, the ions of  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ , as well as  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Li}^+$ . They contain hydroacids of the  $(\text{OH})^-$  group and other additional anions (and, occasionally, water).

Their structure can be regarded as a result of the combination of tetrahedral and octahedral layers. The first type represents a hexagonal net of silicon-oxygenous or aluminium-oxygenous tetrahedrons, in which three of the four oxygen ions are common (see Fig. 91*h*). The second layer is of the brucite-hydrargillite type and is formed by the ions of aluminium, magnesium or iron, that are in the octahedral coordination of  $2\text{OH}^-$  and  $4\text{O}^{2-}$  ions of the neighbouring tetrahedral layer.

Two-, three- and multilayer structural types of layered silicates and aluminosilicates can be distinguished in accordance with the kind of relationship that exists between the tetrahedral and octahedral layers (Fig. 108). The packets in the two-layered silicates are composed of

one tetrahedral and one octahedral layers (Fig. 108e). Minerals of the group of serpentine and the family of kaolinite belong here too. In two-layered silicates silica is never replaced by aluminium. In three-layered silicates and aluminosilicates the packets consist of two tetrahedral layers and one octahedral situated between them (Fig. 108a).

In minerals of montmorillonite, as distinct from the minerals of the group of talc-pyrophyllite, the molecules of water are located between the packets (Fig. 108c). The quantity of water between the packets can vary within a wide range, which is connected with their ability to swell in water. There is also a change of distance between the packets when saturation of other polar liquids (ethylene glycol, glycerine, etc.).

Minerals of this group are characterized by wide isomorphic replacements of silica by aluminium; the redundant negative charges are compensated by  $\text{Ca}^{2+}$ ,  $\text{Na}^{2+}$  and  $\text{K}^+$  ions, located together with the molecules of water between the packets.

In minerals of the family of micas, the tetrahedral layers are usually composed of silicon- and aluminium-oxygenous tetrahedrons, while the place between the three-layered packets is filled by  $\text{K}^+$  ions, compensating for the redundant charges of the packets (Fig. 108b). In hydromicas together with ions between the packets there are ions of oxonium compound  $(\text{H}_3\text{O})^+$ , molecules of water or hydrated ions of magnesium  $\text{Mg}(\text{OH})^+$  (Fig. 108d).

Alternation of three-layered packets with octahedral layers of the brucite-hydrargillite type are characteristic of multilayer aluminosilicates. This also includes copious family of chlorites.

Layered minerals often form complex mixed-layered formations, particularly characteristic of *clays*. The latter usually include minerals with two-layered packets of the family of kaolinite, and with three-layered packets, mainly of the montmorillonite family. In *mixed-layered clays* the packets of the kaolinite and montmorillonite types can alternate with the packets of talc, pyrophyllite, hydromicas, and chlorite.

Layered silicates and aluminosilicates are characterized by a variety of polytypes distinguished by the order of alternation and the orientation of packets.

## Silicates with Two-Layered Packets

### With Additional Anions

#### SERPENTINE $\text{Mg}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$

It usually contains the impurities of  $\text{Fe}^{2+}$ . In the crystalline structure of serpentine the layers of hexagonal nets, composed of silicon-oxygen tetrahedrons, form two-layered packets, thus combining with the brucite octahedral layer, in which the  $\text{Mg}^{2+}$  ions are in an octahedral environment of  $2\text{O}^{2-}$  and  $4(\text{OH})^-$  ions. Several polytypes are known to exist. The bonds between the packets are those of the van der Waals type.

The system is monoclinic. The mineral form compact cryptocrystalline masses and parallel-fibrous veinlets.

The colour is yellow-green, dark-green, white, yellowish. The lustre



is vitreous, greasy, waxy, or silky. The hardness is 2.5-4, and the density is 2.2-2.7.

*Varieties.* The yellow-green variety of serpentine, transparent at the edges, and with a waxy lustre is called *ophite*, or noble serpentine.

*Bastite* is found as pseudomorphs of serpentine after enstatite. *Antigorite* is a foliated serpentine. *Chrysotile-asbestos* is a fibrous variety of serpentine. *Revdinskite* and *garnierite* are cryptocrystalline mixtures of serpentine with other layered minerals, containing up to 11% of NiO, and forming compact and earthy masses of pale-blue colour.

*Origin.* The mineral is formed at the expense of olivine as a result of the action of hydrothermal solutions upon ultrabasic (peridotites, dunites) and carbonate rocks. The usual mineral associates of serpentine are asbestos, magnesite, chromite, magnetite, talc and others. *Revdinskite* and *garnierite* are formed in the weathering crusts of ultrabasic rocks.

*Deposits.* Serpentine rocks are widely spread in the Middle and the Southern Urals, the Northern Caucasus, in Kazakhstan, in Eastern Siberia. The deposits of chrysotile-asbestos in the USSR include: Bazhenovo (the Urals), Laba (Northern Caucasus), Ulchir (Eastern Sayan), Aktovrak (Tuva), Molodyozhnyi (Buryatiya). In countries outside the USSR, this mineral is found in Canada, from the deposits in South Africa, etc. There are *revdinskite* and *garnierite* deposits in the USSR, e. g. in the Southern Urals (Akkerman, Khalilovo, etc.); in other countries these minerals are also mined in the island of New Caledonia.

*Practical use.* Asbestos fibre is used in many branches of industry. It is made use of the production of heat-stable fabrics, heat insulators and automobile brake bands. Both *revdinskite* and *garnierite* are important ores of nickel.

#### The Family of Kaolinite

#### KAOLINITE $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$

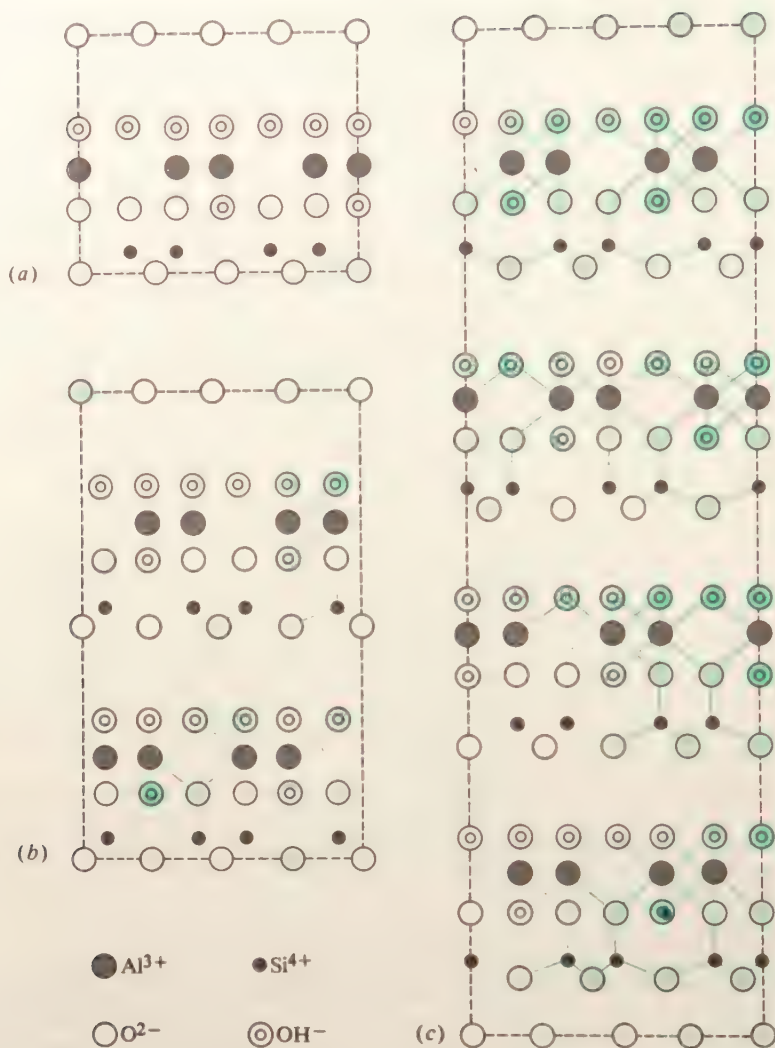
Its crystalline structure is similar to the structure of serpentine, differing from it in that in the octahedral layer the  $\text{Al}^{3+}$  ions occupy not all, but only  $\frac{2}{3}$  of octahedral voids. The ratio Si : Al equals 1 : 1. Depending on the position of the packets of the composition  $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$ , the following polymorphic modifications are singled out: kaolinite—one packet, dickite—two packets, and nacrite—four packets (Fig. 109).

The system is monoclinic. The mineral forms fine-dispersed compact, as well as earthy, powdery masses.

The colour is white, but can be of various shades, depending on the content of impurities. The hardness equals 1, and the density is 2.6. The mineral is greasy to the touch, and hygroscopic. When it is dry, it sticks to the tongue, otherwise, when it contains moisture, it forms a plastic mass.

*Origin.* The mineral is formed under the weathering of feldspars, micas and other aluminosilicates. It enters into the composition of clays, marls, and clay shales. Rocks, consisting of kaolinite, are called *kaolins*. The following kaolin rocks are distinguished: residual kaolin rocks formed at the place of the decomposition of aluminosilicate rocks, and the redeposited kaolin rocks, connected with the washing away of the

Fig. 109. The structures of kaolinite (a), dickite (b), and nacrite (c)



residual kaolin rocks, the transportation of kaolinite in streams and the subsequent sedimentation.

*Deposits.* In the USSR there are deposits in the Ukraine, e.g. Chasov-Yarskoye (the Donetsk Region), Glukhovets (the Vinnitsa Region), along the eastern slopes of the Urals, e.g. Troitsko-Bainovsk, in the Leningrad Region, in the Caucasus and Eastern Siberia. *Practical use.* Kaolin clays are utilized in construction, the ceramic, paper, and rubber industry, in the production of refractory materials, linoleum, paints, etc.

#### HALLOYSITE $Al_4[Si_4O_{10}](OH)_8 \cdot 4H_2O$

In the crystalline structure, as distinct from the structure of kaolinite, there are molecules of water between the packets. The mineral forms opal-like white masses with a waxy lustre. The mineral is typical of the weathering crusts of basic rocks and some ore deposits.

## Silicates and Aluminosilicates with Three-Layered Packets

### With Additional Anions

TALC (steatite, soap rock, soapstone)  $Mg_3[Si_4O_{10}](OH)_2$

This mineral usually contains the impurities of  $Fe^{2+}$ , and sometimes of  $Cr^{3+}$ . The structure of talc comprises alternating three-layered packets with weak van der Waals bonds between them. The octahedral (brucite) layer of  $Mg(OH)_2O_4$ -octahedrons is between two tetrahedral layers of  $[Si_4O_{10}]^{4-}$  (Fig. 110).

The system is monoclinic. The mineral forms foliated or fibrous solid compact masses.

The colour is green, light-green, white, and grey-green in block masses. The lustre is vitreous, purple, greasy or dull. The cleavage {001} is perfect. The hardness is 1, and the density is 2.8. The leaves are soft and are easily deformed. Talc is greasy to the touch.

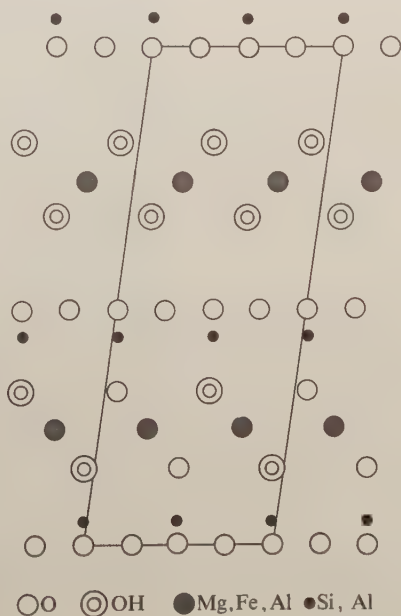
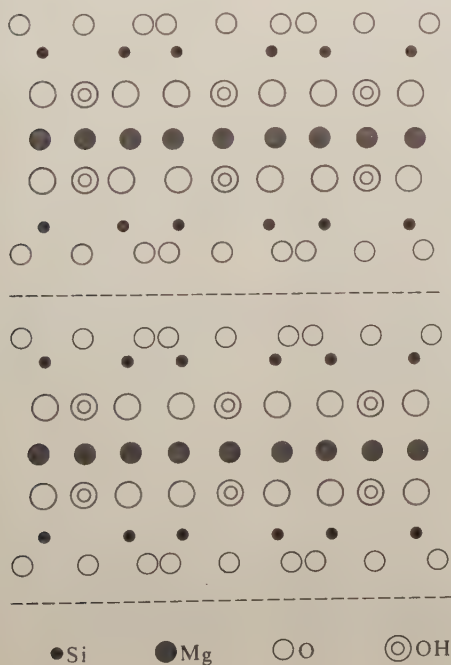
*Origin.* Talc is formed as a result of hydrothermal alteration of ultrabasic rocks rich in magnesium, as well as the magnesium-carbonate and silicate sedimentary rocks. Its mineral associates are serpentine, magnesite, breunnerite, dolomite, actinolite, magnetite, and hematite. Talc and talc-actinolite and other schists are most widespread.

*Deposits.* In the USSR talc is found in the Urals (Shabry and other deposits), in the Eastern Sayan (Onot). Other countries, where talc is deposited are: China, Canada, Austria, Afghanistan, and SAR.

*Practical use.* In the granulated form talc is used in paper, textile, rubber, leather, perfume and other branches of industry. Lumpy talc is a refractory material.

Fig. 110. Talc structure

Fig. 111. Chlorite structure in its projection on {100}



**PYROPHYLLITE**  $\text{Al}_2[\text{Si}_4\text{O}_{10}](\text{OH})_2$ 

The mineral often contains the impurities of  $\text{Fe}^{3+}$  and others. The crystalline structure resembles that of talc. However, the distinguishing feature is that the  $\text{Al}^{3+}$  ions occupy only  $2/3$  of octahedral positions in the hydrargillite layer.

The system is monoclinic. The mineral is found in the form of foliated, scale, compact, and cryptocrystalline aggregates, forming, sometimes, pseudomorphs after various minerals.

The colour is white, light-grey, light-green, sometimes brownish, at the expense of foreign inclusions. The cleavage is perfect, parallel to  $\{001\}$ . The fracture is uneven. The mineral is brittle, though its leaves are elastic. It is also greasy to the touch. The hardness equals 1, and the density is 2.6-2.9.

*Varieties.* *Agalmatolite* is a cryptocrystalline compact variety of pyrophyllite.

*Origin.* The mineral is formed during the hydrothermal alteration of aluminosilicate rocks in secondary quartzites and under the dehydration of kaolinite sedimentary rocks.

*Deposits.* In the USSR, there are deposits in the Ukraine, the Urals, and Tuva. In other countries the mineral is deposited in China, the USA, and elsewhere.

*Practical use.* Talc has the same application as talc. Agalmatolite is used as a semiprecious stone.

**The Family of Micas**

Micas include layered silicates and aluminosilicates, containing  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , and the alkaline ions of  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ . In the crystalline structure of micas the silica-oxygenous three-layered packets are interconnected by alkaline cations (Fig. 112). Micas are characterized by polytypes.

The system is monoclinic. The crystals are foliated, scale, and of the pseudo-hexagonal form. Sometimes they are characterized by an elongation perpendicular to the cleavage. The size of crystals varies from microscopic to plates measuring several square metres. Muscovite crystals weighing one ton have been found in the Chuya deposit. Phlogopite crystals of similar weight have also been discovered in the southern part of the Baikal region (the Slyudyanka deposit).

The colour of micas is different for various members of this family, e.g. colourless, yellowish, greenish, green, brown, black, and violet.

The cleavage is most perfect and parallel to  $\{001\}$ . The leaves are elastic, some of which luminesce in the darkness when split. When watched through a thin mica plate against a shining object, there appears a 6 or 12-ray star (particularly in some phlogopites of the Slyudyanka deposit), which can be explained by the oriented inclusions of the rutile needles.

The hardness is approximately two, and the density reaches 3.2. The iron-free micas are characterized by dielectric properties and are fireproof.

Micas are widespread in nature. They account for 3.7% of all the minerals of the Earth's crust. They enter into the composition of a large number of igneous and metamorphic rocks. Micas of pegmatite and contact-metasomatic origin are of industrial importance.

**MUSCOVITE**  $KAl_2[Si_3AlO_{10}](OH,F)_2$ 

In the crystalline structure the  $Al^{3+}$  ions occupy  $2/3$  of octahedral voids of the 'hydrargillite' layer.

The mineral is colourless or yellowish, light-green, light-brown, sometimes with a reddish tinge.

*Varieties.* *Sericite* is fine-crystalline light muscovite, which is the product of the decomposition of aluminosilicates (mainly feldspars), its lustre is silky. *Fuchsite* is a chromium-bearing variety of muscovite of bright-green colour characteristic of listvenites.

*Origin.* Muscovite of magmatic origin is related to igneous rocks. The metamorphic origin is associated with crystalline schists. Large muscovite plates of industrial value are found in the pegmatite veins in association with microcline, oligoclase, biotite, shorl, and apatite. *Deposits.* In the USSR the deposits are in the north of the Irkutsk Region in the basins of the Mama and Chuya Rivers, in Karelia (the Ensk deposits, etc.), and in Eastern Sayan (the Biryusinka deposit). In other countries there are deposits in India and Brazil.

*Practical use.* Muscovite is used in electrical industry, radio engineering and instrument making, where the dielectric properties of this mineral are made use of. Large transparent muscovite plates are inserted into the windows of metallurgical furnaces and chemical stoves. Mica powder (scrap), resulting from the cutting of sheet mica, finds its application as a refractory roofing material, in the production of fireproof wallpaper, paper, paints, lubricants, and automobile tyres.

**PHLOGOPITE**  $KMg_3[Si_3AlO_{10}](OH,F)_2$ 

In the crystalline structure the  $Mg^{2+}$  ions occupy all the octahedral positions of the 'brucite' layer.

The colour is brown, of various shades.

*Origin.* Phlogopite of the contact-metasomatic (skarn) origin, is characteristic of some magnesian contact zones of Precambrian age. The mineral associates with diopside, calcite, apatite, scapolite, spinel, and other minerals.

*Deposits.* In the USSR, the Slyudyanka deposit is on the southern shore of Lake Baikal. The Aldan, Emeldzhak, Leglier, and others are in Yakutia, the Kovdor deposit is in the Kola peninsula. In countries outside the USSR phlogopite is also found in Canada, South Africa, and India.

*Practical use.* They are the same as those of muscovite.

**BIOTITE**  $K(Fe, Mg)_3[Si_3AlO_{10}](OH,F)_2$ 

The crystalline structure is similar to the structure of phlogopite.

The colour is black. Among micas it is the most widespread mineral.

*Varieties.* *Lepidomelane* does not contain magnesium. Its colour is black. The mineral is characteristic of alkaline rocks (the Urals).

*Origin.* The magmatic origin is related to biotite granites; biotite of pegmatite origin is found in veins with or without muscovite; the metamorphic origin is associated with various schists and gneisses. Since biotite contains iron, it cannot be used as a dielectric.

**LEPIDOLITE**  $KLi_{1.5}Al_{1.5}[Si_3AlO_{10}](OH, F)_2$ 

$Rb^+$  is sometimes present. In the crystalline structure the  $Li^+$  ions occupy the octahedral positions.

The colour is pink, light-purple; sometimes the mineral is colourless. The leaves, as distinct from other micas, usually do not yield large plates. It often has curved shell-like forms and fine-grained masses. *Origin.* Lepidolite is found in rare-metal pegmatites and greisens. In pegmatites it associates with cleavelandite, quartz, spodumene, polychromatic tourmaline, and beryl.

*Deposits.* In the USSR there are deposits of this mineral in Kazakhstan, in the Urals, in the Transbaikal region. In other countries the deposits are in the USA, SAR, Sweden, Afghanistan, etc. *Practical use.* When its accumulations are substantial, the mineral serves as an ore of lithium.

### Aquatic

#### The Family of Hydromicas

Hydromicas represent hydrated layered aluminosilicates and are intermediate formations between micas, chlorites, and clay minerals. The crystalline structure of hydromicas is characterized by a deficiency of  $K^+$  ions and its replacement by the molecules of water, the ions of hydroxonium ( $H_3O^+$ ) or the hydrated  $Mg^{2+}$  ions.

The system is monoclinic. The composition is both complex and irregular. Hydromicas resemble micas, but their leaves are not elastic.

**VERMICULITE** ( $Mg, Fe^{2+}, Fe^{3+}$ )<sub>3</sub> [(Si, Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> · 4H<sub>2</sub>O

In its crystalline structure the hydrated  $Mg^{2+}$  ions are located between the packets.

The colour is golden- or bronze-yellow. The hardness is 1-1.5. When heated, the mineral becomes bulged, increases in its volume by 15-25 times. Burned vermiculite becomes very light, and floats in the water.

*Origin.* Vermiculite is formed at the expense of biotite and phlogopite. *Deposits.* In the USSR, the deposits are in the Urals (the Vishnevye Mountains), in Karelia (Kovdor) and elsewhere.

*Practical use.* When calcined, vermiculite is used as a heat-insulating material.

**GLAUCONITE** ( $K, H_2O$ )( $Fe^{3+}, Al, Fe^{2+}, Mg$ )<sub>2</sub> [ $Si_3AlO_{10}$ ] (OH)<sub>2</sub> ×  $nH_2O$ , contains 4.0-9.5% of  $K_2O$

The crystalline structure is transitory between the structures of micas and that of montmorillonite.

The mineral is earthy, and is usually found in sedimentary rocks in the form of irregular grains, particularly in sandy, clay, and clay-carbonate rocks. It functions as cement in sandstones, and is often found in sands (glaucconite sands). The colour is green of various shades.

*Origin.* Glaucconite of sedimentary origin is formed in the seas and oceans, and is possibly connected with the activity of various organisms, as well as in soils.

*Deposits.* Glaucconite sands are known in a large number of places in the European part of the USSR, e.g. in the Ukraine, in the Kursk, Orel and Kirov regions.

*Practical use.* Glaucconite can serve as a potassium fertilizer, and is used as green paint, as well as for water treatment.

### The Family of Montmorillonite

**MONTMORILLONITE**  $(Al, Mg)_2[Si_4O_{10}](OH)_2 \cdot 4H_2O$  and **BEIDELLITE**  $Al_2[Si, Al)_4O_{10}](OH)_2 \cdot 4H_2O$

usually contain  $Na^+$  ions. The crystalline structure is three-layered. In each packet there is an octahedral layer with  $Al^{3+}$  and  $Mg^{2+}$  between the silicon-oxygen hexagonal nets. The bonds between the packets are weak, of van der Waals type. The molecules of adsorptional interlayer water can occur between them.

Montmorillonite enters into the composition of *bentonitic clays*, the characteristic feature of which is their marked swelling in the presence of water.

The colour is white, pink, and grey. The lustre is dull. The hardness equals one.

*Origin.* The mineral is formed under the weathering of effusive rocks (tuff, ash) and by means of sedimentation.

*Practical use.* Montmorillonite is used as a whitening material in textile industry, for the fixing of drilling holes, etc.

**NONTRONITE**  $(Fe, Al)_2[(Si, Al)_4O_{10}](OH)_2 \cdot 4H_2O$

The composition is not constant. The mineral usually contains the ions of  $Na^+$ ,  $Ca^{2+}$ , and Ni. In terms of its structure, it is analogous to montmorillonite, and is found in earthy masses.

The colour is grey-green and yellow-green. The lustre is dull. The hardness is about two.

*Origin.* The mineral is formed in weathering crust of ultrabasic rocks.

*Deposits.* In the USSR, there are deposits in the Southern Urals and in West Kazakhstan (the Buruktaus, Buranovsk, Chuguev and other deposits).

*Practical use.* Nickel-bearing nontronites are a splendid ore of nickel.

**CHRYSOCOLLA**  $Cu_4[Si_4O_{10}](OH)_2 \cdot 4H_2O$

The structure is cryptocrystalline. It is found in opaline-like sintered masses in the form of crusts, powder with bubble surface.

The colour is light-blue or greenish-blue. The streak is greenish-white. The lustre is vitreous or waxy. The hardness equals 2-3, and the density is 2.0-2.3.

*Origin.* Chrysocolla is a typical mineral of the oxidation zone of copper and other ore deposits, containing the sulphides of copper. It is found together with malachite, azurite, cuprite, native copper, gypsum, opal, and hydroxides of iron.

As far as its implementation is concerned, it is practically of no value; only occasionally it is used in melting with other oxygenous minerals of copper. It is a prospecting mineral of copper, and is particularly widespread in copper and other deposits in Kazakhstan and Central Asia.

## Silicates and Aluminosilicates with Multilayered Packets

### With Additional Anions

#### The Family of Chlorites

Chlorites comprise layered aluminosilicates of magnesium, iron, and aluminium, and sometimes contain nickel and chromium. In the crystalline structure of most of the chlorites the three-layered packets

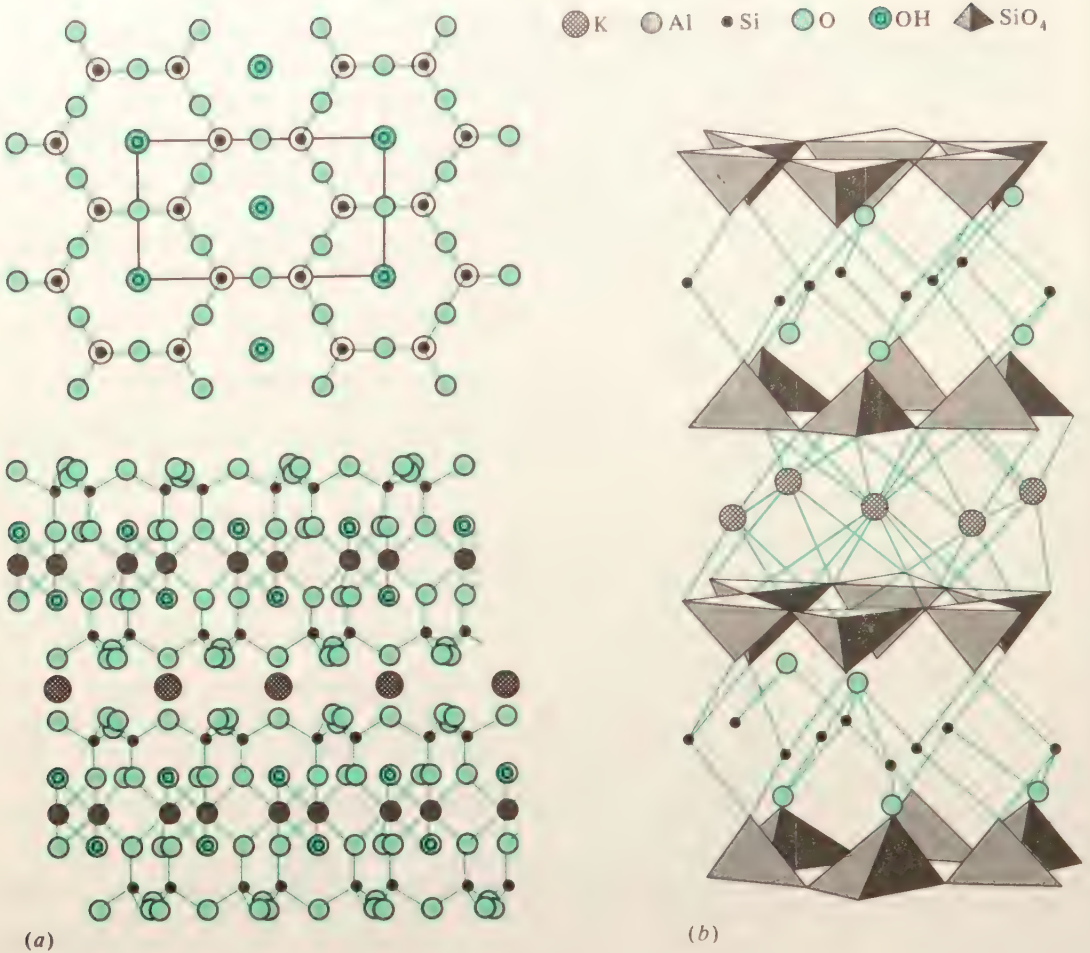


Fig. 112. The structure of muscovite in its projection on {001} (a) and {100} (b), and the general aspect of the structure (c)

of the talc type  $Mg_3[Si_4O_{10}](OH)_2$  alternate with the layers of the brucite type  $Mg(OH)_2$ , or of hydrargillite type  $Al(OH)_3$  (see Fig. 108, 111), which finds its expression in the crystallochemical formulae. A large number of polytypes has been established for chlorites. The variety of chemical composition of chlorites is conditioned by wide isomorphous replacements of the main elements:  $Mg^{2+} \rightarrow Fe^{2+} \rightarrow Mn^{2+} \rightarrow Ni^{2+}$ ,  $Al^{3+} \rightarrow Fe^{3+} \rightarrow Cr^{3+}$  as well as  $Si + Mg \rightarrow Al_2$  and  $Mg_3 \rightarrow Al_2$  both in the three-layered packets and in the octahedral layers. Chlorites also form mixed-layered minerals, which are characterized by the alternation of multilayered packets of chlorite, different in their composition, and other layered minerals.

Chlorites are crystallized in a monoclinic system. They usually form foliated, scale aggregates and block masses. Some of them (e.g. chamosite) are characterized by cryptocrystalline aggregates and oölites. The colour of chlorites is green (the term is derived from the Greek word 'chloritis', which means 'green') of various shades to greenish-black, though sometimes it is white and yellowish. The cleavage parallel to {001} is perfect; the leaves are flexible, but, as



distinct from micas, they are not elastic. The hardness is 2-3, and the density is 2.6-2.9.

In accordance with the composition and structural characteristics, magnesian and ferrous chlorites are singled out. It is practically impossible to distinguish the two without chemical analyses and special X-ray-structural, physical and thermal investigations.

PENNINE (Mg, Al)<sub>6</sub>[Si<sub>3.5</sub>Al<sub>0.5</sub>O<sub>10</sub>](OH)<sub>8</sub>, CLINOCHLORE (Mg, Al)<sub>6</sub>[Si<sub>3</sub>AlO<sub>10</sub>](OH)<sub>8</sub> and PROCHLORITE (tripidolite) (see Fig. 111) (Mg, Fe, Al)<sub>6</sub>[Si<sub>2.5</sub>Al<sub>1.5</sub>O<sub>10</sub>](OH)<sub>8</sub>

usually have a characteristic colour, which is green. They are widely spread in nature and the main rock-forming minerals of talc-chlorite, sericite-quartz-chlorite, chlorite-actinolite and other rocks of metamorphic origin. The process of chloritization, which is widespread in nature, consists in the transformation of hornblende and biotite into chlorite. The presence of chlorites can also be relevant in determining the low-temperature hydrothermal conditions in which rocks, containing the silicates of magnesium and iron undergo changes. Chlorites are often formed in the veins of Alpine type. Chrome-bearing varieties of pennine and chlinochlore are found together with chromites. They are *kaemmererite* and *kotschubeite*. Both of them are of purple colour.

CHAMOSITE (Fe<sup>2+</sup>, Mg, Fe<sup>3+</sup>)<sub>6</sub>[Si<sub>3</sub>AlO<sub>10</sub>](OH)<sub>8</sub> and THURINGITE (Fe<sup>2+</sup>, Mg, Fe<sup>3+</sup>, Al)<sub>6</sub>[Si<sub>2</sub>Al<sub>2</sub>O<sub>10</sub>](OH, O)<sub>8</sub>

are prevalent among the ferrous chlorites. They have a darker colour as compared with the magnesium chlorites. Chamosite is distinguished by its greenish-black streak and oölitic structure, while thuringite usually forms earthy, cryptocrystalline and dispersed masses of dark-green colour.

*Origin.* Their origin is connected with the formation of sedimentary and sedimentary metamorphic deposits of iron in conditions of restoration.

*The deposits* of ferrous chlorites are known in FRG and in France.

*Practical use.* Both chamosite and thuringite serve as an orer of iron.

## Aluminosilicates and Their Analogues of Frame Structure (Tectosilicates)

The composition of aluminosilicates with frame structure include, besides silica and aluminium, large cations of alkaline and alkaline-earthly metals, mainly the ions of Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup>, and much more rarely those of Ba<sup>2+</sup>, Sr<sup>2+</sup>, and Cs<sup>+</sup>, which occupy large cavities in the structure and are in coordination of 8, 9 and more oxygen ions, as well as of additional anions (OH)<sup>-</sup>, Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> or S<sup>2-</sup>. Sometimes, as an impurity, there is the presence of Fe<sup>3+</sup> and Ti<sup>+</sup> ions, replacing the positions of Al<sup>3+</sup> and Si<sup>4+</sup> ions. In rare beryl-silicates the cations are represented by the ions of Mn<sup>2+</sup>, Fe<sup>2+</sup> and Zn<sup>2+</sup>.

In frame aluminosilicates the Al<sup>3+</sup> ions, occupying the tetrahedral positions of Si<sup>4+</sup> ions, produce a negative charge of the frame, which is equivalent to the number of Al<sup>3+</sup> ions. The limits of replacement of the

positions of  $\text{Al}^{3+}$  ions by  $\text{Si}^{4+}$  ions depend on the total number of tetrahedrons in the elementary cell of the frame structure. In the general formula of the frame radical  $[\text{Si}_{n-p}\text{Al}_p\text{O}_{2n}]^{p-}$  this number is indicated by the index  $n$ . With the increase of the number  $n$  in the frame, there can also be an increase in the number of  $\text{Al}^{3+}$  ions (marked by the index  $p$ ), replacing the positions of  $\text{Si}^{4+}$  ions, but not more than by half, i.e.  $p \leq 1/2n$ . The negative charge of the frame is equal to the number  $p$ .

The number of tetrahedral groups in cell  $n$  serves as a distinguishing feature in singling out the structural types of frame radicals and, consequently, the more rational subdivisions into subclasses with radicals of the type  $[\text{SiAlO}_4]^-$ ,  $[\text{Si}_2\text{AlO}_6]^-$ ,  $[\text{Si}_3\text{AlO}_8]^-$ ,  $[\text{Si}_2\text{Al}_2\text{O}_8]^{2-}$ ,  $[\text{Si}_4\text{AlO}_{10}]^-$ ,  $[\text{Si}_3\text{Al}_2\text{O}_{10}]^{2-}$  etc. Among them together with simple and complex types, we have aluminosilicates, containing additional anions or molecules of water, which are distributed in the large voids of the frame structure.

## Aluminosilicates with Radicals $[\text{SiAlO}_4]^-$ (Feldspathoids)

*Feldspathoids* include frame aluminosilicates of  $\text{Na}^+$  and  $\text{K}^+$  which are close, as far as their composition is concerned, to feldspars, but differ from them in that their content of silicic acid is low, and that of alkaline is considerably higher.

### Complex

NEPHELINE  $\text{KNa}_3[\text{SiAlO}_4]_4$  (up to 17% of  $\text{Na}_2\text{O}$ ; up to 11% of  $\text{K}_2\text{O}$ ; up to 34.6% of  $\text{Al}_2\text{O}_3$ )

The mineral also contains the impurities of Rb, Ga, etc. In the crystalline structure (Fig. 113) the aluminosilico-oxygenous tetrahedrons form a frame with the ratio  $\text{Al}:\text{Si} = 1:1$ . The  $\text{K}^+$  and  $\text{Na}^+$  cations are distributed in the large voids with the coordination number 9 and 8 respectively.

The system is hexagonal. The crystals are small, prismatic (Fig. 113); or as embedded grains they form block confluent masses.

The colour is grey, reddish, greenish; sometimes the mineral is colourless. The lustre is greasy. There is no cleavage. The hardness equals 5.5, and the density is 2.6. As a result of weathering, there appears at the surface of nepheline a friable white crust, consisting of hydroxides  $\text{Al}^{3+}$  and zeolites (spreustein).

*Varieties.* *Eleolite* is a coarse-crystalline variety of nepheline with a greasy lustre of the meat-red colour.

*Origin.* The magmatic origin is related to rocks, poor in silicic acid, but rich in sodium (in nepheline sienites and alkaline pegmatites), in association with apatite, aegirine, feldspar, biotite, ilmenite, sphene, zircon and other minerals pertaining to alkaline rocks. It is not found with quartz.

The products of hydrothermal alteration of nepheline are: albite, cancrinite, sodalite and zeolites. In hypogene conditions nepheline is easily destroyed and is replaced by spreustein.

*Deposits.* Nepheline is found in the Kola peninsula, where it is

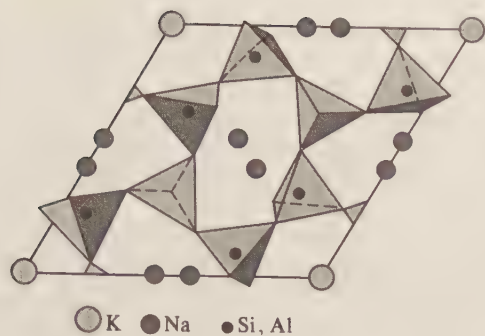


Fig. 113. Nepheline structure

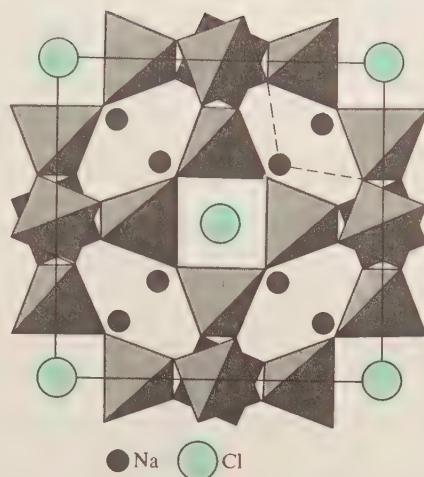


Fig. 114. Sodalite structure projected on {001}

recovered together with apatite. There are nepheline deposits in the Ilmen and Vishneve Mountains in the Urals. A large deposit of nepheline has been discovered at the foothills of the Kuznetsk Alatau Mountains (Belogorsk).

*Practical use.* This mineral serves as an ore of aluminium. Nepheline is used in the production of sodium carbonate and potash. Rare alkaline metals and gallium can be extracted.

#### With Additional Anions

#### The Family of Cancrinite-Sodalite

**CANCRINITE**  $\text{Na}_6\text{Ca}_2[\text{SiAlO}_4]_6[\text{CO}_3, \text{SO}_4](\text{OH})_2$  with a wide isomorphic miscibility between  $[\text{CO}_3]^{2-}$  and  $[\text{SO}_4]^{2-}$ . Besides,  $\text{Cl}_2$ ,  $\text{K}^+$ , and  $\text{Ba}^{2+}$  are sometimes present. In the crystalline structure the hexagonal rings of alumo- and silica-oxygenous tetrahedrons are combined with the formation of large channels. The hexagonal rings contain  $[\text{CO}_3]^{2-}$  or  $[\text{SO}_4]^{2-}$ , while the group of  $(\text{OH})^-$  are located in the channels.

The system is hexagonal. The crystals are of tabular and prismatic form. The mineral forms crystalline-granular aggregates, as well as edges of replacement around nepheline and pseudomorphs after it.

The colour is white, yellowish, pink, with a latticed distribution of colour, and light-blue. The lustre is vitreous to purple. The cleavage is perfect and parallel to the prism {1010}. The fracture is step-like, uneven. The hardness is 5-5.5, and the density is 2.4-2.5.

*Varieties.* *Vishnevite* is a blue variety of sulphate-cancrinite.

*Origin.* The magmatic origin is related to the alkaline rocks and pegmatites. It is also formed at the expense of nepheline (metasomatic).

*Deposits.* In the USSR there are deposits in the Urals (the Vishneve and Ilmen Mountains), in the Kola peninsula (the Lovozerskii Massif), in Tuva, and Yakutia. Outside the USSR the mineral is also mined in Sweden.

**SODALITE**  $\text{Na}_8[\text{SiAlO}_4]_6\text{Cl}_2$  also contains  $\text{K}^+$ ,  $\text{Fe}^{3+}$ ,  $[\text{CO}_3]^{2-}$ ,  $(\text{OH})^-$ , sometimes  $[\text{MoO}_4]^{2-}$ , and  $\text{S}_2^{2-}$ . In the crystalline structure of sodalite (Fig. 114) the frame

consists of four-, or six-fold rings of alumo- and silica-oxygenous tetrahedrons. In the large cavities there are additional anions, each of which is tetrahedrally surrounded by four cations of  $\text{Na}^+$  or  $\text{Ca}^{2+}$ .

The system is cubic. The crystals are rarely found in the form of rhombic-dodecahedrons  $\{110\}$ . The mineral usually has the form of granular aggregates, replacing nepheline, and more seldom as disseminations in effusive and irregular concentrations.

The colour of sodalite is white; in semitransparent extractions it is colourless; greenish, bluish, and sometimes pink; the mineral is photochemically unstable. The cleavage is distinct, parallel to  $\{110\}$ . The fracture is uneven. Sodalite is brittle, its hardness is 5.5-6, and the density is 2.1-2.4. The mineral luminesces in the ultraviolet light. *Varieties.* *Hackmanite* is the sulphur-bearing sodalite with pink, unstable to the light colouring, changing into greyish-green, and with bright orange luminescence.

*Origin.* The mineral is found in the form of phenocrysts in lavas, as well as in alkaline rocks, and pegmatites together with nepheline, aegirine, microcline, arfvedsonite, sphene, and eudialyte. It is also formed at the expense of nepheline (the metasomatic origin).

*Deposits.* In the USSR sodalite is found in the Kola Peninsula, in the Urals. Outside the USSR there are deposits of this mineral in the lavas Vesuvius (Italy).

#### LAZURITE $\text{Na}_6\text{Ca}_2 [\text{SiAlO}_4]_6(\text{SO}_4, \text{S}, \text{Cl}_2)$

The crystalline structure is analogous to the structure of sodalite.

The system is cubic. The crystals are rare, and are usually in the form of granular masses.

The colour is bright dark-blue to blue-purple. The cleavage is distinct. The fracture is uneven. The hardness equals 5.5, and the density is 2.3-2.4.

*Origin.* The metasomatic origin is related to magnesian skarns with phlogopite, diopside, forsterite, calcite, and pyrite.

*Deposits.* In the USSR the mineral is recovered from the deposits in the southern Baikal region along the Malaya Bystraya River (the Irkutsk Region), and in the Pamir Mountains. In other countries, there are deposits in Afghanistan.

*Practical use.* Lazurite is a beautiful semiprecious stone.

#### HELVITE $(\text{Mn}^{2+})_4 [\text{SiBeO}_4]_3\text{S}$ (up to 14% of BeO)

There are wide isomorphic replacements of  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Zn}^{2+}$ . The crystalline structure is similar to that of sodalite, the difference between them consisting in that the place of  $\text{Al}^{3+}$  is occupied by  $\text{Be}^{2+}$  in tetrahedral coordination.

The system is cubic. The crystals are of tetrahedral habit, and the aggregates are granular.

The colour is yellow, yellow-green, yellow-brown, reddish to brown. The lustre is vitreous to resinous. The cleavage is distinct, parallel to the  $\{111\}$  tetrahedron. The hardness is 6-6.5, and the density is 3.2-3.7.

*Origin.* The mineral is formed in granites and alkaline pegmatites, in skarns together with magnetite, fluorite, chrysoberyl, and bertrandite, in hydrothermal quartz veins.

*Deposits.* In the USSR there are deposits of this mineral in Kazakhstan, the European part of the USSR, and in Siberia. In other

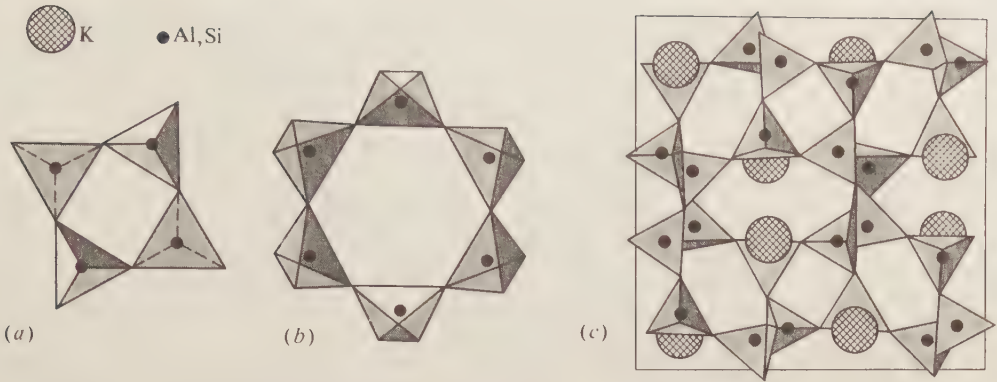


Fig. 115. Leucite structure:  
*a*—fourfold and *b*—sixfold rings; *c*—projection on {001}

countries, helvite is mined in the USA (Butte, Montana), Sweden, Norway, and elsewhere.

*Practical use.* When substantially accumulated, the mineral is used as an ore of beryllium.

## Aluminosilicates with Radical $[\text{Si}_2\text{AlO}_6]^-$

### Simple

#### LEUCITE, $\text{K} [\text{Si}_2\text{AlO}_6]$

also contains  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ti}^{4+}$ , etc. In the crystalline structure of leucite (Fig. 115) the frame is composed of four-, and six-fold rings of aluminosilicate tetrahedra. The  $\text{K}^+$  ions with coordination number 12 are distributed in the channels formed by hexagonal rings. The high-temperature (cubic) modification is distinguished by a greater symmetry of hexagonal rings and the location of  $\text{K}^+$  ions in the centre of the channels. The transition to a low-temperature modification at  $660^\circ$  is accompanied by the symmetry dropping down and becoming tetragonal with polysynthetic twinning.

The system is pseudocubic. The mineral usually occurs as isometric crystals in the form of tetragonal-trioctahedrons {210}, often fused, and spherical.

The colour is white, ash-grey. The lustre is vitreous. There is no cleavage. The hardness is 5.5-6, and the density is 2.5.

*Origin.* Leucite is a mineral of young effusive rocks. It is found in lavas, tuffs, and volcanic ash. The mineral is formed under the solidification of lavas rich in potassium and poor in silicic acid. Hence, it is not found with quartz.

*Deposits.* Large beautiful crystals are known in Italy (Mount Vesuvius), and are rarely found in the Transcaucasus.

*Practical use.* When the rock contains a considerable amount of leucite, the former may serve as a raw material for the production of aluminium and potassium fertilisers.

### Aquatic

#### ANALCITE $\text{Na} [\text{Si}_2\text{AlO}_6] \cdot \text{H}_2\text{O}$

An inconsiderable redundancy of  $\text{Si}^{4+}$  and the impurity of  $\text{Ca}^{2+}$ , as well as  $\text{K}^+$  are known to be common with this mineral. In its

crystalline structure, the silica-oxygenous frame radical, which is similar to that of leucite, and the  $\text{Na}^+$  ions occupy small, sectionally square, voids (voids in leucite). In large voids (the place of  $\text{K}^+$  ions in leucite) there are molecules of water. Analcite is found in its two structural varieties, distinguished by the regularity with which  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  are distributed.

The system is pseudocubic. Analcite is found in the form of regular tetragonal-trioctahedron crystals, and often forms druses.

The colour is white, light-grey, sometimes reddish-pink or greenish at the expense of the inclusions of other minerals. The lustre is vitreous, the cleavage is absent. The fracture is uneven. The hardness equals 5-5.5, and the density is 2.3.

*Origin.* Analcite of magmatic origin forms disseminations in middle and alkaline rocks, and fills the amygdules in basalts. As a product of the hydrothermal change, it is widely spread among igneous rocks of the basic and middle composition. This mineral is also formed in sedimentary rocks.

#### POLLUCITE $\text{Cs}_{1-n}\text{Na}_n[\text{Si}_2\text{AlO}_6] \cdot n\text{H}_2\text{O}$

The mineral is characterized by an incomplete isomorphic miscibility with analcite, and usually contains a redundancy of silica, and the  $\text{K}^+$  and  $\text{Rb}^+$  ions. The crystalline structure resembles the structures of analcite and leucite. The  $\text{Na}^+$  ions occupy the small voids, as is the case with analcite and  $\text{Cs}^+$  cations are large voids and are likely to  $\text{K}^+$  ions in leucite, in which the  $\text{H}_2\text{O}$  molecules are also present. Both analcite and pollucite are represented by two structural varieties, the distinguishing feature of which is the regularity with which  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  are distributed.

The system is pseudocubic. Pollucite is found in block granular or confluent masses, sometimes in porcelain-like accumulations in the form of large xenomorphic extractions and pseudomorphs after spodumene and other minerals of lithium. The crystals are exceptionally rare.

The colour is white; in its transparent varieties the mineral is colourless; it is often light-grey or pink at the expense of the inclusions of other minerals and the products of its alteration. The lustre is vitreous; in compact masses it is dull. The cleavage is absent. The fracture is uneven and shelly. The hardness equals 6.5, and the density fluctuates depending on the composition between 2.65 and 3.0.

*Origin.* Pollucite is formed exclusively in the granite pegmatites of the rare-metal-replacement type together with lepidolite, spodumene, petalite, green and pink tourmaline, cleavelandite, amblygonite, etc.

*Deposits.* In the USSR there are deposits in Eastern Kazakhstan, the Pamir Mountains, and in the Kola peninsula. In other countries the mineral is deposited in the Island of Elba, the USA, South Africa, Sweden, and Afghanistan.

*Practical use.* Pollucite is the most important ore of caesium.

## Aluminosilicates with Radicals $[\text{Si}_3\text{AlO}_8]^-$ , $[\text{Si}_2\text{Al}_2\text{O}_8]^{2-}$ , $[\text{Si}_2\text{B}_2\text{O}_8]^{2-}$ , etc.

### Simple (Feldspars)

*Feldspars* include frame aluminosilicates of alkaline and alkaline-earth cations of  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , as well as  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ . Besides, it has been discovered that the composition contains the impurities of  $\text{Cs}^+$ ,  $\text{Rb}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Tl}^+$ , etc. In the formula of the alumo-silica-oxygenous radical of feldspars  $[\text{Si}_{4-p}\text{Al}_p\text{O}_8]^{p-}$  the index  $p$  can take the values from 1 to 2; consequently, the charge of the radical also changes, and is compensated by one-, or two-valent cations with coordination number between 8 and 10. In the crystalline structure of feldspars we can single out four-member ring links, which form chains elongated along the  $C$  axis and interconnected by the common ions of oxygen (Fig. 116). The tetrahedrons located along the axis of these chains are not identical to the lateral tetrahedrons. This is closely connected with the structural organization of  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  ions in feldspars. The irregularly organized structures of minerals, formed in high-temperature conditions, are congruous with a greater degree of symmetry.

Feldspars are characterized by a wide isomorphous miscibility of the isoivalent type between potassium and sodium feldspars (potassium-sodium feldspars, anorthoclases) and the heterovalent type between sodium and potassium feldspars (sodium-potassium feldspars, plagioclases). The degree of miscibility depends on the temperature of crystallization (see Fig. 12). More restricted isomorphous replacements have been determined between K- and Ca- feldspars, as well as in the K-Sr-Ba-feldspars series.

Fig. 116. Feldspar structure in globular (left) and polyhedral models (right): the fourfold ring links bound into chains by common oxygen ions

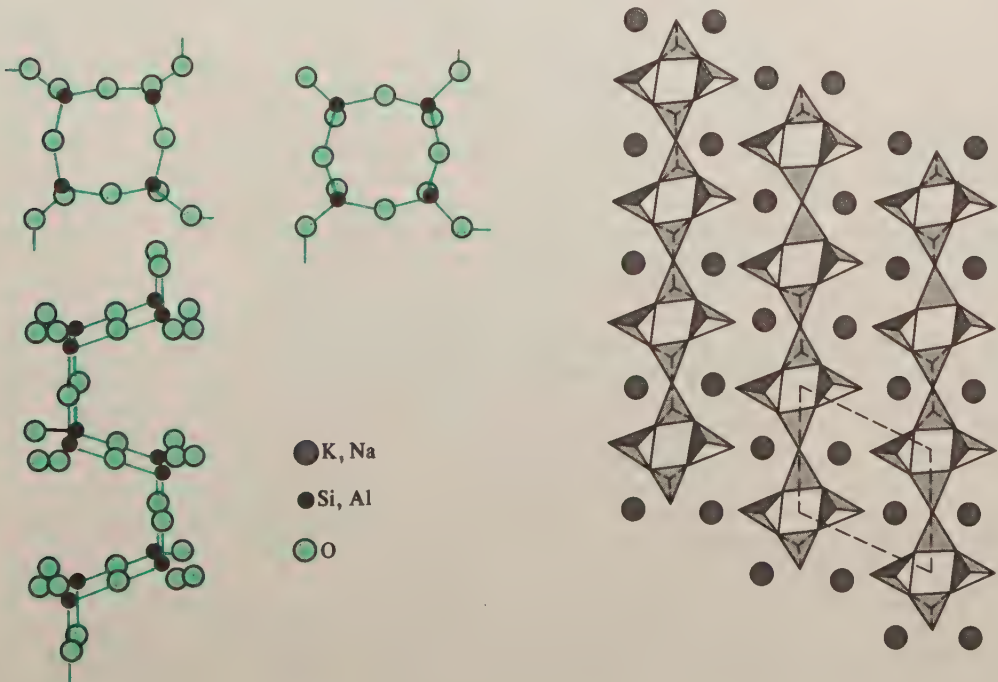
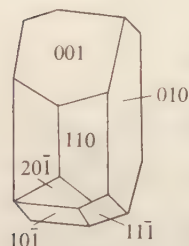
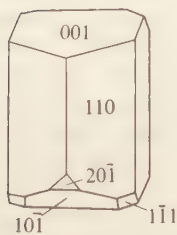
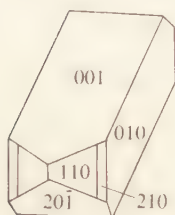
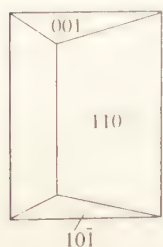


Fig. 117. Feldspar crystals



SANIDINE (K, Na)  $[\text{Si}_3\text{AlO}_8]$ , ORTHOCLASE (K, Na)  $[\text{Si}_3\text{AlO}_8]$ , and MICROCLINE (K, Na)  $[\text{Si}_3\text{AlO}_8]$

are, in all respects, potassium representation of the isomorphous series of K-Na-feldspars. They contain the isomorphous impurity of  $\text{Ca}^{2+}$ ;  $\text{Cs}^+$ ,  $\text{Rb}^+$ ,  $\text{Tl}^+$ ,  $\text{Pb}^{2+}$ , as well as  $\text{Fe}^{3+}$ . In the crystalline structure of the high-temperature K-Na-feldspars  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  are irregularly distributed in the tetrahedrons (sanidine). The lowering of temperature is accompanied by a partial (orthoclase) or complete (microcline) restoration of the regularity with which  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  are distributed along the non-equivalent positions. Besides, with the decrease in temperature in K-Na-feldspars there is an orderly rearrangement of K<sup>+</sup> and Na<sup>+</sup> followed by the disintegration of the solid solution with the formation of decomposition perthites, i.e. inclusions of Na-feldspar in K-feldspar.

The system of sanidine and orthoclase is monoclinic; that of microcline is triclinic. The crystals are usually well formed (Fig. 117), and are often found in the form of twins (see Fig. 31); they form crystalline grains and crystalline-granular masses, as well as crystal druses of gigantic dimensions (weighing many tons).

The colour is light-grey, yellow, light-pink to red; sometimes it is green, white or altogether colourless; the colour is often unevenly distributed, mottled.

Not infrequently the mineral is semitransparent and transparent. The lustre is vitreous. The cleavage is perfect and parallel to  $\{001\}$ ,  $\{010\}$ . The angle between the cleavage planes of sanidine and orthoclase equals 90, while with microcline it differs by less than 0.5. The hardness is 6-6.5, and the density is 2.5-2.6.

*Varieties.* Water-transparent crystals of orthoclase that are usually found in the veins of the Alpine type are called *adular*. *Moonstone* is a variety of adular of a tender light-blue colour with a silvery-purple tinge. *Amazonite* (the amazon stone) is a variety of green or bluish-green microcline. *Perthite* is K-Na-feldspar crystals, containing regularly oriented inclusions of the decomposition of albite, of usually white colour, sometimes distinguished by the naked eye.

*Origin.* The magmatic origin is related to acid, middle, and alkaline rocks, as well as to pegmatites, and apogranites. It is found in high-temperature hydrothermal veins and in the veins of the Alpine type. It also enters into the composition of metamorphic rocks, i.e. gneisses and crystalline schists.

*Deposits.* In the USSR there are large deposits of ceramic pegmatites in Karelia. Amazonite is found in the pegmatites of the Ilmen Mountains in the Urals, in the pegmatites and granites in Kazakhstan, the Transbaikalian region, and the Kola peninsula. In other countries large deposits of ceramic pegmatites are known in the USA, Canada, and in Scandinavian countries. Transparent amazonite is found in the pegmatites in Madagascar.

*Practical use.* K-Na-feldspars from pegmatites serve as a raw material for ceramic and glass industries. Moonstone and amazonite are used as semiprecious stones.

ALBITE  $\text{Na}[\text{Si}_3\text{AlO}_8]$  and ANORTHITE  $\text{Ca}[\text{Si}_2\text{Al}_2\text{O}_8]$

are the extreme members of the isomorphous series of *plagioclases*. The intermediate members of the series that have been singled out, are



distinguished by their composition, which is designated by the molar per cent of anorthite content or by a corresponding number:

Albite No. 0-10	}	acid plagioclases
Oligoclase No. 11-30		
Andesine No. 31-50	}	middle plagioclases
Labradorite No. 51-70		
Bytownite No. 71-90	}	basic plagioclases
Anorthite No. 91-110		

Thus, for instance, plagioclase No. 36 corresponds to andesine, containing 36 molar per cent of anorthite and 64 molar per cent of albite (36% of An, 64% of Ab). Plagioclases are distinguished in that they contain from 68.8 molar per cent of silicic acid in albite to 43.28% molar per cent of the same in anorthite. Hence, acid plagioclases are more often found in the acid igneous rocks, the middle ones in the middle and the basic acid plagioclases in the basic or ultrabasic rocks.

In the crystalline structure the  $\text{Na}^+$  ions have their coordination number 7; with Ca the coordination number is 8. The high-temperature structural varieties of plagioclases of any composition, with the exception of anorthite, have the same type of disordered monoclinic structure of albite. The high-temperature anorthite is characterized by a body-centered elementary cell. The mid- and low-temperature plagioclases are characterized by a variety of structural types, representing the products of the disintegration of solid solutions of various degree of organization and their fine intergrowths.

The system of the low-temperature varieties of plagioclase is triclinic. The well-formed crystals are rare. The phenocrysts and grains of irregular form are usually twinned. Polysynthetic (see Fig. 26) and complex twins are very common. Acid plagioclases often form druses, brushes, and tabular-radiated aggregates, particularly in pegmatites, as well as crystalline-granular monomineral rocks (albites and anorthosites). In the form of perthite intergrowths or along the metasomatic veinlets they are found in potassium-sodium feldspars.

The colour of plagioclase is usually white, not infrequently grey, and pink, at the expense of various inclusions. The lustre is vitreous. Orthoclase is characterized by blue iridescence, which is yellow, blue, or green with labradorite. The cleavage is perfect, parallel to  $\{001\}$  and  $\{010\}$  at an angle of approximately  $70^\circ$ . The hardness is 6-6.5. The density is from 2.6 (albite) to 2.76 (anorthite).

*Varieties.* *Saccharoidal albite* (fine-grained aggregates) and *cleavelandite*, which has the form of foliated and radiated aggregates of white or bluish albite found in pegmatites. *Labradorite* is a dark coarse-crystalline rock with bright iridescence of labradorite at the cleavage  $\{010\}$  surfaces. *Belomorite* is a variety of oligoclase with a beautiful tender-blue iridescence.

*Origin.* The magmatic origin is associated with various igneous rocks. The mineral is formed in pegmatites at the early stages, and later in the process of albitization. It is a rock-forming mineral of a large number of metamorphic rocks, and is a metasomatic mineral in skarns and greisens.

*Deposits.* The mineral is not a rare find. In the USSR labradorite deposits are developed in the Ukraine (the Turchin deposit, etc.).

*Practical use.* Labradorite is used as a facing material. Belomorite serves as a semiprecious stone.

#### With Additional Anions (scapolites)

MARIALITE  $\text{Na}_4[\text{Si}_3\text{AlO}_8]_3\text{Cl}$  and MEIONITE  $\text{Ca}_4[\text{Si}_2\text{Al}_2\text{O}_8]_3 \times (\text{CO}_3, \text{SO}_4)$

are the extreme members of the isomorphic series of *scapolites*. In the frame crystalline structure of scapolites the alumo- and silica-oxygenous tetrahedrons form chains of the wollastonite type amalgamated into four-fold columns, between which the ions of calcium and additional anions find their place in the large voids.

The system is tetragonal. The crystals are prismatic and elongated along the *C* axis. Of simple forms tetragonal prisms and dipyrramids can be properly distinguished. The size of the crystals reaches several tens of centimetres; they sometimes form druses (Fig. 118). The aggregates are massive and granular.

The colour of scapolite is white, grey with greenish tinge, and sometimes violet. The lustre is vitreous. The prism cleavage  $\{100\}$  is distinct. The fracture is uneven. The hardness is 5-6, and the density is 2.6-2.75.

*Varieties.* *Glaucolite* is a pale-violet variety of marialite.

*Origin.* Scapolites are found in contacts with limestone, together with diopside, calcite, phlogopite, apatite, tremolite, titanite, in iron-ore and scheelite-bearing skarn deposits and in some metamorphic rocks.

*Deposits.* In the USSR, there are deposits in the Baikal region (Slyudyanka), in Khakasia (Anzas), in Azerbaidzhan (Dashkesan), and in Central Asia (Chorukh-Dairon).

#### Alumosilicates with Radicals $[\text{Si}_3\text{Al}_2\text{O}_{10}]^{2-}$ , $[\text{Si}_4\text{Al}_2\text{O}_{12}]^{2-}$ , etc.

#### Aquatic (Zeolites)

Zeolites include frame alumosilicates with volume and interconnecting cavities, in which large cations, mainly those of Ca, Na, K, Sr, Ba, and the molecules of water, are located. Zeolites are characterized by

Fig. 118. A druse of scapolite crystals. Slyudyanka (the Near-Baikal region)



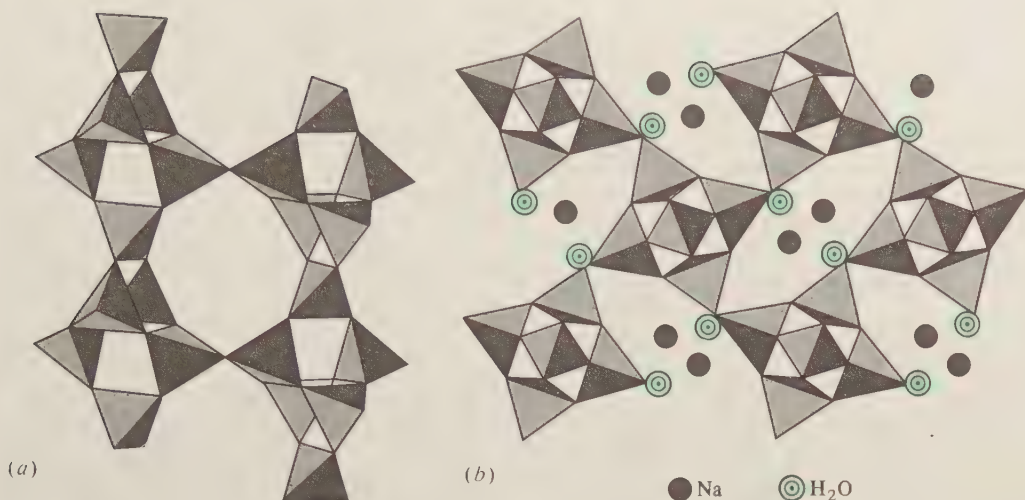


Fig. 119. Natrolite structure in a polyhedral model in its projection on  $\{100\}$  (a), and  $\{001\}$  (b)

a high degree of mobility of cations and their ability involving the replacement of ions. In zeolite radicals  $[\text{Si}_{n-p}\text{Al}_p\text{O}_2]^{p-}$  the index  $n$  can acquire the values from 5 to 24, while with  $p$  it is from 1 to 5. The content of zeolite water is connected with the ratio Al:Si, and in a vast majority of cases regularly decreases from purely potassium to sodium zeolites.

The crystalline structure of zeolites (Fig. 119) is characterized by the combination of alumo- and silica-oxygenous tetrahedrons, forming chains, consisting of four-fold links and interconnected into six-fold rings and other elements, forming isometric, layered, and chain motifs. The size of the voids and channels in the frame radical of zeolites is associated with the chemical composition. Larger voids are typical of highly siliceous zeolites, comprising larger cations and more molecules of water. In most of the zeolites the  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  ions occupy fixed positions, i.e. their structure can be regarded as organized. The isomorphic replacements between the cations in zeolites, as is the case with plagioclases, are basically of the heterovalent type ( $\text{Ca}^{2+}\text{Al}^{3+} \rightleftharpoons \text{Na}^+\text{Si}^{4+}$ ), and more seldom of the isovalent type ( $\text{Ca}^{2+} \rightleftharpoons \text{Sr}^{2+}$ ). In the communicating voids of the crystalline structure of zeolites the dipole molecules of water surround the cations, thus forming aqua-complexes of a big radius; while they themselves are distributed between the cations and ions of oxygen, belonging to the alumo-oxygen tetrahedrons with a redundant negative charge.

When moderately heated the 'zeolite water' can gradually be relieved with the crystalline structure remaining intact. Desiccated zeolites again acquire the properties to absorb water (with the extraction of heat!) and to adsorb the molecules of various substance, e.g.  $\text{H}_2\text{S}$ , hydrocarbons, alcohol, ammonia, etc. which is utilized in the draining of gases, the division of products of petro-chemical industry, the recovery of deep vacuum. The high density surface of the micropores of desiccated zeolites makes it possible to use them as carrying material for catalysts activating the processes of cracked petroleum products. Zeolites with large channels in the structure are used as thermostable 'molecular sieves', which help to separate the large

TABLE 4  
*Classification of Zeolites (a Brief Outline)*

Mineral	Formula	System	Crystal Habit	Colour	Cleavage	Hardness	Density
Laumontite	$\text{Ca}[\text{Si}_4\text{Al}_2\text{O}_{12}] \cdot 4\text{H}_2\text{O}$	mon.	prismatic crystals	white, pink	perfect {010}, {110}, and {001}	3.5-4	2.2-2.3
Chabasite	$(\text{Ca}, \text{Na}_2)[\text{Si}_4\text{Al}_2\text{O}_{12}] \cdot 6\text{H}_2\text{O}$	hex.	rhombohedral (pseudo- cubic) crystals	white	perfect {1011}	4-5	2.1-2.2
Heulandite (clinoptilolite)	$\text{Ca}[\text{Si}_7\text{Al}_2\text{O}_{18}] \cdot 6\text{H}_2\text{O}$	mon.	tabular, wedge-like, split crystals	white, pink	perfect {010}	3.5-4	2.2
Desmine (stilbite)	$(\text{Ca}, \text{Na})_2[\text{Si}_7\text{Al}_2\text{O}_{18}] \cdot 7\text{H}_2\text{O}$	mon.	bladed, split, sheaflike crystals and aggregates	white	perfect {010} indistinct {100}	3.5-4	2.2
Mordenite (ptilolite)	$(\text{Na}_2, \text{Ca})[\text{Si}_{10}\text{Al}_2\text{O}_{24}] \cdot 7\text{H}_2\text{O}$	ortho- rhomb.	acicular and matted-fib- rous aggregates		perfect {100}	up to 4.5	2.15

organic molecules from the small ones. One of the characteristic features of zeolites is that the cations are highly mobile, and are apt to ionic exchange. These properties are employed in water purification and the regeneration of stagnant and service water, in agrochemistry, as well as to enhance the effectiveness of fertilizers and the retention of moisture in the soil. Zeolite properties pertaining to the processes of adsorption and ion-exchange are also connected with the use of zeolites in cattle-breeding as an addition to fodder, thus improving the productivity and quality of meat. The properties of heulandite (clinoptilolite), chabasite, as well as their high-silicon synthetic properties are most widely used.

NATROLITE  $\text{Na}_2[\text{Si}_3\text{Al}_2\text{O}_{10}] \cdot 2\text{H}_2\text{O}$  and SCOLECITE  
 $\text{Ca}[\text{Si}_3\text{Al}_2\text{O}_{10}] \cdot 3\text{H}_2\text{O}$

The crystalline structure is characterized by clear-cut four-member chains of alumo-silico-oxygenous tetrahedrons, elongated along the C axis (see Fig. 119).

The system is orthorhombic. The minerals form long prismatic crystals, sometimes intergrowing into druses; they are often found in radiated aggregates and granular masses.

The minerals are colourless or white. The lustre is vitreous. The prism cleavage {110} is perfect. The hardness is 5-5.6. The density is nearly 2.

*Varieties.* *Spreustein* is the product resulting from the alteration of nepheline, consisting of natrolite and hydroxides of  $\text{Al}^{3+}$ .

*Origin.* The mineral is formed in amygdaloidal voids of basalts, and as a later mineral in alkaline pegmatites, skarns, and hydrothermal veins.

*Deposits.* In the USSR, there are deposits in the Urals (the Vishnevye Mountains), in the Kola peninsula (Khibiny), in Siberia (Nizhnaya Tunguska), and elsewhere.

A brief classification of some other zeolites is given in Table 4.

## Borates

The function of species-forming cations of borates is mainly shared by alkaline-earth ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ), alkaline ( $\text{Na}^+$ ), as well as transition metals ( $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ) and others; while the function of additional anions is undertaken by the groups of  $(\text{OH})^-$ ,  $\text{Cl}^-$ , more seldom by  $\text{F}^-$ , etc. A large number of borates are aquatic.

Borates pertain to minerals with various types of bonds. Thus, covalent bonds are characteristic of borate anion complexes; ionic and hydrogen bonds are typical of those between them and cations. The isomorphism in borates is restricted; with the exception of ludwigite and boracite, which are characterized by wide isomorphic replacements between  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$ .

As far as their structure is concerned, borates are similar to silicates and are characterized by a variety of anion radicals, which are mainly based on triangular and tetrahedral complexes. In borates they are found in the form of single anion groups (islands), or in combination with one another, form more complex island (paired or ring), chain, layered, and frame radicals (Fig. 120). In anion radicals of a complex structure in the environment of  $\text{B}^{3+}$  together with  $\text{O}^{2-}$  ions the groups of  $(\text{OH})^-$  take part. In borates of the island structure, as is

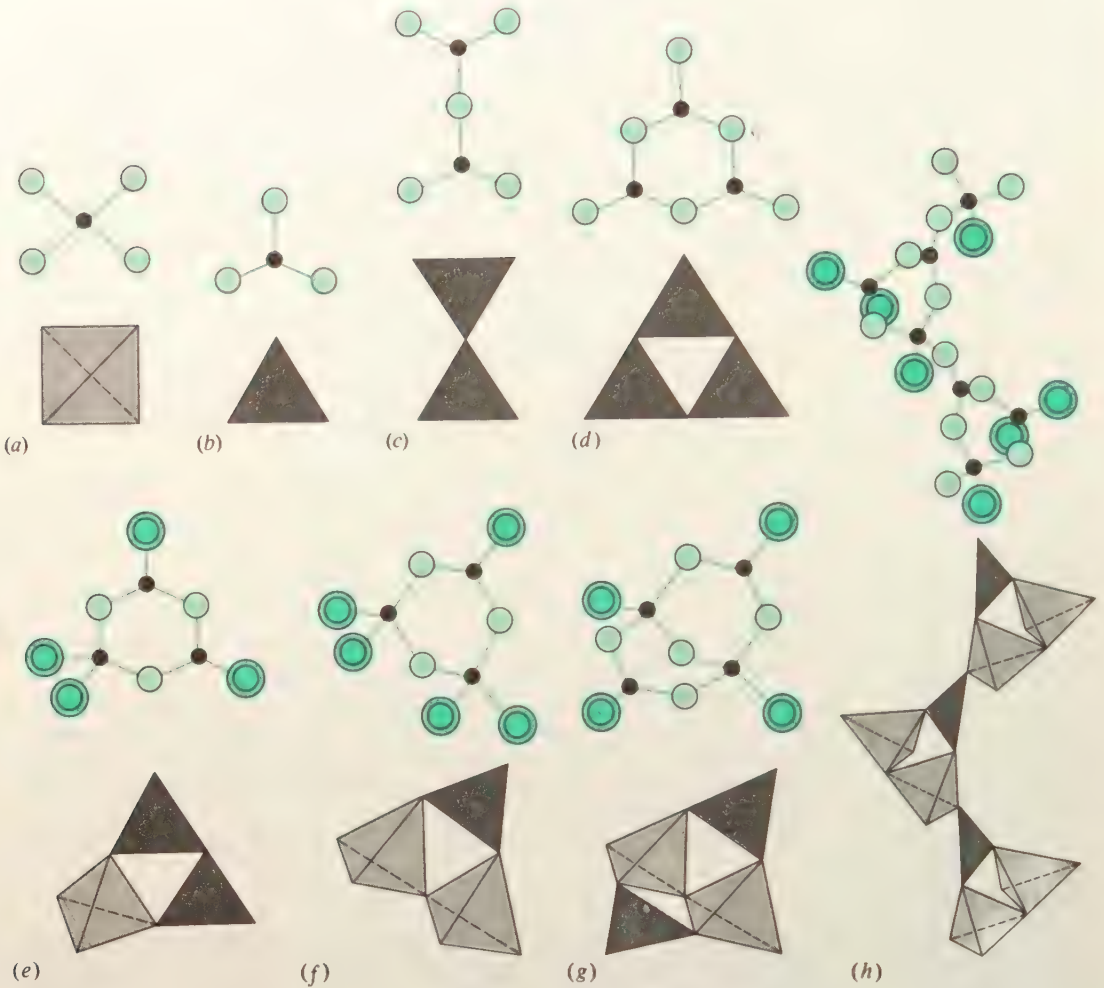


Fig. 120. Main types of anion radicals in borates:  
*a*—tetrahedron  $[\text{BO}_4]^{5-}$ ;  
*b*—triangle  $[\text{BO}_3]^{3-}$ ;  
*c*—paired triangle  $[\text{B}_2\text{O}_5]^{4-}$ ; *d*—three-fold ring  $[\text{B}_3\text{O}_6]^{3-}$ ; *e*—three-fold ring  $[\text{BB}_2\text{O}_6(\text{OH})_4]^-$ ;  
*f*—three-fold ring  $[\text{B}_2\text{O}_3(\text{OH})_5]^{2-}$ ;  
*g*—four-fold ring  $[\text{B}_2\text{B}_2\text{O}_3(\text{OH})_4]^{2-}$ ;  
*h*—chain  $[\text{B}_2\text{BO}_4(\text{OH})_3]^{2-}$

often the case, the cations form chain motifs (ludwigite, ascharite, and borax). Borates with chain and layered anions are characterized by corresponding cation motifs (hydroboracite, colemanite). Borates form crystalline-granular, earthy and compact cryptocrystalline, not infrequently radiated, spherulite, fibrous aggregates, crystalline crusts and druses of perfect crystals. Elongated-and-prismatic and fibrous crystals and aggregates are more characteristic of minerals with chain structure or chain motif.

Most of the borates are white, grey or yellowish, with the exception of Fe-bearing ludwigite and boracite. Borate crystals are often transparent. The hardness with most of them is low and medium (from 1 to 3-4). In very rare cases it reaches 7 (boracite with a frame structure). The diagnosis of borates is by no means simple, particularly in earthy and compact aggregates. Many of them resemble sulphates, carbonates, phosphates, and clay minerals. Some borates tend to be

luminescent in the ultraviolet light and under X-rays. The formation of borates is related to magnesian skarns (ludwigite, kotoite, etc.), and the volcanic activity. The main bulk of borates is of the sedimentary origin and is accumulated in non-drainage lakes and lagoons of the sea basins in hot climate conditions, as well as it is associated with the leaching zones of salt domes, the weathering crusts of gypsum-bearing strata, and with vulcano mud.

In large concentrations borates serve as a raw material in the production of boron. The boron salts and boric acid are used in glass industry, metallurgy, medicine, food industry and in other branches of economy.

## Systematization

### Borates of Island Structure

#### Simple

*The group of sinhalite*

Borates with Isolated Radicals  $[\text{BO}_4]^{5-}$  and  $[\text{BO}_3]^{3-}$   
sinhalite  $\text{Mg}[\text{BO}_4]$  (orthorhombic).

*The group of kotoite*

KOTOITE  $\text{Mg}_3[\text{BO}_3]_2$  (orthorhombic).

#### With Additional Anions

*The group of jeremejevite*

jeremejevite  $\text{Al}_6[\text{BO}_3]_5(\text{OH})_3$  (hexagonal).

*The group of ludwigite*

LUDWIGITE  $(\text{Mg}, \text{Fe}^{2+})_2\text{Fe}^{3+}[\text{BO}_3]\text{O}_2$  (orthorhombic).

*The group of fluoborite*

fluoborite  $\text{Mg}_3[\text{BO}_3](\text{OH}, \text{F})_3$  (hexagonal).

#### Aquatic

*The group of pentahydroborite*

pentahydroborite  $\text{Ca}[\text{B}(\text{OH})_4]_2 \cdot \text{H}_2\text{O}$  (triclinic).

*The group of sulphoborite*

sulphoborite  $\text{Mg}_3[\text{BO}_2(\text{OH})_2][\text{SO}_4] \cdot 4\text{H}_2\text{O}$  (orthorhombic).

#### Simple

*The group of suanite*

Borates with Double and Cycle Radicals  $[\text{B}_2\text{O}_5]^{4-}$ ,  $[\text{B}_2\text{O}_4(\text{OH})]^{3-}$ , etc.  
suanite  $\text{Mg}_2[\text{B}_2\text{O}_5]$  (monoclinic),  
pinnoite  $\text{Mg}[\text{B}_2\text{O}(\text{OH})_6]$  (tetragonal).

#### With Additional Anions

*The group of ascharite*

ascharite  $\text{Mg}_2[\text{B}_2\text{O}_4(\text{OH})](\text{OH})$  (orthorhombic).

#### Aquatic

*The group of inderite*

inderite  $\text{Mg}[\text{B}_2\text{BO}_3(\text{OH})_5] \cdot 5\text{H}_2\text{O}$  (monoclinic),  
inyoite  $\text{Ca}[\text{B}_2\text{BO}_3(\text{OH})_5] \cdot 4\text{H}_2\text{O}$  (monoclinic).

*The group of kaliborite*

kaliborite  $\text{KMg}_2[\text{B}_3\text{O}_3(\text{OH})_5]_2 \cdot [\text{B}_5\text{O}_6(\text{O})_4] \cdot 2\text{H}_2\text{O}$  (monoclinic).

**Borates of Chain Structure****Simple**

*The group of  
calciborite*

calciborite  $\text{Ca}[\text{B}_2\text{O}_4]$  (orthorhombic).

**Aquatic**

*The group of  
hydroboracite*

HYDROBORACITE  $\text{CaMg}[\text{B}_2\text{BO}_4(\text{OH})_3]_2 \cdot 3\text{H}_2\text{O}$  (monoclinic).

*The group of  
colemanite*

colemanite  $\text{Ca}[\text{B}_2\text{BO}_4(\text{OH})_3] \cdot \text{H}_2\text{O}$  (monoclinic).

*The group of  
pandermite*

pandermite  $\text{Ca}[\text{B}_4\text{BO}_7(\text{OH})_5] \cdot \text{H}_2\text{O}$  (monoclinic).

*The group of ulexite*

ulexite  $\text{NaCa}[\text{B}_2\text{B}_2\text{O}_7(\text{OH})_4] \cdot 6\text{H}_2\text{O}$  (triclinic),  
preobrazhenskite  $\text{Mg}_3[\text{B}_3\text{B}_2\text{O}_7(\text{OH})_4]_2 \cdot \text{H}_2\text{O}$  (orthorhombic).

*The group of borax*

borax  $\text{Na}_2[\text{B}_2\text{B}_2\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$  (monoclinic),  
kernite  $\text{Na}_2[\text{B}_2\text{B}_2\text{O}_6(\text{OH})_2] \cdot 3\text{H}_2\text{O}$  (monoclinic).

**Borates of the Layered Structure****Simple**

*The group of  
sassolite*

sassolite  $\text{H}_3[\text{BO}_3]$  (triclinic).

**Borates of the Frame Structure****Simple**

*The group of  
metaborite*

metaborite  $\text{HBO}_2$  (cubic).

**With Additional Anions**

*The group of  
boracite*

boracite  $\text{Mg}_3[\text{B}_3\text{B}_4\text{O}_{12}]\text{OCl}$  (orthorhombic).

**Borates of Island Structure****Simple**

KOTOITE  $\text{Mg}_3[\text{BO}_3]_2$  (36.5% of  $\text{B}_2\text{O}_3$ )

Sometimes there is an impurity of  $\text{Fe}^{2+}$ . In the crystalline structure of kotoite the  $\text{Mg}^{2+}$  ions in the octahedral coordination form zigzag chains, fixed by triangular radicals  $[\text{BO}_3]^{3-}$ .

The system is orthorhombic. The mineral forms granular marble-like aggregates.

The colour is white. The lustre is vitreous. The cleavage is perfect in one direction. The hardness equals 6.5, and the density is 3.1. *Origin.* The origin is contact-metamorphic. The mineral is found in magnesian skarns together with forsterite, spinel, and ludwigite. *Deposits.* In the USSR kotoite is recovered from the deposits in Eastern Siberia. In other countries there are deposits of this mineral in KPDR (Hol-Kol).

*Practical use.* In large accumulations kotoite is an ore of borax.



### With Additional Anions

**LUDWIGITE**  $(\text{Mg}, \text{Fe}^{2+})_2 \text{Fe}^{3+} [\text{BO}_3] \text{O}_2$  (14-17% of  $\text{B}_2\text{O}_3$ )

Besides a complete miscibility of  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  there have been established considerable impurities of Al, Sn, Ti,  $\text{Mn}^{2+}$ , and  $\text{Mn}^{3+}$ . In the crystalline structure of ludwigite the octahedrons with  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$  form chains interconnected by flat anion radicals  $[\text{BO}_3]^{3-}$  and additional anions  $\text{O}^{2-}$ .

The system is orthorhombic. The mineral forms rod-like, radiate, and more seldom granular aggregates.

The colour is greenish-black to black. The streak is green. The lustre is vitreous to adamantine. Ludwigite is brittle, its hardness equals 5, there is no cleavage, the fracture is uneven, and its density is 3.6-4.7. The outer form of this mineral resembles hedenbergite and tourmaline (short).

*Origin.* The mineral is found in magnesian skarns together with tourmaline, magnetite, and other borates.

*Deposits.* In the USSR, ludwigite is recovered from the skarn iron-ore deposits in Yakutia (the Tayozhnoye deposit), and Gornaya Shoriya, as well as in the Primorski Krai and Central Asia. Outside the USSR, there are deposits in KPDR (Hol-Kol), and elsewhere.

*Practical use.* This mineral can possibly be an ore of boron.

## Borates of the Chain Structure

### Aquatic

**HYDROBORACITE**  $\text{CaMg}[\text{B}_2\text{BO}_4(\text{OH})_3]_2 \cdot 3\text{H}_2\text{O}$  (50.5% of  $\text{B}_2\text{O}_3$ ). Sometimes there is a presence of  $\text{Na}^+$ . In the crystalline structure (Fig. 121) the anion radical  $[\text{B}_2\text{BO}_4(\text{OH})_3]$  represents a chain, each link of which is composed of two tetrahedrons and one triangle (see Fig. 120h). Elongated along the C axis, they alternate with lenticular chains of Mg-octahedrons, which have common apexes, and with the columns, comprising Ca-polyhedrons.

The system is monoclinic. Radiating and fibrous aggregates are common.

The colour is white; more seldom it is yellowish. The mineral is transparent. The lustre is vitreous, silky, and purple. Hydroboracite is brittle, its cleavage is perfect along the line of elongation; the fracture is uneven and hackly. The hardness is 2-3, and the density is 2.7. *Origin.* The origin is associated mainly with the leaching zone of salt domes together with other borates.

*Deposits.* In the USSR the mineral is known in Western Kazakhstan.

*Practical use.* Hydroboracite series serves as a raw material for the production of boron.

A brief classification of other borates is adduced in Table 5.

Fig. 121. A fragment of hydroboracite structure in its projection on {010}: the boron ions in triangular (grey) and tetrahedral (light green) coordination. The magnesium ions are in octahedral coordination; calcium ions marked by black circles

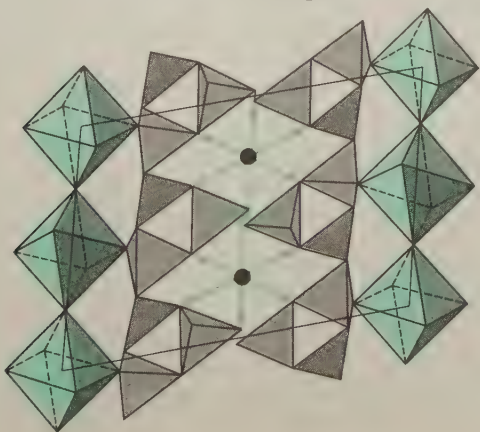


TABLE 5  
Classification of Borates (A Brief Outline)

Mineral	Formula	Content of $B_2O_3$ , %	System	Crystalline structure	Outer form	Colour	Lustre	Hardness	Cleavage	Density
Ascharite	$Mg_2[B_2O_4(OH)](OH)$	40.4	orthorhomb.	island	fine-fibrous aggregates	white, yellowish	silky, dull	4-4.5	not determined	2.6-2.7
Inyonite	$Ca[B_2BO_3(OH)_5] \cdot 4H_2O$	37.6	mon.	island	short-prismatic, columnar crystals	white, colourless	vitreous	2	perfect	1.9
Borax	$Na_2[B_2B_2O_5(OH)_4] \cdot 8H_2O$	36.5	mon.	chain	short-prismatic crystals, granular aggregates and earthy masses	white	white	2-2.5	perfect	1.7
Kernite	$Na_2[B_2B_2O_6(OH)_2] \cdot 3H_2O$	51.0	mon.	chain	coarse-grained aggregates	white	white	3	perfect	1.95
Colemanite	$Ca[B_2BO_4(OH)_3] \cdot H_2O$	50.8	mon.	chain	growths of short-columnar, rarely rod-like and flattened crystals	white, colourless	white	4	perfect	2.4
Pandermite	$Ca[B_4BO_7(OH)_5] \cdot H_2O$	49.8	mon. (?)	chain	nodular aggregates, compact, porcelain-like and earthy masses	white	tar-nished	3.5-4	poor	2.4
Ulexite	$NaCa[B_2B_2O_7(OH)_4] \times 6H_2O$	42.9	tricl.	chain	nodular and fibrous aggregates	white, colourless	dull, silky	3-3.5	perfect	2
Boracite	$Mg_3[B_3B_4O_{12}]OCI$	62.15	orthorhomb.	frame	pseudocubic (tetrahedral) crystals and marble-like masses	white, grey, yellowish, etc.	vitreous	7-7.5	none	2.9

# Carbonates

Minerals of the class of carbonates represent salts of carbonic acid, in which the function of cations is distributed among the ions  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ , copper, uranium, alkaline and rare-earth metals. The composition of carbonates also includes additional anions  $(\text{OH})^-$ ,  $\text{F}^-$ , and more seldom  $\text{Cl}^-$ . Carbonates are characterized by a mixed kind of bond, e.g. in anion radicals  $[\text{CO}_3]^{2-}$  ( $sp^2$ -hybridization) there is a covalent bond, while between anions and cations the bond is ionic. In carbonates with additional anions  $(\text{OH})^-$  and aquatic carbonates hydrogen bonds are by no means uncommon.

Carbonates are characterized by wide isomorphous replacements of the isovalent type between  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Mn}^{2+}$  in minerals of the calcite group (more restricted for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ), between  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Pb}^{2+}$  in minerals of the aragonite group, etc.

In carbonates with additional anions, the composition of which is complex, there are isovalent replacements between  $(\text{OH})^-$  and  $\text{F}^-$ ,  $(\text{OH})^-$  and  $\text{Cl}^-$ .

In terms of their structure all carbonates pertain to one island type, viz. anions  $[\text{CO}_3]^{2-}$ , and represent isolated radicals in the form of flat triangles. In most of the carbonates these radicals have identical (antiparallel) plane orientation. According to the distribution of cations and anions  $[\text{CO}_3]^{2-}$  the carbonate structures can be classified into coordinate (calcite, siderite, etc.), and chain (aragonite, malachite, etc.) structural motifs. The layered motif is characteristic of rare carbonates  $[\text{UO}_2]^{2+}$  and some others, mainly of the aquatic carbonates of complex composition.

The carbonates of divalent ions, that are distinguished in size, serve to illustrate the phenomenon of *morphotropy*. In the morphotropic series of carbonates with an increasing dimensions of cations (in nm):

## Hexagonal

- $\text{Mg}[\text{CO}_3]$  (0.078) magnesite
- $\text{Zn}[\text{CO}_3]$  (0.083) smithsonite
- $\text{Fe}[\text{CO}_3]$  (0.08) siderite
- $\text{Mn}[\text{CO}_3]$  (0.091) rhodochrosite
- $\text{Ca}[\text{CO}_3]$  (0.104) calcite

## Orthorhombic

- $\text{Ca}[\text{CO}_3]$  (0.104) aragonite
- $\text{Sr}[\text{CO}_3]$  (0.127) strontianite
- $\text{Pb}[\text{CO}_3]$  (0.132) cerussite
- $\text{Ba}[\text{CO}_3]$  (0.143) witherite

The border-line between the two structural types corresponds to calcium carbonate, forming two widespread polymorphic modifications, viz. calcite  $\text{Ca}[\text{CO}_3]$  (hexagonal-R) and aragonite  $\text{Ca}[\text{CO}_3]$  (orthorhombic system), as well as a less stable form, vaterite  $\text{Ca}[\text{CO}_3]$  (hexagonal system). Carbonates not infrequently form double compounds with an ordered distribution of cations, which is characteristic, for example, of minerals pertaining to the dolomite group with an equal content of  $\text{Ca}^{2+}$  ions and the sum of  $(\text{Mg}^{2+} +$

+  $\text{Fe}^{2+}$  +  $\text{Mn}^{2+}$ ) ions. They differ from the corresponding disorganized minerals of the non-constant composition in that their symmetry is markedly lower.

The morphology of carbonates is, in many respects, connected with the structural characteristic features and the conditions in which they are formed. Carbonates the structure of which is simple are mainly found in the crystalline-granular aggregates and in the form of crystals of various habit. The carbonates of the calcite series are characterized by rhombohedral crystals. The morphology of calcite crystals is particularly variegated (see Fig. 16). Carbonates with a chain structural motif (the aragonite group) have a regularly recurrent elongated-and-prismatic habit of crystals and spherulite aggregates. Sinter, reniform, compact porcelain-like aggregates are mainly typical of carbonates formed in hypergene conditions.

Most of the carbonates are either colourless or white. Their colour is predominantly connected with the chromophore ions of the species-forming transitory elements, coordinated with the ions of  $\text{O}^{2-}$ ,  $(\text{OH})^-$ , and sometimes,  $\text{Cl}^-$ . The relationship can be expressed by means of the following binary terms:  $\text{Cu}^+$  – green, light-blue, or blue;  $\text{Co}^{2+}$  – crimson-coloured; and  $\text{Mn}^{2+}$  – pink colour. The yellowish-brown or brown colour of siderite  $\text{Fe}[\text{CO}_3]$  is connected with a partial oxydation of iron.

The variety of colour in calcite and other carbonates, colourless in their pure form, also depends on the radiated defects of the centres of colour (blue, pink, yellowish-brown, etc.) or is of allochromatic nature. Thus, the dark-blue and the black colour of calcite in marble is connected with the impurity of the carbonified bitumens. Its green colour is associated with the micro-inclusions of chlorite or actinolite, while the red variety can be related to hematite. The carbonates of the alkaline-earth metals tend to luminesce in the ultraviolet light. Most of the carbonates have a vitreous lustre on the edges and the planes of cleavage. A stronger lustre (up to adamantine) is found with Fe and Pb carbonates, e.g. siderite and cerussite.

Regular plane orientation of triangular radicals  $[\text{CO}_3]^{2-}$  is related to the anisotropy of the physical properties of a large number of carbonates characterized, in particular, by a strong double refraction of light (calcite, aragonite, etc.), pleochroism (malachite, azurite, etc.), dissimilar degrees of hardness in different directions, etc.

Carbonates are distinguished by a high degree of solubility in hydrochloric acid with the extraction of  $\text{CO}_2$ . In natural conditions calcite, aragonite, azurite, malachite, and some other minerals are easily soluble. However, most of them react with HCl only when heated or in a powder form. Carbonates of the sodium carbonate group are soluble in water too.

Carbonates are formed both within the endogene and the exogenetic processes. Magmatic origin is shared by calcite and the dolomite of carbonatites; the metamorphic processes are associated with the formation of calcite and the dolomite of marble. The hydrothermal changes undergone by carbonate metamorphic strata can be related to the formation of magnesite and siderite deposits. The carbonates of the alkaline-earth and transitory metals basically have a hydrothermal origin, and, besides, are frequently found in skarn deposits. The main bulk of carbonates of calcium are of sedimentary, organogenic and of

hemogenic origin. Sodium carbonate and other water-soluble carbonates have a lake-sedimentary origin. Many minerals are formed in the oxidation zone of sulphide deposits (malachite, azurite, smithsonite, cerussite), in the weathering crusts of ultrabasic rocks (magnesite), in karst caves and mineral sources (aragonite, calcite).

Carbonates are pertinent to the widely-spread minerals of the Earth's crust, though the total number of mineral species does not exceed one hundred. Some of them form industrial accumulations and are used as construction material (limestone, marble) or for the production of cement (dolomite), in chemical industry in the production of sodium carbonate, in metallurgical industry as a refractory raw material (magnesite), as a flux in the melting of iron (limestone).

Carbonates are also an ore of iron (siderite), and enter into the composition of polymetallic and copper ores (malachite, azurite, cerussite, smithsonite), serve as a valuable optical raw material (the Iceland spar) and is used as an ornamental and semiprecious stone (marble onyx, malachite, azurite). Azurite and malachite, owing to their bright colour, can function as a reliable exploratory feature of copper ores, and are also used in the production of paints. Parisite and bastnäsite are a valuable ore of rare earths, while dawsonite is an ore of aluminium.

## Systematization

### Carbonates of the Island Structure

#### Simple

*The group of calcite*  
(hexagonal-R)

CALCITE  $\text{Ca}[\text{CO}_3]$ ,  
RHODOCHROSITE  $\text{Mn}[\text{CO}_3]$ ,  
SIDERITE  $\text{Fe}[\text{CO}_3]$ ,  
SMITHSONITE  $\text{Zn}[\text{CO}_3]$ ,  
MAGNESITE  $\text{Mg}[\text{CO}_3]$ .

*The group of aragonite*  
(orthorhombic)

ARAGONITE  $\text{Ca}[\text{CO}_3]$ ,  
strontianite  $\text{Sr}[\text{CO}_3]$ ,  
witherite  $\text{Ba}[\text{CO}_3]$ ,  
CERUSSITE  $\text{Pb}[\text{CO}_3]$ .

*The group of vaterite*

vaterite  $\text{Ca}[\text{CO}_3]$  (hexagonal).

#### Complex

*The group of dolomite*  
(hexagonal-R)

DOLOMITE  $\text{CaMg}[\text{CO}_3]_2$ ,  
ankerite  $\text{CaFe}[\text{CO}_3]_2$ .

#### With Additional Anions

*The group of malachite*

MALACHITE  $\text{Cu}_2[\text{CO}_3](\text{OH})_2$  (monoclinic),  
AZURITE  $\text{Cu}_3[\text{CO}_3]_2(\text{OH})_2$  (monoclinic),  
aurichalcite  $\text{Zn}_3\text{Cu}_2[\text{CO}_3]_2(\text{OH})_6$  (orthorhombic),  
hydrozincite  $\text{Zn}_5[\text{CO}_3]_2(\text{OH})_6$  (monoclinic).

*The group of bastnäsite*  
(hexagonal)

bastnäsite  $\text{Ce}[\text{CO}_3](\text{F}, \text{OH})$ ,  
parisite  $\text{CaCl}_2[\text{CO}_3]_3(\text{F}, \text{OH})_2$ .

*The group of dawsonite*

dawsonite  $\text{NaAl}[\text{CO}_3](\text{OH})_3$  (monoclinic).

**Aquatic**

The group of sodium carbonate

The group of hydro-talcite

The group of uranium carbonates

thermonatrite  $\text{Na}_2[\text{CO}_3]\text{H}_2\text{O}$  (orthorhombic),  
 trona  $\text{Na}_3\text{H}[\text{CO}_3]_2 \cdot 2\text{H}_2\text{O}$  (monoclinic),  
 sodium carbonate  $\text{Na}_2[\text{CO}_3] \cdot 10\text{H}_2\text{O}$  (monoclinic),  
 hydrotalcite  $\text{Mg}_6\text{Al}_2[\text{CO}_3](\text{OH})_{16} \cdot 4\text{H}_2\text{O}$  (hexagonal-R).

zellerite  $\text{Cu}(\text{UO}_2)[\text{CO}_3]_2 \cdot 5\text{H}_2\text{O}$  (orthorhombic),  
 andersonite  $\text{Na}_2\text{Ca}(\text{UO}_2)[\text{CO}_3]_3 \cdot 6\text{H}_2\text{O}$  (hexagonal-R), etc.

## Carbonates of the Island Structure

### Simple

#### CALCITE $\text{Ca}[\text{CO}_3]$

The impurities of  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Fe}^{2+}$  are common. Sometimes  $\text{Pb}^{2+}$ ,  $\text{TR}^{3+}$ ,  $[\text{SO}_4]^{2-}$  and others are present too. The crystalline structure of calcite is derived from the NaCl structure, deformed along the C axis (Fig. 122). The  $\text{Na}^+$  positions in it are occupied by  $\text{Ca}^{2+}$  ions, while those of  $\text{Cl}^-$  by the  $[\text{CO}_3]^{2-}$  anions, which are distributed parallel to each other in the plane  $\{0001\}$ . The  $\text{Ca}^{2+}$  ions are in the octahedral coordination of oxygen ions, belonging to the apexes of the triangular anion  $[\text{CO}_3]^{2-}$ .

The system is hexagonal-R. The crystals are variegated, mainly of the rhombohedral and scalenohedral type (Fig. 123). Occasionally they are twinned. The aggregates are granular (marble), earthy (chalk), and often represent sinter forms of stalactites and stalagmites.

The colour is white. Lighter shades of various colours also become

Fig. 122. Calcite structure

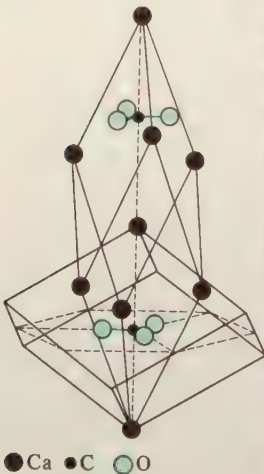


Fig. 123. Scalenohedrons of calcite crystals, twinned according to  $\{0001\}$ . The Primorski Krai. Natural size



apparent. Sometimes the mineral is transparent. The rhombohedral cleavage  $\{10\bar{1}1\}$  is perfect. The hardness is 3, and the density is 2.7. Calcite reacts most turbulently even when in contact with diluted hydrochloric acid.

*Varieties.* Transparent colourless crystals of calcite have acquired the name of *Iceland spar*, or *optical calcite*. It is characterized by a strong double refraction of light (see Fig. 41).

*Origin.* Calcite is widely spread in nature in the form of limestone, chalk, and marble. Limestones are chemical or biogenic sea sediments. Marble is a recrystallized limestone, and is formed under regional or contact metamorphism. Calcite enters into the composition of carbonates as the main species-forming mineral. It is found as a low-temperature hydrothermal mineral in ore veins and skarns. It is formed in karst caves, as well as in the weathering crusts.

*Deposits.* In the USSR there are deposits of marble in Georgia, Armenia, Central Asia, in the Urals. Iceland spar is found along the Nizhnaya Tunguska River. It is hydrothermal in connection with traps. In other countries marble is deposited in Italy, and Iceland spar is found in the basalt voids in Iceland.

*Practical use.* Limestone is used in construction, chemical (limestone, cement, glass, and the recovery of soda) and metallurgical (flux) industry. Their deposits are numerous. Marble is a valuable facing material. Iceland spar is utilized in optical instruments (polarizing microscopes, etc.).

#### MAGNESITE $\text{Mg}[\text{CO}_3]$

$\text{Fe}^{2+}$  impurities are occasionally present. The crystalline structure is similar to that of calcite.

The system is hexagonal-R. It is found in the form of crystalline-granular aggregates and porcelain-like compact cryptocrystalline masses.

The colour is white. The hardness is 4-4.5. The density is 3. In HCl it undergoes disintegration only when heated in the form of powder.

*Origin.* The metasomatic origin is associated with the replacement of limestone by the solutions containing magnesium (this process presupposes that magnesium is being leached from dolomite strata). The mineral also originates under hydrothermal processing of ultrabasic rocks rich in magnesium, and under weathering.

*Deposits.* In the USSR this mineral is recovered in Satka, to the southwest of Zlatoust (the Urals), and Savinskoye in the Irkutsk Region. In countries outside the USSR, there are deposits in China, Austria, and Canada.

*Practical use.* Magnesite is used in the production of refractory bricks.

#### SIDERITE $\text{Fe}[\text{CO}_3]$ (48.2% of Fe)

The mineral often contains the impurities of Mn and Mg. The crystalline structure is analogous to the structure of calcite.

The system is hexagonal-R. The aggregates are granular, earthy, compact, and sometimes in globular-form nodules (sphaerosiderite).

The colour is brownish-yellow, brown. The rhombohedral cleavage  $\{1010\}$  is perfect. The hardness is 3.5-4.5. The density is 4. In HCl it easily lends itself to decomposition, this being accompanied by a drop of HCl becoming yellow as a result of  $\text{FeCl}_3$  formation.

*Origin.* The hydrothermal origin occurs in polymetallic deposits as

a veined mineral. Under the replacement of limestone, the mineral forms metasomatic deposits. It can be of sedimentary origin (oölite structure), as well as of metamorphic origin, when the metamorphism of sedimentary deposits of iron takes place. In the oxidation zone it is easily disintegrated and is transferred into hydrates of iron oxides, thus forming gossans.

*Deposits.* In the Southern Urals there is the largest Bakal deposit of siderite in the USSR. Its hydrothermal origin is connected with the replacement of dolomites. In other countries there are deposits of siderite in Austria, Spain, and elsewhere.

*Practical use.* Siderite is an important ore of iron.

#### RHODOCHROSITE $\text{Mn}[\text{CO}_3]$ (47.7% of Mn)

The crystalline structure is similar to that of calcite.

The system is hexagonal-R. The aggregates are granular, complete, and botryoidal.

The colour is pink, under weathering it becomes brownish. The hardness is 3.5-4. The density is 3.6. In HCl the mineral undergoes gradual decomposition; when heated, this process becomes turbulent.

*Origin.* The hydrothermal origin is related to ore veins (the Dzhida deposit in Buryat ASSR). Rhodochrosite is more often of sedimentary origin, e.g. the deposits of manganese in Chiatura, in Georgia.

*Practical use.* This mineral enters into the composition of manganese ores.

#### SMITHSONITE $\text{Zn}[\text{CO}_3]$ (52% of Zn)

The structure is that typical of calcite.

The system is hexagonal-R. It is usually found in sinter forms, as crusts and reniform aggregates.

The colour is white with greenish or bluish tinge resulting from the impurity of copper. The hardness is 4-4.5. The density is 4.3. In HCl the mineral is easily decomposed.

*Origin.* Being of exogenous origin, smithsonite is a typical mineral of the oxidation zone of polymetallic sulphide deposits. It is formed at

Fig. 124. Branched aggregates of aragonite. The Bakal deposit (the Urals)





Fig. 125. An aggregate of rod-like cerussite crystals. The Achisai deposit (Kazakhstan)



the expense of sphalerite, often together with cerrusite, calamine, and limonite.

*Deposits.* In the USSR, the mineral is known in the polymetallic deposits of the Karatau mountain Range (Southern Kazakhstan), in the ores of the Klichka group (the Chita Region), and in the Dalnegorsk deposit in the Primorski Krai.

*Practical use.* Smithsonite is an ore of zinc.

#### ARAGONITE $\text{Ca}[\text{CO}_3]$

This mineral often contains the impurities of  $\text{Sr}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $[\text{SO}_4]^{2-}$ . The crystalline structure, as distinct from the structure of calcite, has a chain motif. The triangular anions  $[\text{CO}_3]^{2-}$  are distributed on top of one another, thus forming, as is the case with  $\text{Ca}^{2+}$  ions whose coordination number is 9, columns, elongated along the *C* axis.

The system is orthorhombic. The crystals are prismatic and acicular. The aggregates are rod-like, divergent. Sintered forms, oölites ('aragonite oölite', see Fig. 36), and dendritic forms ('flowers of iron', Fig. 124) can be regarded as characteristic features.

The colour is white. The lustre is vitreous. The cleavage is distinct along the line of elongation. The hardness equals 4.5, and the density is 2.5. In HCl the mineral lends itself to turbulent disintegration, a process similar to calcite under these circumstances.

*Origin.* Aragonite is formed in the sediments of hot springs and in the amygdules of effusive rocks. It is basically of exogenous origin, composes organogenic limestones and is formed in karst caves, in the weathering crust of rocks, and in the oxidation zone of ore deposits.

#### CERUSSITE $\text{Pb}[\text{CO}_3]$ (77% of Pb)

The structure is the same as that typical of aragonite.

The system is orthorhombic. The crystals are tabular, acicular, and rod-like (Fig. 125). The aggregates are predominantly solid, granular,

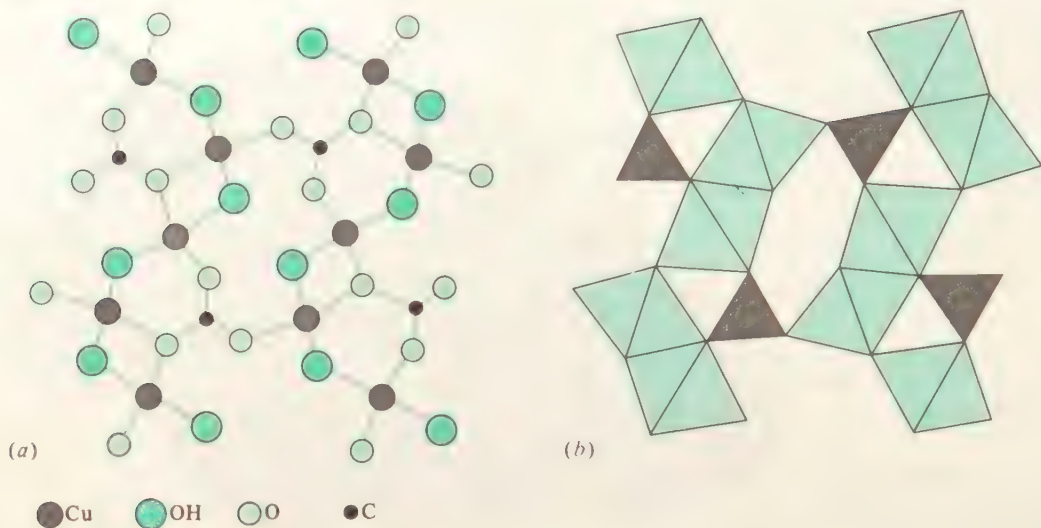


Fig. 126. Malachite structure in globular (a), and polyhedral (b) models

oft en of sinter form. Reticulated fibrous aggregates are found too. The mineral is brittle.

Cerussite can be colourless, white or grey. The lustre is adamantine. The hardness is 3-3.5. High density (6.5) has been found to be a characteristic feature. In  $\text{HNO}_3$  the mineral is dissolved with hissing. *Origin.* It is a typical mineral of the oxidation zone of lead-zinc deposits, and is formed at the expense of galena and anglesite. *Deposits.* The mineral is found in polymetallic deposits of the Karatau mountain range (the Achisai deposit), Rudni Altai (Zmeinogorsk), in the deposits of the Chita Region (Kadainskoye), and elsewhere. *Practical use.* When the oxidation zone is considerable, cerussite is used as an ore of lead.

### Complex

#### DOLOMITE, $\text{CaMg}[\text{CO}_3]_2$

This mineral often contains the impurities of  $\text{Fe}^{2+}$ . The crystalline structure is similar to the structure of calcite with the organized distribution of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions.

The system is hexagonal-R. It is usually found in the form of crystalline-granular aggregates; it also forms porous and earthy masses.

The colour is white, light-brown. The hardness is 3.5-4. The density is 2.9. Its reaction to hydrochloric acid is weak.

*Origin.* The origin is basically sedimentary. However, the mineral can also originate at the expense of limestone transformation which takes place under the influence of magnesian solutions. The hydrothermal origin is related to ore veins.

*Deposits.* Dolomite is widely spread in Paleozoic rock massifs in the Urals, Donbass, the Near-Moscow Region, along the Volga River, in Central Asia, and Siberia.

*Practical use.* This mineral is used in the production of cement and refractory bricks, and as flux in metallurgy.

### With Additional Anions

**MALACHITE**  $\text{Cu}_2[\text{CO}_3](\text{OH})_2$  (57.4% of Cu)

The  $\text{Zn}^{2+}$  impurity is sometimes present. In the crystalline structure of malachite the  $\text{Cu}^{2+}$  ions are in the distorted octahedral (pseudo-square) coordination of  $(\text{OH})^{2-}$  and  $\text{O}^{2-}$  ions, thus forming polyhedra of two types, which, being interconnected by common edges, and  $[\text{CO}_3]^{2-}$  anions, produce sinuous chains along the  $a$  axis (Fig. 126).

The system is monoclinic. The mineral is found in sinter forms, reniform formations, that have a concentrically-zonal structure (Fig. 127), earthy masses and coatings. Sometimes it forms fibrous divergent aggregates with a characteristic silky lustre. The earthy variety of malachite is called chrysocolla.

The colour is green, and the streak is pale-green. The lustre is vitreous, and silky. The cleavage is perfect. The hardness equals 3.5, and the density is 4. The mineral easily dissolves in HCl.

*Origin.* The mineral is formed in the oxidation zone of copper and other deposits, containing in primary ores the sulphides of copper together with azurite, chrysocolla, native copper, cuprite, limonite, gypsum, etc.

*Deposits.* The best specimens of malachite have been recovered from the Gumeshevsk and the Mednorudnyansk deposits (the district of Nizhni Tagil). In other countries there are deposits in the Republic of Zaïre.

*Practical use.* Sintered accumulations of malachite are used as a valuable semiprecious stone material. Together with other minerals

Fig. 127. Concentrically-zonal structure of malachite spherulite aggregates. A polished sample (the Urals)



of the oxidation zone it is melted and serves as an ore of copper. It is also used in the production of green paint. Bright-green stains and crusts of malachite can function as an important indicator of copper ores.

**AZURITE**  $\text{Cu}_3[\text{CO}_3]_2(\text{OH})_2$  (55.2% of Cu)

In the crystalline structure of azurite the  $\text{Cu}^{2+}$  ions of one type are in a four-fold (rectangular), while there are twice as much of the  $\text{Cu}^{2+}$  ions of the other type in a five-fold (tetragonal pyramid) coordination and form continuous chains along the *b* axis, thus being interconnected by  $[\text{CO}_3]^{2-}$  anions.

The system is monoclinic. The crystals are small, columnar or tabular. The mineral usually forms fine-crystalline crusts and druses. It is found in the form of coatings and earthy masses (copper blue).

The colour is dark-blue, in earthy masses it is light-blue. The streak is light-blue. The lustre is vitreous. The hardness is 3.5-4, and the density is 3.8. In acids it is dissolved with the hissing effect. *Origin.* The origin and the mineral associates of azurite are those of the malachite. It is of rarer occurrence than malachite. Azurite is an indicator of copper, and is used in the production of blue paint.

## Nitrates

Nitrates are the salts of nitrous acid. Minerals pertaining to this class, which is small in number, are rare. Those of the nitrates that are more widely spread include sodium nitrate and potassium nitrate. Nitrates are found in the form of soil blooms, coatings, and crusts. Since they are easily soluble in water, they usually occur in arid hot places.

Their origin is mainly biogenic, i.e. they are formed at the expense of the decay of organic remains and the activity of nitrato-bacteria.

**SODA-NITER (Chilesalt-peter)**  $\text{Na}[\text{NO}_3]$

The structure is similar to the structure of calcite.

The system is hexagonal-R. It is found in the form of crusts, as well as in granular and friable masses.

The colour is white, resulting from impurities it is grey, yellow, or reddish-brown. The cleavage rhombohedral is perfect (the crystals resemble calcite). The mineral is dissolved in water. Its taste is salty. The hardness is 1.5-2. The density is 2.25. When heated with coal powder, the mineral ignites, but to a lesser extent than potassium nitrate.

*Deposits.* The deposits of sodium nitrate in Chile (approximately 200 million tons) are world famous. The origin is biogenic, and sedimentary, though not completely clear. It has been established that in the formation of nitrate the physico-geographical factors are of greatest importance. The content of iodine, a by-product recovered in large quantities, is found to be a characteristic feature.

*Practical use.* Potassium nitrate is used as the best kind of fertilizer, in food industry, in the production of nitrous acid, and explosives.

## Sulphates

Minerals of this class represent salts of sulphuric acid, the composition of which includes alkaline (Na, K) and alkaline-earth (Mg, Ca, Sr, Ba) metals, as well as Pb, Cu, Fe, and Al. A considerable part of sulphates are basic and hydrated salts.

In the tetrahedral anion  $[\text{SO}_4]^{2-}$  sulphur finds itself in the highest degree of oxidation. Sulphates are characterized by a substantially ionic type of chemical bond. In basic and hydrated sulphates the function of hydrogen bonds can hardly be overestimated. The isovalent and heterovalent replacements have a restricted character. Perfect isomorphism has been established only between barite  $\text{Ba}[\text{SO}_4]$  and celestite  $\text{Sr}[\text{SO}_4]$ . Besides, in barite  $\text{Ba}^{2+}$  is often replaced by  $\text{Pb}^{2+}$  and  $\text{Ra}^{2+}$  ions. In anhydrite the presence of  $\text{TR}^{3+}$  and  $\text{Mn}^{2+}$  impurities is common. Wide replacements between cations are highly developed in hydrate sulphates of Fe, Cu, and Zn.

The basic structural element of sulphates is the isolated  $[\text{SO}_4]^{2-}$  anion. Hence, all sulphides pertain to one structural type. According to their compositional features sulphates can be classified into a particular number of types, viz. simple anhydrous, complex with additional anions and hydrous, also distinguished by their structural motif. A coordination motif of anion and cation distribution is characteristic of simple sulphates with a weak manifestation of the anisodesmic bonds between cations and anions. That is why simple sulphates often have a tabular and flattened-and-elongated form and perfect cleavage.

The layered motif is particularly clearly apparent in the basic and some hydrous sulphates with hydrogen bonds, which form fine-scaly aggregates, as is the case with jarosite, or tabular crystals (gypsum) with an absolutely perfect cleavage in one direction. Sulphates, as a class, are characterized by moderate and low hardness.

Most of the sulphates are colourless. The bright colour of some of them is mainly connected with the chromophore ions of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Fe}^{2+}$ ; with radiated centres, e. g. in anhydrite, celestine, and barite or is allochromatic (for instance, the red colour of barite is associated with fine scales of hematite). Sulphates of alkaline metals and hydrous sulphates are easily soluble in water and have a specific salty, bitter or astringent taste.

The origin of sulphates is connected with both the exogenous and the endogenous mineral formation. In hydrothermal conditions barite, often together with sulphide veins, more seldom celestite and anhydrite, as well as alunite are formed. The process of sedimentation in enclosed sea basins leads to the formation of the deposits of gypsum, anhydrite, simple and hydrous sulphates of alkaline metals and magnesium; carbonate rocks are also associated with the accumulation of barite and celestite. Large stratiform barite-polymetallic deposits are formed in the conditions of underwater sedimentation at the bottom of sea basins from the concentrated hot solutions, connected with the underwater volcanism.

The process of oxidation of sulphide deposits leads to the formation of Pb, Cu, Fe sulphates, other metals, and also gypsum. The dehydration of strata is associated with the formation of anhydrite in metamorphic rocks.

A large number of sulphates serve as a raw material for chemical industry in the production of Ba, Sr, Al, Mg and other metals, some of which are used in construction (gypsum), and as weighing material (barite), etc.

## Systematization

### Sulphates of Island Structure

#### Simple

*The group of thenardite*

THENARDITE  $\text{Na}_2[\text{SO}_4]$  (orthorhombic).

*The group of anhydrite*

ANHYDRITE  $\text{Ca}[\text{SO}_4]$  (orthorhombic).

*The group of barite (orthorhombic)*

CELESTITE  $\text{Sr}[\text{SO}_4]$ ,

BARITE  $\text{Ba}[\text{SO}_4]$ ,

ANGLESITE  $\text{Pb}[\text{SO}_4]$ .

#### Complex

*The group of langbeinite*

langbeinite  $\text{K}_2\text{Mg}_2[\text{SO}_4]_3$  (cubic).

*The group of glauberite*

glauberite  $\text{Na}_2\text{Ca}[\text{SO}_4]_2$  (monoclinic),

vanthoffite  $\text{Na}_6\text{Mg}[\text{SO}_4]_4$  (monoclinic),

glaserite  $\text{K}_2\text{Na}[\text{SO}_4]_3$  (hexagonal-R).

#### With Additional Anions

*The group of brochantite*

brochantite  $\text{Cu}_4[\text{SO}_4](\text{OH})_6$  (orthorhombic),

antlerite  $\text{Cu}_3[\text{SO}_4](\text{OH})_4$  (monoclinic).

*The group of alunite (hexagonal-R)*

ALUNITE  $\text{KAl}_3[\text{SO}_4]_2(\text{OH})_6$ ;

JAROSITE  $\text{KFe}_3^{3+}[\text{SO}_4]_2(\text{OH})_6$ .

*The group of berkeyite*

berkeyite  $\text{Na}_8[\text{SO}_4]_2[\text{CO}_3]$  (orthorhombic).

#### Aquatic

*The group of gypsum*

GYPSUM  $\text{Ca}[\text{SO}_4] \cdot 2\text{H}_2\text{O}$  (monoclinic).

*The group of mirabilite*

mirabilite  $\text{Na}_2[\text{SO}_4] \cdot 10\text{H}_2\text{O}$  (monoclinic).

*The group of kieserite*

kieserite  $\text{Mg}[\text{SO}_4] \cdot \text{H}_2\text{O}$  (monoclinic),

pentahydrate  $\text{Mg}[\text{SO}_4] \cdot 5\text{H}_2\text{O}$  (hexagonal-R),

hexahydrate  $\text{Mg}[\text{SO}_4] \cdot 6\text{H}_2\text{O}$  (monoclinic).

*The group of chalcantite*

chalcantite  $\text{Cu}[\text{SO}_4] \cdot 5\text{H}_2\text{O}$  (triclinic),

boothite  $\text{Cu}[\text{SO}_4] \cdot 7\text{H}_2\text{O}$  (monoclinic),

melanterite  $\text{Fe}[\text{SO}_4] \cdot 7\text{H}_2\text{O}$  (monoclinic),

goslarite  $\text{Zn}[\text{SO}_4] \cdot 7\text{H}_2\text{O}$  (monoclinic),

epsomite  $\text{Mg}[\text{SO}_4] \cdot 7\text{H}_2\text{O}$  (orthorhombic).

*The group of astrakhanite (monoclinic)*

astrakhanite  $\text{Na}_2\text{Mg}[\text{SO}_4] \cdot 10\text{H}_2\text{O}$ ,

löweite  $\text{Na}_2\text{Mg}[\text{SO}_4]_2 \cdot 2\text{H}_2\text{O}$ ,

leonite  $\text{K}_2\text{Mg}[\text{SO}_4] \cdot 4\text{H}_2\text{O}$ ,

schoenite  $\text{K}_2\text{Mg}[\text{SO}_4]_3 \cdot 6\text{H}_2\text{O}$ .

*The group of polyhalite*

polyhalite  $\text{K}_2\text{Ca}_2\text{Mg}[\text{SO}_4]_4 \cdot 2\text{H}_2\text{O}$  (triclinic),

görgeyite  $\text{K}_2\text{Ca}_5[\text{SO}_4]_6 \cdot \text{H}_2\text{O}$  (monoclinic),

syngenite  $\text{K}_2\text{Ca}[\text{SO}_4] \cdot \text{H}_2\text{O}$  (monoclinic).

*The group of alum:*

alum  $\text{KAl}[\text{SO}_4]_2 \cdot 12\text{H}_2\text{O}$  (cubic).

*The group of kainite*

kainite  $\text{KMg}[\text{SO}_4]\text{Cl} \cdot 3\text{H}_2\text{O}$  (monoclinic).

## Sulphates of Island Structure

### Simple

**THENARDITE**  $\text{Na}_2[\text{SO}_4]$  (56.3% of  $\text{Na}_2\text{O}$ ; 43.7% of  $\text{SO}_3$ )

In the crystalline structure the  $\text{Na}^+$  ions are in the octahedral environment of oxygen ions, belonging to the neighbouring  $[\text{SO}_4]^{2-}$  anions.

The system is orthorhombic and is found in the form of crystalline aggregates, crusts and blooms. The mineral is hygroscopic, absorbs moisture from the air, is covered with white and powdery coating of hydrated sulphates and becomes friable. The cleavage is imperfect. The hardness is 2-3, and the density is 2.7. The mineral is colourless and its taste is salty.

*Origin.* The origin is chemogenic. Thenardite is formed together with other water-soluble sulphates in the lakes and lagoons of the sea basins, as well as under dehydration of mirabilite.

*Deposits.* In the USSR there are deposits in Turkmenia (Kara-Bogaz-gol), in Eastern Siberia (the lakes of Barabinskaya and Kulundinskaya Steppes). In other countries the mineral is found in Chile (in the nitre deposits); in the USA (boric and sodium lakes in the states of Nevada and California).

*Practical use.* In chemical industry thenardite is used as the main raw material in the production of soda.

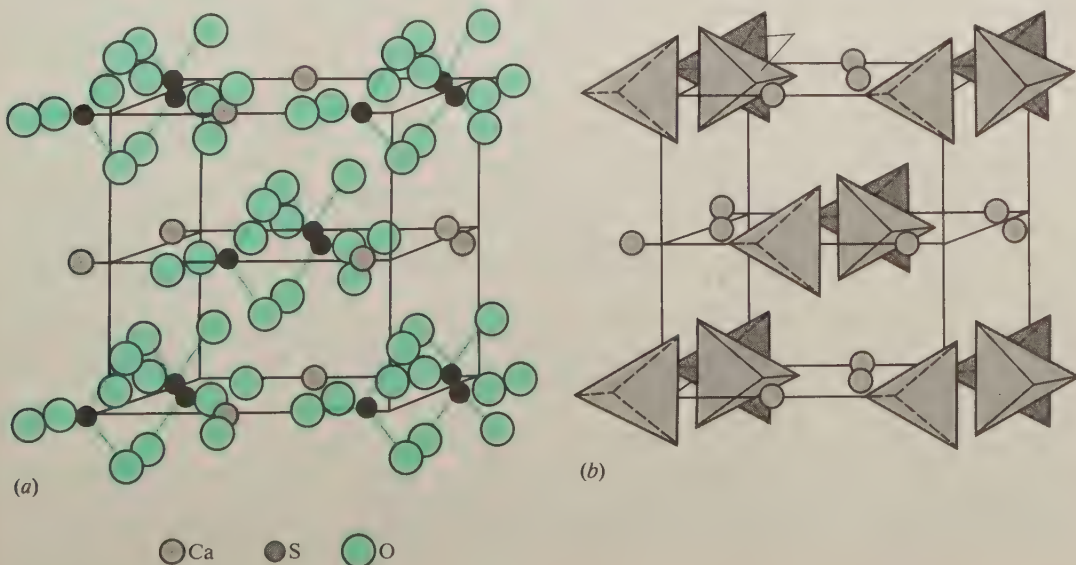
**ANHYDRITE**  $\text{Ca}[\text{SO}_4]$ ,

sometimes contains the impurities of Mn, Mg, Sr, Ba, TR. In the crystalline structure the  $\text{Ca}^{2+}$  ion finds itself in the environment of eight oxygen ions, which belong to the six neighbouring ions of  $[\text{SO}_4]^{2-}$  (Fig. 128).

The system is orthorhombic. The crystals are columnar, nearly isometric. The aggregates are solid and fine-grained.

The colour is white, grey, and bluish. The streak is white. The lustre

Fig. 128. Anhydrite structure in globular (a) and polyhedral (b) models



is vitreous, occasionally weakly purple at the surface of perfect cleavage. The hardness is 3.5 and the density is 3.0.

*Origin.* Anhydrite is an important mineral of sedimentary rocks, which is found together with gypsum and halite. It sediments from the sea water at the temperature higher than 42°. At a lower temperature gypsum  $\text{Ca}[\text{SO}_4] \cdot 2\text{H}_2\text{O}$  is deposited. In those cases when the concentration of salts ( $\text{NaCl}$  and particularly  $\text{MgCl}_2$ ) is very high, anhydrite can also be deposited at much lower temperatures (20-30°).

Under normal pressure and in the presence of water anhydrite is transformed into gypsum with a marked increase in its volume (by 30%). The depth of the bedding, at which such a transformation becomes possible, does not exceed 100-150 metres, the pressure of the overlying rocks being taken into account. Anhydrite is also formed under the dehydration of gypsum in the processes of metamorphism. *Deposits.* The deposits of anhydrite are connected with the deposits of salts that originate in the seas. In the USSR anhydrite is found in the Ukraine (the Artemovsk deposit). In countries outside the USSR there are deposits of this mineral in GDR, FRG, and in India (Punjab state). *Practical use.* Anhydrite is used in the production of cement.

#### CELESTITE $\text{Sr}[\text{SO}_4]$ (56% of $\text{SrO}$ )

The mineral often contains Ba. In the crystalline structure of celestite as distinct from the structure of anhydrite, the large  $\text{Sr}^{2+}$  ions are in the environment of 12 oxygen atoms, belonging to seven  $[\text{SO}_4]^{2-}$  anions, ten of which are located along the edges of five tetrahedra, while two find their place in the apexes of the remaining two tetrahedra.

The system is orthorhombic. The crystals are tabular, prismatic (Fig. 129), pyramidal, sometimes markedly elongated. The aggregates are rod-like, granular, compact, not infrequently in druses, and secretions.

The colour is light-blue, bluish-white, grey, often transparent. The perfect cleavage is parallel to  $\{001\}$ . The lustre is vitreous; it can also be up to purple at the surface of cleavage. The hardness is 3-3.5, and the density is 4. After ignition and wetting it turns the flame into a carminite-red colour (a reaction to strontium).

*Origin.* The origin of celestite is mainly sedimentary, and is related to the paragenesis with gypsum, calcite, barite, and native copper. The low-temperature hydrothermal origin is also possible.

*Deposits.* In the USSR there are deposits in Central Asia (the Lyakkan deposit in the Ferghana valley), in Mangyshlak, in the Volga River district. The Arkhangelsk Region, and elsewhere. In other countries the deposits are in Italy (the Island of Sicily), in FRG, England, and the USA.

*Practical use.* Celestite is the basic raw material in the production of strontium and strontium salts, used in sugar industry and in pyrotechnical engineering.

#### BARITE (heavy spar) $\text{Ba}[\text{SO}_4]$ (65.7% of $\text{BaO}$ )

The origin of the term can be traced back to the Greek word 'barytes', which means 'weight'. The mineral usually contains Sr, sometimes Pb, Ra, etc. The crystalline structure is similar to the structure of celestite.

The system is orthorhombic. The crystals are tabular (Fig. 130); the

Fig. 129. Celestite crystals

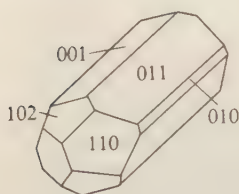
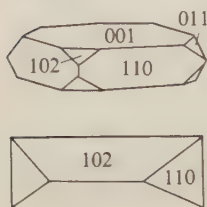


Fig. 130. Barite crystals





aggregates are granular, compact, and foliated. The mineral is also found in the form of druses.

Barite is colourless, though sometimes it is water-transparent, more often white, grey, and not infrequently, acquires red, bluish, brown, and other colours, as a result of the presence of impurities. The streak is white. The cleavage is perfect and parallel to {001}. In two other directions it is less perfect. The lustre is vitreous, sometimes purple. The hardness is 3-3.5, and the density is 4.5.

*Origin.* The hydrothermal origin is related to ore veins with galena, sphalerite, pyrite, cinnabar, fluorite; independent barite veins are often formed. Barite of the exogenous origin is formed in the zone of the iron cap at the expense of the reactions of the soluble salts of barium to the sulphates of other metals to  $H_2SO_4$ .

*Deposits.* The mineral is recovered from the deposits in the Kutaisi district in Georgia, in Turkmenia (Kopetdag), and in the Urals. Simultaneously it is extracted from the polymetallic deposits of the Altai and Kazakhstan.

*Practical use.* In its pure form and as barium preparations, barite is used in industry. It is employed in the drilling of holes as a weighting of clay solutions, in paint and varnish industry (lithopone), as a weighting material in the manufacturing of wall-paper, oil-cloth, and linoleum. Barium salts are utilized in the production of pesticides and in medicine, as well as for radiation-protection purposes (barite plaster).

#### ANGLESITE $Pb[SO_4]$ (68.3% of Pb)

The crystalline structure is similar to that of celestite.

The system is orthorhombic. The mineral forms small fine-tabular, elongated crystals, as well as compact granular masses.

The mineral is colourless or white. The lustre is adamantine. The hardness is 2.5-3, and the density is 6.3.

*Origin.* The origin is related to the oxidation zone of lead deposits in association with galena, cerussite and other secondary minerals of lead. The mineral is known in the polymetallic deposits of the Transbaikal region and Kazakhstan.

*Practical use.* Anglesite enters into the composition of oxidized ores of lead.

#### With Additional Anions

##### ALUNITE $KAl_3[SO_4]_2(OH)_6$ (11.4% of $K_2O$ ; 37.0% of $Al_2O_3$ ; 38.6% of $SO_3$ )

The mineral sometimes contains the isomorphic impurity of Na. In the crystalline structure the Al ions are in the octahedral environment of four groups of  $(OH)^-$  and two oxygen ions. Large cations  $K^+$  have their coordination number 12, i.e.  $6O_2^- + 6(OH)^-$ , and form layers with  $[SO_4]^{2-}$  anions. The layered motif is conditioned by the alternation of these layers with those composed of  $AlO_2(OH)_4^-$  octahedra.

The system is hexagonal-R. It is found in compact, earthy and solid masses, often with a breccia texture.

The colour is white, greyish, yellowish, or reddish. The hardness is 3.5-4. The density is 2.8.

*Origin.* The hydrothermal origin is associated with volcanic activity. The mineral is formed while being processed by sulphate solutions of the effusive rocks, rich in alkalines. This process (alunitization) is accompanied by kaolinization and silicification of rocks.

*Deposits.* In the USSR the deposits are located in Azerbaidzhan (Zaglik). Other well-known deposits occur in China (Taichow deposits), and in Italy, etc.

*Practical use.* Alunite rocks are used in the production of alum, and as ores of aluminium.

#### JAROSITE $KFe_3^+ [SO_4]_2(OH)_6$

The mineral sometimes contains the isomorphic impurity of Na, Pb, etc. The structure is of the same type as that of alunite.

The system is hexagonal-R. It is found in the form of solid granular or earthy masses, as well as in concretions of ochre-yellow or brown colour. The streak is yellow, and sparkling. The lustre is silky; the cleavage is perfect and parallel to  $\{0001\}$ . The hardness is 2.5-3.5, and the density is 3.2.

*Origin.* Jarosite is formed in the oxidation zone when the disintegration of sulphurous compounds of iron, mainly those of pyrite, takes place.

*Deposits.* In the USSR this mineral is known in the form of concretions and nodules in the oxidation zone of the gold-bearing deposits of Maikain in Northern Kazakhstan.

*Practical use.* Jarosite is used as a raw material in the production of fine polishing powder.

### Aquatic

#### GYPSUM $Ca[SO_4] \cdot 2H_2O$

In the crystalline structure of gypsum the ions of calcium, forming coordination polyhedra eight summits, have common edges with one another and with  $[SO_4]^{2-}$  tetrahedra, and are also surrounded by oxygen ions, belonging to the molecules of water. The layered motif is conditioned by the alternation of double layers, composed of  $Ca^{2+}$  and  $[SO_4]^{2-}$  ions with layers, consisting of  $H_2O$  molecules (Fig. 131).

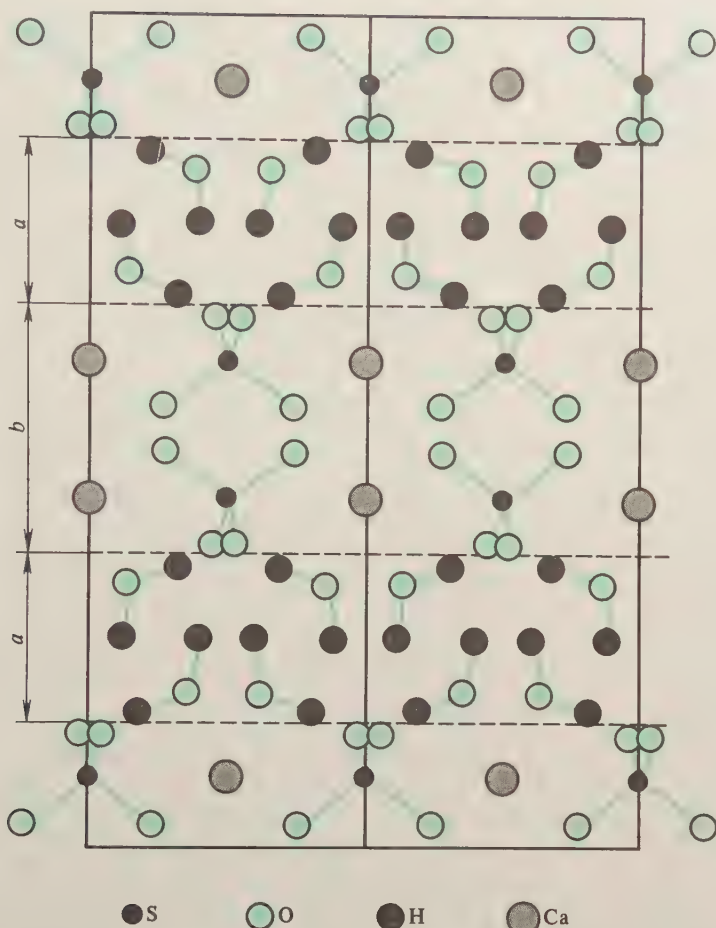
The system is monoclinic. The crystals are of the thick- and fine-tabular type; large crystals are very rare. Twins, e.g. 'swallow's tail' (see Fig. 32) are found to be characteristic. The aggregates are compact, granular, foliated and fibrous.

The colour is white, often transparent, as well as grey and pink, resulting from the impurities. The streak is white. The lustre is vitreous, with the fibrous varieties it is silky. The cleavage  $\{010\}$  is perfect, and can be flaked into thin leaves. The hardness is 2, and the density is 2.3.

*Varieties.* A compact fibrous variety of gypsum with a characteristic silky lustre is called *selenite*.

*Origin.* By its origin and location in nature gypsum is closely connected with anhydrite. It is a typical chemical sediment pertaining to seas. Among sedimentary rocks it forms layers, and is often associated with anhydrite, halite, native sulphur, sometimes with petroleum, can occur under the hydration of anhydrite, as well as in the weathering zone of sulphide minerals and native sulphur with the

Fig. 131. The structure of gypsum in its projection on  $\{010\}$ :  
 $a$ —the layer of  $H_2O$  molecules;  
 $b$ —the layer of  $Ca^{2+}$  and  $[SO_4]^{2-}$  ions



formation of compact and friable masses, usually polluted by clay and other admixtures, the so-called gypsum caps. As is the case with anhydrite, gypsum is found in the products of fumarole activity. *Deposits.* In the USSR, there are gypsum deposits in Arkhangelsk, Vologda and Vladimir Regions, in the Western Ural region, Bashkiria and Tatar ASSR (the deposits of Permian age), in the Irkutsk Region, in the Northern Caucasus, in Dagestan and Central Asia (the deposits of Jurassic age). In other countries, there are deposits in the USA, Canada, Italy, FRG, GDR, and France.

*Practical use.* Gypsum is used in its raw and burnt forms. When heated to 120-140° it is transformed into semi-hydrate,  $CaSO_4 \cdot 1/2H_2O$  (semi-burnt gypsum or alabaster); at higher temperatures burnt gypsum, or gypsum used in construction, is produced. Burnt gypsum is used in sculpture, architecture, plastering, in medicine, in the cement and paper industry. Crude gypsum is also employed in the production of Portland cement, in sculpture, and in agriculture. Fibrous gypsum, or selenite, particularly from the districts of Kungura in the Urals, is widely utilized for ornamental purposes.

A brief outline of some of the water-soluble sulphates of Na, Mg, Fe, and Cu are adduced in Table 6.

TABLE 6 *The Classification of Water-Soluble Sulphates (A Brief Outline)*

Mineral	Formula	System	Outer form	Colour	Cleavage	Hardness	Density	Taste
Mirabilite (glauberite salt)	$\text{Na}_2[\text{SO}_4] \cdot 10\text{H}_2\text{O}$	mon.	blooms and salt-like masses	colourless, white	perfect {100}	1.5-2	1.49	bitter and salty
Astrakhanite (bloedite)	$\text{Na}_2\text{Mg}[\text{SO}_4] \cdot 4\text{H}_2\text{O}$	mon.	granular, compact masses, parallel-rod-like aggregates	colourless, grey, yellowish	none	3-3.5	2.27	weakly bitter and salty
Epsomite	$\text{Mg}[\text{SO}_4] \cdot 7\text{H}_2\text{O}$	orthorhomb.	acicular, fibrous crystals and aggregates	colourless, white	perfect {010}, distinct {101}	2.5	1.70	astringent, bitter, salty
Chalcanthite	$\text{Cu}[\text{SO}_4] \cdot 5\text{H}_2\text{O}$	tricl.	sinters, crusts, parallel-rod-like aggregates	bright blue	perfect {110}	2.5	2.28	unpleasant, metallic, astringent
Melanterite	$\text{Fe}[\text{SO}_4] \cdot 7\text{H}_2\text{O}$	mon.	sinters, crusts, powdery and parallel-rod-like aggregates	bottle-green	perfect {001}	2.5	1.9	metallic, astringent
Goslarite	$\text{Zn}[\text{SO}_4] \cdot 7\text{H}_2\text{O}$	mon.	crusts and nodular sinters	colourless, greyish-white	perfect {010}	2.5	1.58	astringent, unpleasant

## Phosphates, Arsenates and Vanadates

This vast class, featuring more than 300 species, amalgamates minerals, representing, mainly salts of the phosphoric, arsenic, and, to a lesser extent, vanadium acids. The prevalent species, forming cations in the minerals pertaining to this class, are the  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $(\text{UO}_2)^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Al}^{3+}$  ions, as well as some of the alkaline metals.

In phosphates and their analogues the radicals are represented mainly by the tetrahedral oxygen complexes  $[\text{PO}_4]^{3-}$ ,  $[\text{AsO}_4]^{3-}$ , and  $[\text{VO}_4]^{3-}$ . The polymerization of anion radicals is characteristic only of a restricted group of vanadates. The radicals  $[\text{V}_2\text{O}_8]$  have been found, for instance, in uranium micas with a considerable number of minerals comprising this particular class. The function of additional anions is also shared by the groups of  $(\text{OH})^-$ , the  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{O}^{2-}$ , more seldom  $[\text{CO}_3]^{2-}$ ,  $[\text{SO}_4]^{2-}$  ions, etc. About half of all the representatives of this class contain crystallized water. All the minerals of this class under discussion are characterized by a covalent bond within the limits of anion complexes and by the anion bond between anions and cations. In hydroxyl-bearing and hydrated phosphates and their analogues a considerable role is allotted to hydrogen bonds.

A large number of phosphates and their analogues are characterized by the iso- and heterovalent isomorphic replacements in both the cation and anion parts. The  $\text{Ca}^{2+}$  ions in apatite and other phosphates are often replaced by the  $\text{Sr}^{2+}$  and  $\text{TR}^{3+}$  ions, and the  $\text{Fe}^{2+}$  ions by  $\text{Mn}^{2+}$  ions, in erythrite there can be a replacement of  $\text{Co}^{2+}$  ions by those of  $\text{Ni}^{2+}$ . Wide isomorphic replacements have been established in many minerals between additional anions of  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ , and  $\text{O}^{2-}$ . The isomorphism between the anions of  $[\text{PO}_4]^{3-}$  and  $[\text{AsO}_4]^{3-}$  is restricted, though it is infrequently that the radical  $[\text{PO}_4]^{3-}$  is replaced by the anions of  $[\text{SiO}_4]^{4-}$ ,  $[\text{SO}_4]^{2-}$ , and even  $[\text{CO}_3]^{2-}$ , as is the case in apatite.

In phosphates and their analogues the complex anions are represented by the island groups bound by cations. Hence, they all pertain to one, island, type of structure. In accordance with the characteristic features of the spatial distribution of cations and additional anions, as well as the molecules of water, phosphates and their analogues are characterized by coordination, chain, layered and frame structural motifs. Minerals with coordination and frame motifs usually have an isometric form of crystals. Minerals of chain motif, as a rule, have an elongated-and-prismatic habit. Hydrous phosphates and their analogues with a layered structural motif have a foliated-flattened or tabular habit of crystals or scaly aggregates of plates.

Dehydrated phosphates, simple, as far as their composition is concerned, and their analogues with coordination and chain motifs are distinguished from the hydrous phosphates with a layered motif by a higher degree of hardness.

The content of ions-and-chromophores is connected with various colours of phosphates and their analogues. A large number of phosphates and their analogues are characterized by luminescence.

Hypogene mineral formation is typical of a considerable part of phosphates. Magmatic processes are connected with their formation, predominantly in the form of accessory minerals in igneous rocks. Phosphates are also characteristic of pegmatites, skarns, greisens and

hydrothermal veins. In hypogene conditions a considerable number of phosphates are formed, as well as all arsenates and vanadates. Large accumulations of phosphates are associated with the process of sedimentation (phosphorites). Many rare phosphates, containing rare-earth and radioactive elements, are accumulated in river and coastal placers. The uraniferous phosphates and their analogues of hypogene origin serve as a source of radioactive raw material. Vanadates are also ore minerals of vanadium. The bright colour of some of the phosphates and their analogues containing chromophore elements (uranium micas, erythrite, annabergite, etc.) are used as an exploratory feature of U, Co, Ni and other ores.

## Systematization

### Phosphates, Arsenates and Vanadates of Island Structure

#### Simple

*The group of heterosite*

heterosite  $(\text{Mn, Fe})\text{PO}_4$  (orthorhombic).

*The group of xenotime*

xenotime  $(\text{Y, La ...})[\text{PO}_4]$  (tetragonal).

*The group of monazite*

MONAZITE  $(\text{Ce, La ...})[\text{PO}_4]$  (monoclinic).

#### Complex

*The group of triphylite*

triphylite  $\text{Li}(\text{Mn, Fe})[\text{PO}_4]$  (orthorhombic).

#### With Additional Anions

*The group of apatite*

APATITE,  $\text{Ca}_5[\text{PO}_4]_3(\text{F, Cl, OH, O})$  (hexagonal).

*The group of pyromorphite (hexagonal)*

PYROMORPHITE  $\text{Pb}_5[\text{PO}_4]_3\text{Cl}$ ;

mimetesite  $\text{Pb}_5[\text{AsO}_4]_3\text{Cl}$ ;

vanadinite  $\text{Pb}_5[\text{VO}_4]_3\text{Cl}$ .

*The group of amblygonite (hexagonal-R)*

amblygonite  $\text{LiAl}[\text{PO}_4]\text{F}$ ,

montebrasite  $\text{LiAl}[\text{PO}_4](\text{OH})$ .

*The group of pseudomalachite*

pseudomalachite  $\text{Cu}_5[\text{PO}_4]_2(\text{OH})_6$  (monoclinic),

libethenite  $\text{Cu}_2[\text{PO}_4](\text{OH})$  (orthorhombic),

olivenite  $\text{Cu}_2[\text{AsO}_4](\text{OH})$  (orthorhombic),

adamite  $\text{Zn}_2[\text{AsO}_4](\text{OH})$  (orthorhombic),

triplite  $(\text{Mn, Fe})_2[\text{PO}_4]\text{F}$  (monoclinic).

*The group of lazulite*

lazulite  $(\text{Mg, Fe})\text{Al}_2[\text{PO}_4]_2(\text{OH})_2$  (monoclinic).

*The group of herderite*

herderite  $\text{CaBe}[\text{PO}_4](\text{OH, F})$  (monoclinic).

#### Aquatic

*The group of churchite*

churchite  $\text{Y}[\text{PO}_4] \cdot 2\text{H}_2\text{O}$  (monoclinic).

*The group of vivianite (monoclinic)*

VIVIANITE  $\text{Fe}_3[\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$ ;

ERYTHRITE  $\text{Co}_3[\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$ ,

ANNABERGITE  $\text{Ni}_3[\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$ .

The family of  
uranium micas

The group of  
scorodite  
(orthorhombic)  
The group of  
turquoise

TORBERNITE  $\text{Cu}(\text{UO}_2)_2[\text{PO}_4]_2 \cdot 12\text{H}_2\text{O}$  (tetragonal);  
AUTUNITE  $\text{Ca}(\text{UO}_2)_2[\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$  (tetragonal);  
zeunerite  $\text{Cu}(\text{UO}_2)_2[\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$  (tetragonal);  
CARNOTITE  $\text{K}_2(\text{UO}_2)_2[\text{V}_2\text{O}_8] \cdot 3\text{H}_2\text{O}$  (monoclinic);  
tyuyamunite  $\text{Ca}(\text{UO}_2)_2[\text{V}_2\text{O}_8] \cdot 8\text{H}_2\text{O}$  (orthorhombic).  
SCORODITE  $\text{Fe}[\text{AsO}_4] \cdot 2\text{H}_2\text{O}$ ,  
variscite (Al, Fe)[ $\text{PO}_4$ ]  $\cdot 2\text{H}_2\text{O}$ .

TURQUOISE  $\text{Cu}(\text{Al, Fe})_6[\text{PO}_4]_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$  (triclinic);  
eosphorite (Mn, Fe),  $\text{Al}[\text{PO}_4](\text{OH})_2 \cdot \text{H}_2\text{O}$  (orthorhombic).

## Phosphates and Their Analogues of the Island Structure

### Simple

MONAZITE (Ce, La ...) [ $\text{PO}_4$ ]

The mineral usually contains 5-10% of  $\text{ThO}_2$ . In the crystalline structure the  $\text{Ce}^{3+}$  ions are in the coordination of 9 (6 + 3); each of them is surrounded by six isolated anions of [ $\text{PO}_4$ ] $^{3-}$ , the  $\text{Ce}^{3+}$  ion is firmly bound with the three pairs of oxygen ions along the edges of three [ $\text{PO}_4$ ] $^{3-}$  tetrahedra, located in plane {100}; the bonds are less stable with the other ions of oxygen, belonging to the apexes of the three [ $\text{PO}_4$ ] $^{3-}$  tetrahedra of the neighbouring layers.

The system is monoclinic. The crystals are predominantly flattened and tabular, and are found in the form of independent disseminations in the feldspar of pegmatitic veins.

The colour is reddish-brown, yellow-brown. The lustre is vitreous, greasy. The cleavage is perfect, parallel to {100}. The hardness is 5-5.5, and the density, is about 5. The mineral is radioactive.

*Origin.* Monazite is an accessory mineral in granites. In pegmatites there are single crystals the size of which reaches several centimeters in length. The mineral is found together with feldspar, zircon, ilmenite, xenotime, uraninite, etc. The origin of monazite can also be associated with metamorphic rocks, as well as in veins of the Alpine type.

Monazite placers, formed as a result of the weathering of monazite-bearing granites and gneisses are of industrial importance.

*Deposits.* Large sea placers containing monazite are known in India (Travancore), in Sri Lanka, and in Brazil. The mineral is also found in the pegmatites of Madagascar.

*Practical use.* Monazite is an ore of rare earths and thorium.

### With Additional Anions

APATITE  $\text{Ca}_5[\text{PO}_4]_3(\text{F, Cl, OH, O})$

Apatite often contains the isomorphic impurities of  $\text{Sr}^{2+}$ ,  $\text{TR}^{3+}$ ,  $\text{Y}^{3+}$ , and  $\text{Mn}^{2+}$ . In the crystalline structure of apatite (Fig. 132) the chain motif along the *C* axis is determined by the fact that  $\text{Ca}^{2+}$  ions form single and triple columns interconnected by the tetrahedral groups of [ $\text{PO}_4$ ] $^{3-}$ . In the triple columns the calcium ions (Ca I) are found to be in a distorted trigonal-prismatic coordination with the coordination

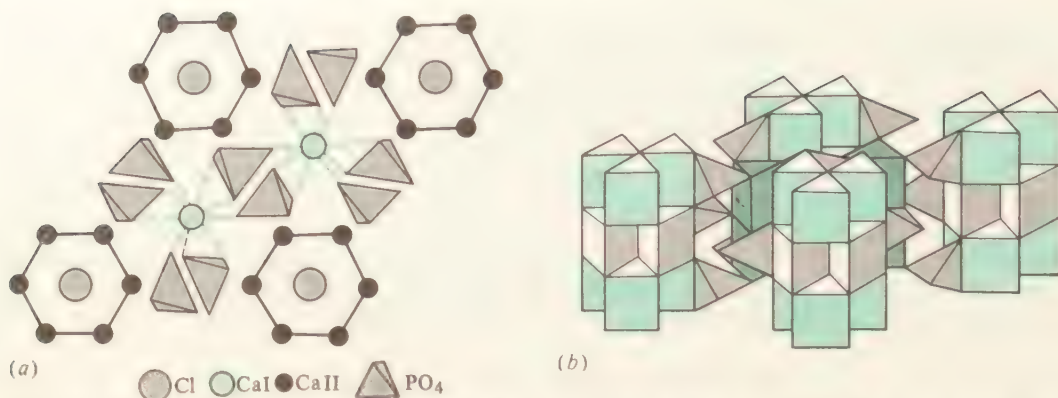


Fig. 132. Apatite structure in its projection on {0001} (a), and in a polyhedral model (b)

number 7 (6O + 1F), while in single columns (Ca II) with the coordination number 9.

The system is hexagonal. The crystals usually represent combinations of a hexagonal prism and a dipyrmaid of the elongated-prismatic or flattened-prismatic habit (Fig. 133). The size covers the range from very small crystals, discernable only under the microscope, to the gigantic ones, weighing 50 kg. Block granular saccharoidal masses are also a characteristic feature.

The colour is yellow-green, white, light-blue, reddish-brown, pink, and black. The streak is light. The lustre is vitreous. The cleavage is imperfect after pinacoid and prism. The fracture is uneven. The mineral is brittle, its hardness equals 5, and the density is 3.2. The luminescence is violet or pink. A certain odour is perceptible when the mineral is struck.

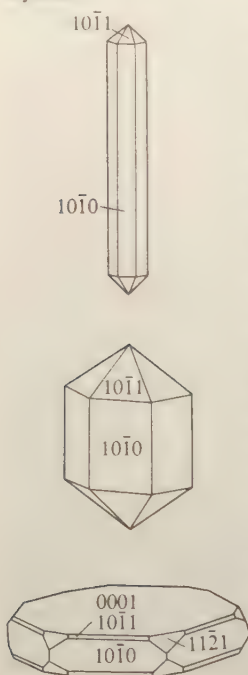
*Varieties.* According to the composition of additional anions the following varieties can be singled out: fluorine-, chlorine-, hydroxyl-, and oxyapatite.

The varieties containing the  $[\text{CO}_3]^{2-}$  group are called carbonate-apatite, or *phosphorite*.

*Origin.* Apatite of magmatic origin is found in acid and middle igneous rocks as an accessory mineral; sometimes it forms industrial concentrations, in alkaline rocks (in nepheline sienites) together with nepheline it is one of the most important rock-forming minerals. This is the most significant industrial type of apatite deposits, where the mineral is represented by light, yellow-green fine-granular masses. Large accumulations of apatite are also in correspondence to carbonatites. Apatite is found in the pegmatite veins with muscovite, and is typical of some of the contact-metasomatic deposits, where well-faced large crystals of light-blue or light-blue and green colour originate in association with diopside, phlogopite, calcite, scapolite; it also forms granular diopside-apatite rocks; and is found in the veins of Alpine type. Phosphorites are of biochemical origin.

*Deposits.* The largest deposit of apatite in the world is Khibiny (USSR). Apatite ores are genetically connected with the complex of alkaline rocks of the Khibiny massif of nepheline sienites. There is a well-known Oshurkovo deposit in Buryatia. Apatite is also recovered together with magnetite from the carbonatite ores of Kovdor deposit in the Murmansk Region. In the Baikal region apatite is found in large crystals in the contact-metasomatic deposits of Slyudyanka. Deposits

Fig. 133. Apatite crystals





of phosphorites are known in the European part of the USSR (Yegoryevsk), and in Kazakhstan (Karatau). In other countries there are large deposits of phosphorites in Morocco, Algeria, and Tunisia. *Practical use.* Apatite is the source of phosphorus and is the basic raw material for the production of phosphorous fertilizers. TR and Sr are recovered as by-products.

#### PYROMORPHITE $Pb_5[PO_4]_3Cl$

The crystalline structure is similar to that of apatite.

The system is hexagonal. Crusts of intergrown crystals of grass-green colour are a characteristic feature. The crystals are of prismatic form with an adamantine lustre. The hardness is 3.5-4.0. There is no cleavage. The density is high: 6.7-7.1.

*Origin.* Pyromorphite originates in the oxidation zone of lead deposits. It associates with galena, anglesite and other minerals of the oxidation zone, and sometimes forms pseudomorphs after galena. There are cases when pyromorphite is found in the low-temperature veins. It is found in small quantities in the oxidation zone of a large number of deposits (in the Transbaikal region, Kazakhstan, and elsewhere).

*Practical use.* When the accumulations are considerable, the mineral is used as a lead ore.

#### Aquatic

#### VIVIANITE $Fe_3[PO_4]_2 \cdot 8H_2O$

In the crystalline structure of vivianite (Fig. 134) the  $Fe^{2+}$  ions are in single  $FeO_2(OH)_4$ -octahedra and the paired along the edge  $FeO_4(H_2O)_2$ -octahedra, which together with the  $[PO_4]^{3-}$  tetrahedra, connecting them, form corrugated layers parallel to  $\{010\}$ . Between the layers there are hydrogen bonds.

The system is monoclinic. Vivianite usually forms radial stellate aggregates. The mineral is also found in the form of earthy masses of white colour.

The colour of pure crystalline vivianite (nonoxidized) is light-green. When the mineral is oxidized it becomes greyish-blue, blue to dark-blue. The lustre is vitreous. The hardness is 1.5-2, and density is 2.6.

*Origin.* Vivianite is an exogenetic mineral, and is found in peat-bogs and iron-bearing deposits originated in the lakes and seas. It is known in the peat-bogs of the Moscow region and in the iron ores of the Kerch deposit in the Crimea.

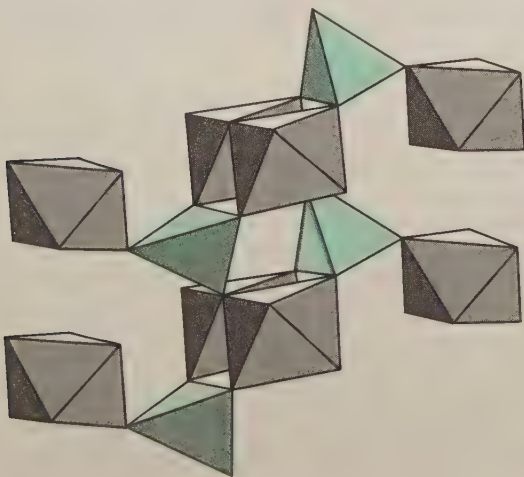
*Practical use.* Vivianite is used as a blue paint.

#### ERYTHRITE $Co_3[AsO_4]_2 \cdot 8H_2O$

The term is derived from the Greek word ('erythros' meaning 'red'). Sometimes this mineral is characterized by the impurities of Ni and Mg. The crystalline structure is of the same type as that of vivianite.

It is spread in the form of earthy fine-powdery masses or crystalline-radiated aggregates of either pink or crimson colour,

Fig. 134. Vivianite structure in a polyhedral model



and is the product of the oxidation of cobaltite and other minerals. The mineral is also an exploratory feature of cobalt.

#### ANNABERGITE $\text{Ni}_3[\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$

The crystalline structure is analogous to that of vivianite.

It forms coatings and earthy masses, of apple-green colour. Annabergite is a secondary mineral, and is formed in the oxidation zone of ores represented by the arsenides of nickel. It is also an exploratory feature of nickel.

#### The Family of Uranium Micas

The family of *uranium micas* comprise more than 50 minerals, representing arsenates, phosphates and vanadates  $(\text{UO}_2)^{2+}$  with Cu, Ca, K and other cations. The crystalline structure of micas is characterized by a layered motif. Between the layers, composed of tetrahedral anions and groups of  $(\text{UO}_2)^{2+}$  there are large cations of  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cu}^+$ , and others, as well as the molecules of water.

The uranium micas usually form fine foliated and powdery accumulations and coatings. The cleavage is perfect to  $\{001\}$ . The mineral is excessively radioactive. The colour is bright, mainly yellow and green. The lustre is purple. The hardness is 1 to 2.5, and the density is approximately 3-4.5. A large number of uranium micas have a bright green luminescence.

*Origin.* The origin is exogenetic. These minerals are of the oxidation zone of uranium deposits. It associates with uraninite and other minerals of uranium, vanadium, with carbonates and barites.

The most important uranium micas are the following:

#### TORBERNITE $\text{Cu}(\text{UO}_2)_2[\text{PO}_4]_2 \cdot 12\text{H}_2\text{O}$ (tetragonal system)

The mineral forms small leaves of the tetragonal form. The colour is emerald-green.

#### AUTUNITE $\text{Ca}(\text{UO}_2)_2[\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$ (tetragonal system)

It is found in the form of fine-scaly or powdery coatings of canary-yellow colour.

#### CARNOTITE $\text{K}_2(\text{UO}_2)_2[\text{V}_2\text{O}_8] \cdot 3\text{H}_2\text{O}$ (monoclinic system)

The mineral forms powdery masses and coatings of a bright-yellow colour.

#### TYUYAMUNITE $\text{Ca}(\text{UO}_2)_2[\text{V}_2\text{O}_8] \cdot 8\text{H}_2\text{O}$ (orthorhombic system)

Fine-scaly and earthy masses of a green-yellow colour.

Under the microscope the three latter minerals are practically undistinguishable.

Uranium micas are spread in a number of deposits in the USSR and in other countries. They serve as a reliable exploratory feature of uranium. When the accumulations of these minerals is considerable, they are used as ores of uranium, radium, and vanadium.

#### SCORODITE $\text{Fe}[\text{AsO}_4] \cdot 2\text{H}_2\text{O}$

In the crystalline structure the  $\text{Fe}^{3+}$  ions are in the octahedral coordination of  $4\text{O} + 2(\text{H}_2\text{O})$  and together with anions form a frame motif, in the voids of which there are molecules of water.

System is orthorhombic. Crystals are very rare. There are usually compact or powdery earthy masses of a dirty-green, grey-green, and sometimes flour-white colour. In the crystals the lustre is vitreous to adamantine, in earthy masses it is dull. The mineral is exceptionally brittle; the fracture is uneven, the hardness is 3.5-4 (usually it is lowered), and the density is 3.3.

*Origin.* The mineral is formed in the process of the decomposition of arsenopyrite and other minerals, and is present in the oxidation zone of a large number of deposits.

*Deposits.* In the USSR, scorodite is known in Uzbekistan (Brig-Mulla), Tadzhikistan (Takeli), in the Eastern Transbaikal region (the Sherlova mountain), and elsewhere. There are deposits of this mineral in Zaire too.

*Practical use.* Perfect crystals of rare occurrence are a raw material in jewellery.

#### TURQUOISE $\text{Cu}(\text{Al}, \text{Fe})_6 [\text{PO}_4]_4 (\text{OH})_8 \cdot 4\text{H}_2\text{O}$

In the crystalline structure of turquoise Al octahedra are connected with the  $[\text{PO}_4]^{3-}$  tetrahedra by common apexes, thus forming a frame motif. In the large cavities the  $\text{Cu}^{2+}$  ions find themselves in the octahedral environment of  $4(\text{OH}) + 2(\text{H}_2\text{O})$ .

The system is triclinic. The mineral is usually found in the form of compact cryptocrystalline concretions and veinlets. The crystals are very rare.

The colour is light-blue to light-blue-green. The lustre is waxy. The fracture is shelly. The hardness is 5-6, and the density is approximately 2.7.

*Origin.* Turquoise is of an exogenetic origin and is found in the form of veinlets in the brecciated volcanic rocks, often together with the hydroxides of iron.

*Deposits.* In the USSR there are deposits in Uzbekistan and Kazakhstan. In other countries this mineral is recovered from the deposits in Iran, Australia, etc.

*Practical use.* Turquoise is a raw material in jewellery.

## Molybdates and Tungstates

The class of molybdates and tungstates comprise a small number (approximately 25) of mineral species, representing mainly the simple and hydrous salts of the molybdenite and tungsten acids containing the ions of  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $(\text{UO}_2)^{2+}$ , as well as some rare minerals of Mo, W,  $\text{UO}_2$ , Al, Si with an undetermined structure. Among the impurities the following are found to be common: Sr, Fe, Mn, TR, Nb, Ta, Si, P, sometimes V, Cr, etc.

Molybdates and tungstates are minerals with an ionic character of bond between the cations and the anions, and the covalent bond that exists within the boundaries of the anion radicals; in hydrous molybdates and tungstates the hydrogen bond becomes markedly apparent. The main species-forming metals, molybdate and tungstate, being in the highest oxidized form, form oxygen anions in the form of tetrahedral (distorted) radicals  $[\text{Mo}^{6+}\text{O}_4]^{2-}$  and  $[\text{W}^{6+}\text{O}_4]^{2-}$ .

The covalent character of the bond in these anions is conditioned by

the hybridization of *s*-, *p*- and *d*-orbitals of Mo and W with 2*p*-orbitals of oxygen ions. Since the charge and dimensions of the anion groups  $[\text{MoO}_4]^{2-}$  and  $[\text{WO}_4]^{2-}$  is identical, the latter are found to be isomorphous in some minerals and replace each other. The restriction of isovalent isomorphous replacements between them, as is the case with the series including scheelite  $\text{Ca}[\text{WO}_4]$ —powellite  $\text{Ca}[\text{MoO}_4]$  is conditioned by the temperature factors and the distinctions in the electronic structure of Mo and W, which is connected with a greater degree of covalence in  $[\text{MoO}_4]^{2-}$  rather than in  $[\text{WO}_4]^{2-}$ . For some of the molybdates and tungstates the isomorphous impurity  $[\text{CrO}_4]^{2-}$  has been established. Isovalent isomorphism is also characteristic of cations. The  $\text{Ca}^{2+}$  ions in scheelite are often replaced by the ions of  $\text{Sr}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ , more seldom by  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$ , as well as rare earths.

Heterovalent isomorphism in molybdates and tungstates becomes apparent when the replacement of both the anions and the cations takes place. The almost permanently existing impurity in scheelite of  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$  during the replacement of hexavalent ions in anion radicals is accompanied by a heterovalent isomorphism in the cation part, with the compensation of redundant charges, for example, in the pattern:  $\text{Ca}_{1-n}(\text{TR}_{\text{Ca}^{2+}}^{3+})_n[\text{WO}_4]_{1-n}\{[\text{NbO}_4]_n^{3-}\}'_n$ .

The marked relationship between the various bonds in molybdates and tungstates is the most important characteristic feature of these minerals. All of them refer to the island structural type; the anion radicals  $[\text{MoO}_4]^{2-}$  and  $[\text{WO}_4]^{2-}$  form isolated groups bound by cations. In simple tungstates and molybdates large cations of  $\text{Ca}^{2+}$  and  $\text{Pb}^{2+}$  have their coordination number 8. In hydrous molybdates and tungstates with hydrogen bonds the layered motif is predominant. It is conditioned by the planar orientation of the hydroxyl groups of  $(\text{OH})^-$  and the crystallization of water  $\text{H}_2\text{O}$ . Cations of small dimensions,  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$ , are found to be in an octahedral orientation.

It should be mentioned that the minerals of the group of wolframite  $(\text{Fe}, \text{Mn})\text{WO}_4$  are usually referred to the class of tungstates. However, in terms of their structure, and what is particularly significant, by all their physical properties, they are affiliated to the complex oxides of the layered structure with a characteristic octahedral coordination of tungsten and iron (manganese).

The physical and morphological characteristic features of molybdates and tungstates are in congruence with the crystalline characteristic features and the type of predominant chemical bonds. Simple molybdates and tungstates with the ionic type of bonds between cations and anions are mainly typified by an isometric form of crystals and crystalline grains. Minerals with a layered structural motif are distinguished by a foliated-flattened habit of fine crystals with an absolutely perfect cleavage, usually forming earthy or radial-scaly aggregates. The hardness of simple molybdates and tungstates is markedly higher than those with a layered structure (3-4.5 and 1-2 respectively). Simple molybdates and tungstates are distinguished by a strong, almost adamantine lustre on the faces and cleaved spallings (the greasy lustre being characteristic of an uneven surface) and also by a high degree of refraction. The colour of molybdates and

tungstates is connected with the presence of ions-chromophores. Molybdates and calcium tungstates lacking in impurities are colourless. However, owing to the presence of TR, Mn, Fe impurities, and radiational defects, they can have various colour. Molybdates and tungstates of lead are distinguished by a bright yellow or orange colour. Hydrated molybdates and tungstates are of yellow and greenish colour, associated with the absorption on the  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$  and  $(\text{UO}_2)^{2+}$  ions, which are surrounded by the groups of  $(\text{OH})^-$  or the  $\text{H}_2\text{O}$  molecules.

The luminescence of molybdates and the tungstates of calcium is connected with the defective anion centres of the type  $[\text{W}^{5+}\text{O}_4]^{3-}$  and the impurity of the active elements of  $\text{Mn}^{2+}$ ,  $\text{TR}^{2+}$ , and  $\text{TR}^{3+}$ .

The origin of molybdates and tungstates in hypogene conditions is connected mainly with the processes of the formation of skarns, greisens, hydrothermal veins (scheelite, molybdoscheelite), while in the hypogene conditions it is related to the oxidation processes of molybdenite and wolframite. Tungstates and molybdates (scheelite, molybdoscheelite, as well as ferrimolybdite, and more seldom wulfenite) form industrial accumulations and are the most important mineral ores of tungstate and molybdate. Powellite, ferrimolybdite, as well as wulfenite serve as exploratory features of molybdenite mineralization.

## Systematization

### Molybdates and Tungstates of the Island Structure

#### Simple

*The group of scheelite-powellite*  
(tetragonal)

SCHEELITE  $\text{Ca}[\text{WO}_4]$ ,  
POWELLITE  $\text{Ca}[\text{MoO}_4]$ .

*The group of stolzite-wulfenite*  
(tetragonal)

stolzite  $\text{Pb}[\text{WO}_4]$ ,  
WULFENITE  $\text{Pb}[\text{MoO}_4]$ ,  
chillagite  $\text{Pb}[(\text{W}, \text{Mo})\text{O}_4]$ .

#### With Additional Anions

*The group of lindgrenite*

lindgrenite  $\text{Cu}_3[\text{MoO}_4]_2(\text{OH})_2$  (monoclinic),  
cuprotungstite  $\text{Cu}_2[\text{WO}_4](\text{OH})_2$  (tetragonal).

#### Aquatic

*The group of ferrimolybdite*  
*The family of hydrous uranium molybdates*

FERRIMOLYBDITE  $\text{Fe}_2^{3+}[\text{MoO}_4]_3 \cdot 7\text{H}_2\text{O}$  (orthorhombic),  
ferritungstite  $\text{Ca}_2\text{Fe}_2^{2+}\text{Fe}_2^{3+}[\text{WO}_4]_7 \cdot 9\text{H}_2\text{O}$  (tetragonal).  
iriginite  $\text{U}(\text{MoO}_4)_2(\text{OH})_2 \cdot 3\text{H}_2\text{O}$  (monoclinic),  
umohoite  $\text{UMoO}_6 \cdot 4\text{H}_2\text{O}$  (triclinic),  
magurmolite  $\text{Mg}(\text{UO}_2)_2[\text{MoO}_4]_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$  (monoclinic).

## Molybdates and Tungstates of the Island Structure

#### Simple

SCHEELITE  $\text{Ca}[\text{WO}_4]$  (80.6% of  $\text{WO}_3$ )

Molybdenum is often present here in the form of an isomorphic impurity, thus forming solid solutions with powellite. Scheelite often

contains the isomorphous impurities of TR, Sr, Mn, Nb, Ta, etc. In the crystalline structure of scheelite (Fig. 135) the tetrahedral groups  $[\text{WO}_4]^{2-}$  are connected with the ions of calcium, which are found in an octahedral coordination (oxygen atoms are in the apexes of the elongated and flattened tetrahedrons). Complex atoms and cations form an adamantine-like packing.

The system is tetragonal. The crystals are usually isometric and in the form of tetragonal dipyramids (pseudo-octahedrons) with an inconsiderable development of other simple forms (Fig. 136). The crystal faces are dull, more seldom mirror-like, sometimes with a granular striation characteristic of the penetration twins. More often the mineral forms fine dissemination or an accumulation of crystalline-granular aggregates of irregular form.

The colour is white, yellow, pink, smoky, etc. Molybdoscheelite is often grey to black at the expense of the inclusions of molybdenite scales. The cleavage is perfect after a dipyramid, distinct after a prism, and pinacoid. The fracture is step-like and uneven. The lustre is adamantine at the mirror faces and surfaces of the perfect cleavage, and greasy at the uneven fracture. The hardness is 4.5. With more brittle molybdoscheelite it is lowered to 3.5. The density is 6, but becomes lower with an increase in the content of molybdenum. Owing to a high degree of light refraction the mineral when in a wet state is easily distinguishable from quartz, feldspar, and calcite by its high relief. Pure scheelite easily lends itself to diagnosis, the bright-

Fig. 135. Scheelite structure in globular (a) and polyhedral (b) models

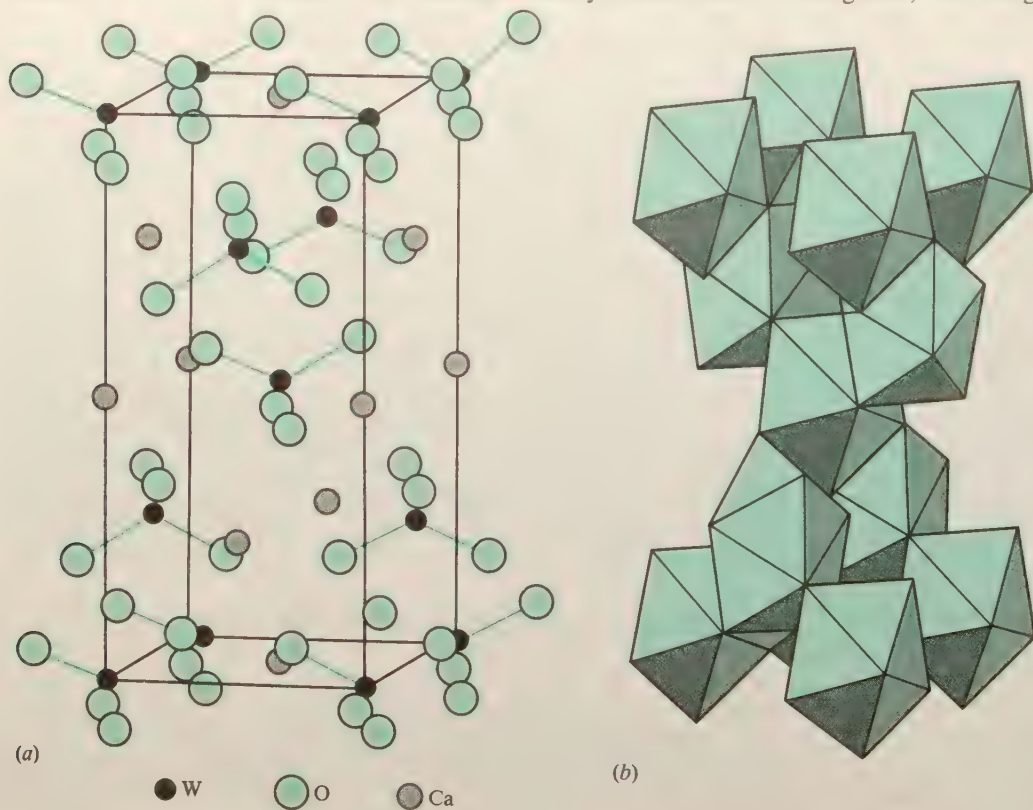
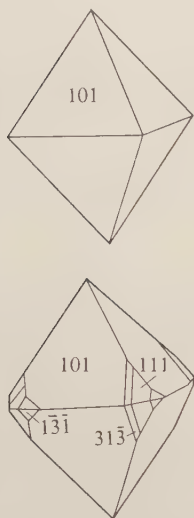


Fig. 136. Scheelite crystals



light-blue luminescence being relevant here. Molybdoscheelite has a white, creamy and yellow crystalloluminescence (not to be confused with powellite!). In HCl and HNO<sub>3</sub> it undergoes decomposition with the extraction of a yellow sediment WO<sub>3</sub>·nH<sub>2</sub>O. When heated in the presence of tin the solution acquires a blue colour. In a drop of HCl and after attrition with a steel needle the surface of scheelite becomes blue.

*Varieties.* *Molybdoscheelite* is a variety containing over 1% of MoO<sub>3</sub> content. *Zeyrigite* comprises more than 24% of MoO<sub>3</sub>.

The *origin* of scheelite (and molybdoscheelite) is mainly connected with the metasomatic processes in skarn deposits, in a characteristic association with hedenbergite, plagioclase, garnet (of the grossular-andradite series), quartz, wollastonite, actinolite, fluorite, calcite, as well as with molybdenite, more seldom with cassiterite, chalcopyrite, sphalerite, etc. In greisen and high-temperature hydrothermal deposits scheelite is found together with wolframite, sometimes replacing it with quartz, muscovite, fluorite, pyrite; in quartz veins, deposited among the amphibolites, scheelite is found together with biotite, amphibole, arsenopyrite; it is a characteristic mineral in quartz veins of some of the gold-bearing deposits. In low-temperature hydrothermal veins it is found with ferberite, antimonite, cinnabar, and tungstenite. Strati-formed deposits of metamorphic genesis, analogous in composition, are also found. Sometimes scheelite is accumulated in placers.

*Deposits.* In the USSR there are skarn deposits in Northern Caucasus (the Tyrnauz deposit with molybdoscheelite, and scheelite with molybdenite), in Central Asia (Chorukh-Dairon, Ingichke, and others), in the Primorski Krai (Vostok-2 and Lermontov); the greisen-veined hydrothermal deposits are in Kazakhstan (Verkhniye Kairakty, Boguty). In other countries there are large skarn deposits in Korea, in Australia, in the USA (Flat River), and elsewhere. The metamorphic deposits are found in Austria.

*Practical use.* Scheelite is the most important mineral of tungsten ores. The synthetic analogues of scheelite are used as luminophorous coverings in illumination engineering and television. Crystals with the impurities of TR are used in lazer engineering as well.

#### POWELLITE Ca[MoO<sub>4</sub>] (72.0% of MoO<sub>3</sub>)

Sometimes the mineral contains the impurities of TR and W. Powellite is an extreme member of the scheelite-powellite series. Its crystalline structure is similar to that of powellite.

The system is tetragonal. Usually in the form of pseudomorphs after molybdenite, this mineral also forms tabular, scaly, spherulite, and earthy aggregates. The crystals are of a tetragonally-bipyramidal habit and rare.

The colour is white, greenish, yellowish, the crystals are sometimes of a blue-green or orange-red colour. The lustre on the crystal faces is adamantine; in scaly aggregates it is purple, and with earthy aggregates the lustre is dull. The cleavage is perfect, particularly in scaly pseudomorphs. The mineral is brittle, its hardness is 3.5, and lower. In a wet state it has a strong lustre and a high relief. Powellite is characterized by a bright-yellow luminescence.

*Origin.* Hypogene powellite is found in syenite pegmatites and in hydrothermal veins together with the Iceland spar and zeolites. As an

isomorphic constituent it enters into molybdoscheelite, and sometimes forms in it the products of disintegration of the solid solution. Hypergene powellite is of a considerably greater occurrence and is developed at the expense of molybdenite.

*Deposits.* Hypogene powellite has been discovered in the pegmatites of the Ilmen mountains in the Urals, in the calcite veins among traps in Eastern Siberia. Hypergene powellite is common to the oxidation zone of a large number of deposits.

*Practical use.* Powellite is a secondary ore mineral of molybdenum. It also serves as an exploratory feature of a hypogene molybdenum mineralization.

**WULFENITE**  $\text{Pb}[\text{MoO}_4]$  (60.7% of  $\text{PbO}$ , 39.3% of  $\text{MoO}_3$ ), sometimes contains the impurities of W, Cr, V, Ca, etc. The crystalline structure is of the type similar to that of scheelite.

The system is tetragonal. The crystals are pyramidal, flattened or fine-tabular.

The colour is yellow, orange-brown to brown. The lustre is adamantine. The streak is white. The cleavage is distinct, and the fracture is uneven. The mineral is brittle, its hardness is 3, and the density is approximately 7.

*Origin.* The mineral originates in the oxidation zone of lead and molybdenum deposits in association with calcite, hydroxides of iron, malachite, etc.

*Deposits.* In the USSR the mineral is recovered from the following deposits: Sulemansai (Kazakhstan), and Chorukh-Dairon (Central Asia). In other countries there is the Trepcha deposits in Yugoslavia, etc.

*Practical use.* Wulfenite can enter into the composition of molybdenum and lead ores, and is an exploratory feature of primary mineralization.

### Aquatic

**FERRIMOLYBDITE**  $\text{Fe}_2^+[\text{MoO}_4]_3 \cdot 7\text{H}_2\text{O}$  (60.2% of  $\text{MoO}_3$ )

The crystalline structure has not yet been fully studied. It can only be presumed that the mineral is of the layered motif.

The system is orthorhombic. The crystals are: earthy, powdery, fine-fibrous, fine-scale, sometimes radially fibrous accumulations and aggregates, and sometimes, the mineral forms pseudomorphs after molybdenite.

The colour is yellow, greenish-yellow. The lustre is silky. The hardness is 1-1.5, and the density is 4.5.

*Origin.* The mineral originates in the oxidation zone at the expense of molybdenite in association with the hydroxides of iron, and sometimes with gypsum.

*Deposits.* In inconsiderable quantities the mineral is found in a large number of places. Large accumulations have been discovered in the Sora deposit in Khakasiya, in the Pervomaisk deposit in Buryatia, and elsewhere.

*Practical use.* Ferrimolybdite is an exploratory feature of molybdenum deposits. It can also be used as a by-product ore mineral of molybdenum.



## Part III

# Geological Processes of Mineral Formation and Mineral Associations

### How Minerals Are Formed

Minerals are the products of natural physicochemical processes, and the conditions in which they originate are various. These conditions are determined by the concentration of the components, temperature, pressure, and the interaction of minerals with country rocks. Since minerals are hard crystalline substances, their origin is reduced to the phasal transitions of a substance from its liquid into solid form, or from its gaseous into its solid form, or from one hard form into another. The phasal transition of a substance from its liquid into its hard form is a particularly widespread means of mineral formation. The crystallization of magma and the formation of igneous rocks can serve as an adequate example. When magma is solidified there appear numerous centres of crystallization, as a result of which the crystalline-granular rock is formed. Another example of crystallization from a liquid is the formation of mineral associations, which appeared during the sedimentation of minerals from hydrothermal solutions. The crystallization of halite during the evaporation of water can also serve as a good example illustrating the formation of minerals from solutions. Minerals can originate in colloidal solutions as well, the latter being characterized by the emergence of typical collomorphic structures.

The formation of sulphur in the volcanoes of Kamchatka and the Kuril Islands, as well as ammonium chloride ( $\text{NH}_4\text{Cl}$ ), sassoline  $\text{H}_3[\text{BO}_3]$ , cinnabar  $\text{HgS}$ , etc. clearly exemplify the emergence of minerals from a gaseous phase. However, the best example, is the formation of snow, the snowflakes representing the skeletal microcrystals of ice.

The formation of minerals during the transition from one solid state into another is typical of the processes of recrystallization, metamorphism and metasomatism, when some minerals are being disintegrated, while others are formed. These processes involve the participation of water solutions. Under metamorphism and the impact of both the pressure and the temperature without any changes in the chemical composition limestone is transformed into marble, quartz sand becomes quartzite, clay schists change into phyllites and mica schists. The recrystallization of glass of effusive rocks and gels in the conditions of their ageing also serve as an example of the formation of minerals from a hard phase.

In metasomatic processes the replacement of previously formed minerals by new ones under the impact of gaseous and water solutions is accompanied by a change in their chemical composition. Metasomatic processes are characteristic of both the deep and the surface conditions of their formation.

In conclusion, it should be said that the formation of minerals can take place in the process of polymorphic transformations and the decomposition of solid solutions.

## Concepts of Natural Associations of Minerals

Minerals are found in nature not in a chaotic state, but in the form of particular conglomerations, or associations. In some places certain mineral associations are discovered, in other places there are other mineral associations. Our knowledge and the correct interpretation of natural associations of minerals make it possible to predict the location of this or that mineral in a given association. If these minerals are of any practical importance, then there is every reason to speak of a discovery of mineral resources. Thus, such secondary minerals as malachite and azurite serve as features of copper ores. They and other minerals of the oxidation zone, or the zone of the 'iron cap', have led to the discovery of a large number of deposits of chalcopyrite, polymetallic and other ores.

The acquaintance of man with various associations of minerals originated in ancient times. Those concerned with the study of ores in the Middle Ages had already known the features by which it was possible to conduct exploratory work pertaining to the discovery of minerals and ores. It was precisely on the basis of such concepts of ore that mineralogy, as a science, began to burgeon. However, in the 17th-19th centuries the science of minerals was, to a considerable extent, descriptive, though the study of mineral associations had always been considered of particular importance. This can be exemplified, for instance, by the fact that a special scientific term 'contiguity of minerals' was first employed by the Russian mineralogist Academician V. M. Severgin (1765-1826) in his book 'Primary Fundamentals of Mineralogy, or the Natural History' (1798). By the term 'contiguity' V. M. Severgin understood 'a combination of two or more minerals in a certain locality, which deserves special attention', i.e. a conglomeration of minerals or mineral associations. Further, V. M. Severgin lay particular stress on the importance of understanding the regularities governing the coexistence of minerals, which is conditioned by the common features of genesis. Many years later A. Breithaupt generalized all the previously known in Western Europe (Saxony, Bohemia and Moravia) information on the coexistence of minerals in nature, and introduced the concept of 'paragenesis' of minerals, which was very close to that of 'contiguity'. Later on the term 'paragenesis' gained more ground and had been established in special mineralogical (and petrological) literature.

Thus, natural mineral associations is the coexistence of minerals in nature. However, the term 'paragenesis' comprises the word 'genesis', which means 'origin'. The answer to the question 'what is the origin of

a mineral' usually suggests a geological process within which it was formed, and the means of its formation. Hence, the *paragenesis of minerals* means their common formation, and, consequently, the location of minerals. However, in one and the same lump of ore we can find minerals, which have appeared as a result of various processes. In this case, we speak of various *paragenetic associations* of minerals. Thus, the coexistence of chalcopyrite, pyrite, quartz, malachite, chrysocolla, goethite are referred to two paragenetic associations: the earlier association, formed, most probably, as a result of a hydrothermal process (pyrite, chalcopyrite, quartz), and the later association, pertaining to the hypergenic process (malachite, chrysocolla, goethite).

The concepts of 'paragenesis of minerals' and 'paragenetic associations of minerals' are actually identical and will further be used as synonyms. However, depending on what should be brought out, it is necessary to use these terms discriminately. If we wish to bring out the common genesis (origin), we should say, for instance, that pentlandite is found in paragenesis with pyrrhotite and chalcopyrite. If, however, we wish to emphasize the common occurrence (as may be the case with a sample), we should say that pentlandite is found in paragenetic association (or simply in association) with pyrrhotite and chalcopyrite.

A great deal of attention to paragenesis of minerals was paid by Academician V.I. Vernadsky. Before his works appeared, mineralogy was, to a considerable extent, only a descriptive science. In his works V.I. Vernadsky gave a number of generalizations concerning the origin and the conditions in which the minerals exist in nature. There is every reason to consider him to be the founder of the genetic trend in mineralogy. In the book 'The History of the Minerals of the Earth's Crust' (Moscow, 1923, in Russian) V.I. Vernadsky wrote: 'The study of paragenesis lies at the very bottom of modern mineralogy'. By paragenesis he understood the common occurrence of minerals, conditioned by their common features of origin, and the genetic bond existing between them.

In the USSR the study of the paragenesis of minerals was most tangibly enriched by the petrological, physicochemical, and experimental works of A. G. Betekhtin, D. S. Korzhinsky, V. S. Sobolev, V. A. Zharikow, A. A. Marakushev, and others. It is due to their research that the methods of paragenetic analysis have been worked out today, diagrams are being constructed representing the compositions of the type: paragenesis, chemical potential-paragenesis and others, which help to establish the paragenetic associations and throw a sufficient amount of light on which of them can be found and which of them are the so-called 'prohibited', i.e. cannot be found.

Each paragenetic association can be regarded as a system that has emerged under absolutely definite values of temperature ( $T$ ), pressure ( $P$ ), and the concentration of matter ( $C$ ). These are the factors that determine the conditions in which the mineral associations are formed, their change leading to the distortion of the equilibrium in the system and the formation of other mineral associations.

According to the principle elaborated by Le Chatelier, *a system in a state of equilibrium counteracts to the forces acting upon it*. Thus, any rise in temperature leads to processes, which in their turn, lead to the

absorption of heat, and, conversely, when the temperature is lowered, processes involving the extraction of heat become apparent. Thus, for instance, when there is a rise in temperature the solubility of salts in salt-bearing basins becomes higher, and is accompanied by the absorption of heat. A rise in pressure is responsible for the formation of minerals that have a greater density. For example, the density of the polymorphic modification  $\text{SiO}_2$ , stishovite, is 4.23; it is unstable at the surface, where quartz  $\text{SiO}_2$  with the density 2.65 is stable. However, stishovite is characteristic of the deeper regions of the Earth, where the pressure is predominantly high. One more example: when the pressure is increased in the deeper zones of metamorphism, at the expense of olivine (density 3.2) and anorthite (density 2.75), garnet (density 4.3), i.e. a mineral with a greater degree of density, is formed:  $(\text{Mg, Fe})_2[\text{SiO}_4] + \text{Ca}[\text{Si}_2\text{Al}_2\text{O}_8] \rightarrow (\text{Mg, Fe, Ca})_3\text{Al}_2[\text{SiO}_4]_3$ . An increase in the concentration of matter helps it to be extracted from the system, as is the case with minerals rich in  $\text{SiO}_2$ , including quartz, in oxidized lavas. Everything becomes much more complicated when fluctuations in  $P$ ,  $T$ , and  $C$  take place simultaneously, and when other components enter into the system.

The study of paragenesis and paragenetic associations of minerals is of great importance in mineralogy, petrology, and the science dealing with mineral resources. The knowledge of mineral paragenesis helps to carry on exploitative works. Thus, for instance, chrome ores are explored only in those places where the ultrabasic rocks are spread. When pyroxene and garnet rocks (skarns) are found in contacts with limestones, it is necessary to examine them very closely so as to ascertain whether there is no scheelite or other ore minerals that are commonly found in the rocks of this type. The discoveries of pyrope in heavy concentrates can serve as a feature showing the presence of diamond-bearing kimberlites. Powellite, ferrimolybdate or the voids of leaching formed after them in quartz veins molybdenite is found at the bottom. The presence of polychromatic tourmaline in pegmatites suggests the possibility of discovering such valuable minerals as lithium, beryllium, caesium, tantalum, and niobium.

It is customary to group the paragenetic associations of minerals according to the main types of genesis. Hence, the following associations of minerals are singled out: those of the magmatic origin (acid, basic, and alkaline rocks), pegmatites (acid and alkaline rocks), skarns, the products of hydrothermal activity, as well as associations of minerals of the chemical sediments in seas, the weathering products, and metamorphism.

### **Typomorphic Minerals, Typomorphic Features, and the Generation of Minerals**

Features by which it is possible to speak of the origin of a mineral are called *genetic*. They reflect the origin of minerals and the mineral association, in which they occur. By studying the specimens of rocks and ores, it becomes essential, first and foremost, to describe the colour, form, and size of the minerals, and the character of their intergrowths in aggregates.

It is of vital importance to properly interpret the structure (constitution) of mineral aggregates. The structures of mineral aggregates are various: granular (coarse-, medium-, fine-granular), for example for intrusive rocks, pegmatites, and sandstones; crystalloblastic, characteristic of metamorphic rocks; the metasomatic rocks are usually characterized by the structure of replacement, etc. Some structures are typical of a certain process; for instance, the graphic structure is typical of pegmatites, while the nodular structure is characteristic of magmatic chromite ores, etc.

The genetic features of minerals are numerous. However, some of them are characteristic to such an extent that they can show exactly the type of geological process to which the mineral belongs. They also furnish a sufficient amount of information on a particular stage in the process of paragenetic association and on the temperature of its formation. These features are called *typomorphic*, and the minerals characteristic of a particular geological process of mineral formation are termed *typomorphic minerals*. The latter can be exemplified by pollucite, which is formed only in pegmatites at the final stage of their development. According to A. Ye. Fersman, typomorphic features are manifested 'in the change of the chemical composition, in the content of isomorphic impurities, in the crystalline form or the polymorphic modification, to be more precise, in the whole complex of morphological characteristic features...'. Typomorphic features of minerals include the crystallographical characteristic features of minerals, their habit, facing, crystallographical forms, the sculpture of their faces, the character of twinning, etc. They also comprise the physical properties and the chemical composition of minerals (also including the elements-impurities), the change of which depends on the conditions of their formation.

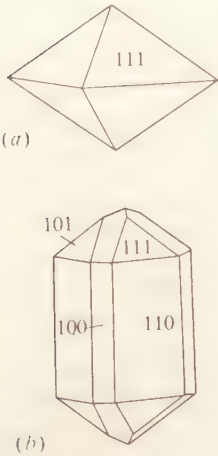
The change of the physicochemical conditions in which the minerals are formed, leads to the change in the composition of minerals, which, in its turn, is reflected in the colour of minerals. Sphalerite could be adduced as an example. There is evidence that the high-temperature sphalerite contains iron and is of a black colour. Sphalerite is usually brown, while the colourless or light-yellow varieties (iron-free, sometimes with cadmium) are characteristic of low-temperature. Thus, the colour of sphalerite can serve as a distinguishing feature of its composition (for instance, the content of iron). It can also approximately be reliable as far as the temperature of the formation of sphalerite is concerned.

Another example, illustrating the dependence of the colour of the mineral on its composition, and, consequently, on the conditions of its formation, can be furnished by garnets. Pyrope (a magnesian-aluminiferous garnet of a bright-red colour) is characteristic of kimberlites; almandine (a ferriferous-aluminiferous garnet of a crimson-red colour) is typical of the crystalline schists and gneisses; uvarovite (an emerald-green chrome garnet) is found exclusively with chromite among the ultrabasic rocks.

A clear-cut typomorphic mineral is tourmaline. Its most widespread variety is the black iron-bearing tourmaline (schorl), which is found in a large number of pegmatitic veins, including the muscovite pegmatites. Comparatively rare varieties of lithium tourmaline of a pink colour or the polychromatic ones are characteristic only of the

Fig. 137. Cassiterite crystals:

*a*—from pegmatite deposits; *b*—from hydrothermal deposits



rare-metal pegmatites, containing the minerals of lithium, and not infrequently those of caesium, tantalum, and niobium.

The appearance of the mineral can also serve as a typomorphic feature. Thus, the crystals of cassiterite from the pegmatitic veins are usually of a dipyramidal form, while the cassiterite extracted from the hydrothermal veins is prismatic (Fig. 137). The high-temperature quartz of the magmatic rocks has a dipyramidal form without or with a very inconsiderable development of the prism, while the quartz recovered from druses in the veins of the 'alpine' type is long-prismatic (see Fig. 87). With the lowering of temperature there is a regular change in the habit of calcite crystals (see Fig. 16).

Each mineral is formed within a particular temperature interval. In some cases this interval is equal to hundreds of degrees, in others the temperature is more or less fixed. This helps to grade the processes of mineral formation. Thus, the low-temperature quartz ( $\beta$ -quartz) is crystallized at a temperature lower than  $575^\circ$ . Consequently, other minerals too, formed synchronically with it, or later, are also crystallized below  $575^\circ$ . Minerals, by which it is possible to estimate the temperature of their formation, are called *mineral-thermometers*.

The interrelationship of minerals, i.e. their interpenetrability, makes it possible, in a number of cases, to determine the order of their segregation. It is not infrequently that one and the same mineral is segregated several times in the process of mineral formation, i.e. has a few *generations* (Fig. 138).

Minerals of various generations are usually distinguished by their chemical composition and external features, viz. colour, the size of grains, facing, etc. Thus, quartz of the earlier generations is often grey, while that of the later generations is white; besides, it is often

Fig. 138. Two generations of quartz.

The Tyzyl deposit (northern Caucasus):

1—quartz of the first generation; 2—quartz of the second generation



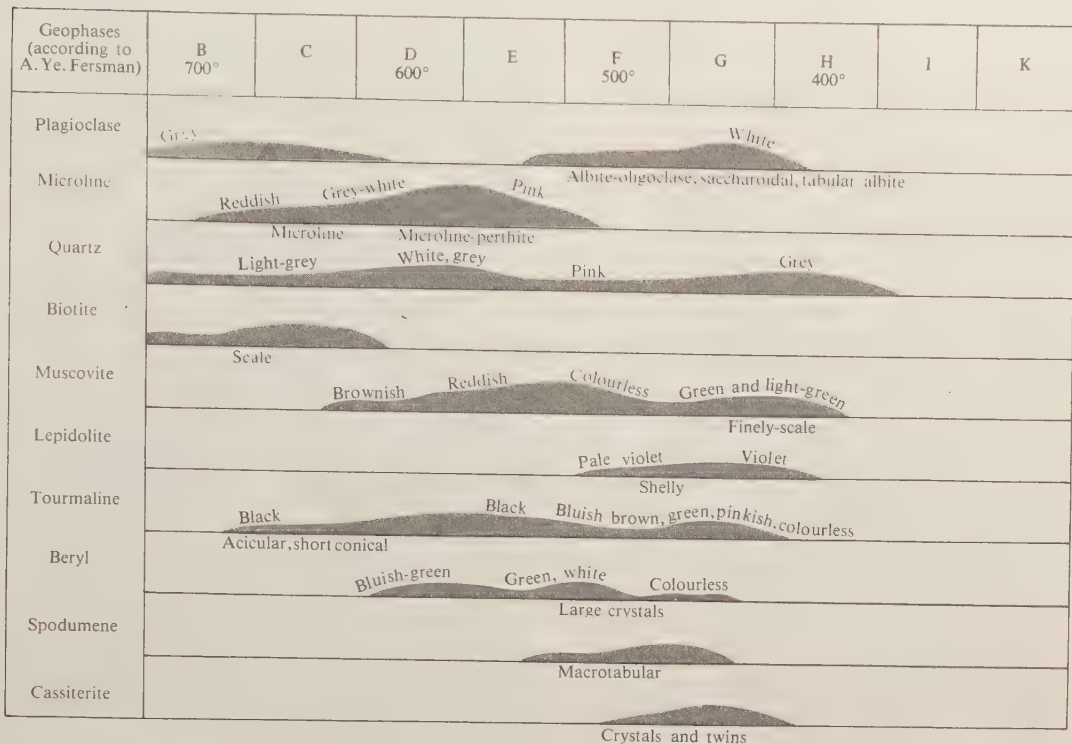


Fig. 139. The segregation order and the typomorphic features of minerals of one of the pegmatite fields in Central Asia

distinguished by a bright facing and transparence (rock crystal).

Detailed mineralogical study of the deposits usually results in the discovery of several generations of quartz, sulphides and other minerals. This kind of research makes it possible to determine the generation that is of a greater industrial value for the given mineral, which in its turn is of no minor significance for the exploratory work.

The order of the segregation of minerals, their generation and paragenetic associations for this or that deposit or ore field are registered in special diagrams. The typomorphic features of minerals are, as far as possible, reflected there too. Figure 139 shows the order of mineral segregation, their typomorphic features and the paragenetic associations of minerals in pegmatite veins of one of the districts in Central Asia. It is clear, for instance, that spodumene is found together with polychromatic tourmaline, tabular albite (cleavelandite), lepidolite, but does not occur with biotite. The succession in which the minerals are formed is established on the basis of vein intersection (Fig. 140), by the relics of the replaced mineral at a later stage, the accretion of crusts of one mineral on another, by the formation of pseudomorphs, and other features.

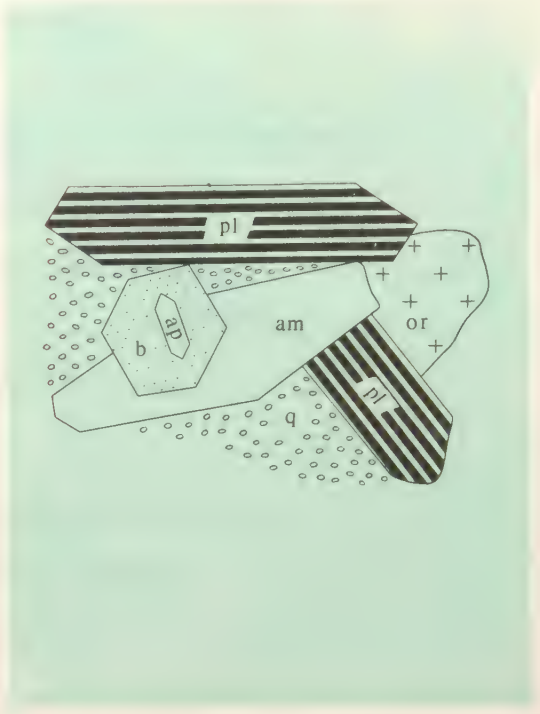
The feature of determining the order in which the minerals are formed that is of particular significance is the degree of the facing of their grains (the degree of idiomorphism), which will be discussed further on the material of an example of crystallization of the minerals of magmatic rocks. Under slow solidification of magma in the deeper regions, the crystallization of minerals begins to take place. First come



Fig. 140. The relationship of veins in biotite hornfels. Scale 1:3. The Tyrnyauz deposit (northern Caucasus):

- 1 - biotite hornfels;
- 2 - quartz; 3 - plagioclase;
- 4 - molybdscheelite;
- 5 - molybdenite;
- 6 - scheelite

Fig. 141. The degree of mineral idiomorphism (according to V.N. Lodochnikov):  
 ap - apatite; b - biotite,  
 am - amphibole;  
 pl - plagioclase;  
 or - orthoclase; q - quartz



the minerals the temperature of which is high. They grow freely in the liquid magma, and, hence, have perfectly well expressed crystallographic contours, and can be called *idiomorphic*. Then the main mass of the magma begins to crystallize, when all of a sudden there appear numerous centres of crystallization. The crystals grow and fill the free space, thus forming a granular rock. In it minerals have partially their own form and, to a certain extent, that conditioned by other minerals. They are called *hypidiomorphic*. Minerals filling the interstices between the earlier formed minerals and those that lack their own crystallographic outlines, are referred to as *xenomorphic*.

The degree of mineral idiomorphism in a rock can be various. Fig. 141 shows that the most idiomorphic minerals are apatite and biotite. Amphibole is restricted by clear-cut lines, i.e. it is more idiomorphic than plagioclase, while the latter is more idiomorphic than orthoclase. Quartz, however, is a xenomorphic mineral since it has no lines of restriction of its own.

The origin of mineral individuals, their aggregates, and age relationships between them constitute the sum and substance of the scientific trend in mineralogy called the *ontogeny* of minerals the founder of which is Prof. D.P. Grigoriev. Problems pertaining to this subject are discussed in detail in D.P. Grigoriev's books, 'The Ontogeny of Minerals' (1961), 'The Ontogeny of Minerals. Individuals' (1975), written in collaboration with A.G. Zhabin, and in the book 'The Ontogeny of Minerals. Aggregates' (1979) by A.G. Zhabin.



## The Classification of Mineral Formation Processes

Geological processes as a result of which minerals are formed fall into two large groups (according to the source of energy): endogenic (inner) processes are connected with the innate energy of the Earth, mainly with the energy of the radioactive decomposition, and the exogenic (external) processes, associated with the activity of the atmosphere, hydrosphere and biosphere, their impact on the lithosphere under the influence of the solar energy.

*Endogenic* (or hypogene, deep) processes take place in the depths of the Earth, and are connected with the magmatic activity or the metasomatic transformations of rocks. The processes of the solidification of magma lead to the formation of various magmatic rocks, while the gaseous and water solutions, which are separated from the magma, transfer various substances, which in certain conditions of the environment, as is the case with fissures, are segregated in the form of minerals.

Endogenic processes take place at high temperatures and pressures. The temperature of the crystallization of magmatic rocks in relation to the content of the melt fluctuates between 1200° and 700°C, with the pressure covering the range from approximately 5500 to 500 bars (or from 550 to 50 MPa). The formation of pegmatites, metasomatic rocks, skarns and greisens, hydrothermal ore veins, etc. connected with the magmatic process, occurs at considerably smaller values of T and P.

*Exogenetic* (or hypergene, surface) processes take place at the surface or close to the surface of the earth, as well as in the atmosphere and the hydrosphere. These processes are manifested in the physical or chemical deterioration of rocks, ores, and minerals, and the formation of such minerals that are stable in the earth's surface conditions. This also includes biogenic processes of mineral formation, i.e. those that are connected with the activity of organisms. Exogenic processes are exceptionally various. Two most important ones should be singled out, they are: the process of weathering and the process of sedimentation.

Minerals and rocks that have originated as a result of endogenic and exogenic processes accompanied by a change in physicochemical conditions, undergo certain transformations, or *metamorphism*. This is closely related to the formation of new minerals and rocks that have acquired the term *metamorphic*.

In what follows the most important endogenic, exogenic and metamorphic processes, as well as natural associations of minerals connected with them, will be discussed. Cosmogenic minerals, such as the minerals of lunar rocks and meteorites will also be dealt with in brief.

## The Magmatic Process and the Associations of Minerals in Magmatic Rocks and Deposits

The magmatic processes of mineral formation proper include those within which minerals originate synchronically with the crystallization of magma. This process comprises all minerals composing magmatic rocks. Thus, granite consists of feldspar, quartz and mica; the origin of

these minerals in the given case is magmatic. Secondary (accessory) minerals of igneous rocks, e.g. apatite, zircon, orthite, etc. are of magmatic origin too.

Magma represents a fiery-liquid silicate melt, containing various elements, oxides and volatile components (fluorine, chlorine, water, carbon dioxide, etc.). Magma can be solidified in the depth of the earth's crust under the cover of the overlying rocks and at the surface or near the surface of the earth. In the former case the process of solidification is slow; it takes the whole of magma enough time to be crystallized, and the holocrystalline granular rocks are formed. When there is a rapid uplift of the magma on to the earth's surface its temperature becomes lower, the pressure drops down to normal, and volatile components are separated. In this case the rocks sometimes have a vitreous structure, i.e. they are not wholly crystallized.

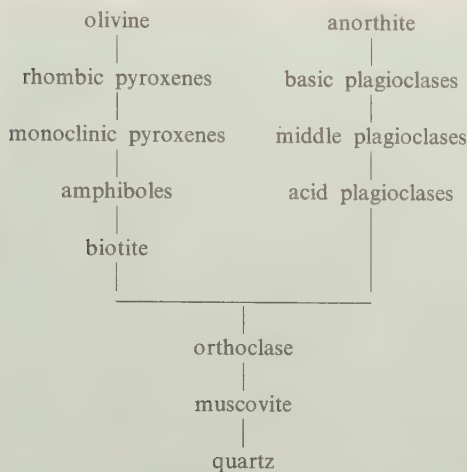
As is known from the course in geology, the magmatic rocks formed in the depths of the Earth, are called *intrusive*, or *deep* rocks. If the solidification of magma takes place at the earth's surface, they are called the *effusive* rocks. Considering the conditions of their formation, we can distinguish the intrusive and the effusive rocks by the conditions in which the deposits originate and the composition of these rocks.

As a result of the cooling of magma there occurs a crystallization of minerals from the magmatic melt. The variety of rocks can be accounted for by the processes connected with the differentiation of magma, the assimilation of the enclosing country rocks, and depends on the geological conditions under which magmatic rocks were formed.

*The differentiation* (segmentation) of magma is a combination of various physicochemical processes, as a result of which the parent magma yields secondary magmas, which in their turn yield magmatic rocks differing in chemical and mineral compositions. The differentiation of magma takes place at considerable depths and leads to the enrichment of various parts of a common magmatic reservoir by a variety of components. Differentiation takes place owing to the processes of crystallization. Minerals that were formed at the first stage of crystallization, float in the melt. If their density is greater than the density of the melt, they sink to the bottom of the magmatic reservoir. Similar differentiation occurs in the case when the viscosity of the magma is not particularly great. As a rule, heavy ferromagnesian minerals, e.g. olivine, fall out first. The olivine crystals gradually submerge to the basis of the magma pocket. However, the crystals formed at the initial stage are not usually accumulated in the lower part of the magma pocket; they can remain in a suspended condition for some time and react to the melt. Thus, olivine, as a result of similar reactions, is transformed into pyroxene. In those cases, when the crystals thus formed are lighter than the melt, they come out on to the surface and are accumulated in the upper parts of the chamber.

From what has been said above, it becomes clear that in the processes of the crystallization of magma there is a redistribution of various components. If the crystals that are being formed are removed from the magmatic hearth, as is the case when they fall into deeper horizons or float out into the upper ones, the composition of magma

will gradually change and various rocks will be crystallized from it. The order of crystallization and the interrelationship of the main rock-forming minerals were established by the American petrologist N. Bowen in the form of the diagram given below:



This diagram shows the main trend in the formation of rocks. N. Bowen distinguishes two reactionary series of minerals, according to the succession in which they fall out of the magma. Each mineral (preceding in descending order), in the reactions with the melt, forms a mineral, that comes below the former in the diagram. If the separation of minerals takes place at the initial stages of crystallization, the basic rocks are formed. The later phases are associated with acid rocks. This is accompanied by a further increase in the complexity of the silicon-oxygen structures from nesosilicates to those of the cyclosilicates, inosilicates, phyllosilicates, and tectosilicates; the degree of the replacement of silica by aluminium is also increased. The process of the crystallization of magma becomes inseparable from the accumulation of silicon, alkaline, and water in the melt.

The processes of magmatic differentiation should be regarded in conjunction with *liquation*, i.e. the separation of one liquid magma into two non-miscible liquids. Under continuous cooling of both liquids they yield rocks different in their composition. This is how, for instance, *schlieren excretions*, or mineral accumulations of a somewhat different composition than the groundmass, are formed. Sometimes, as a result of liquation, the melt, rich in metal compounds, is separated from the silica, which leads to the formation of liquation deposits of copper, nickel, and chromium, highly important for industry.

In the formation of magmatic rocks a substantial part is played by the processes of *assimilation*. Entering the overlying strata, the magma usurps and remelts the remnants of various rocks (xenolites), thus changing its own composition. This kind of change in the composition of magma leads to the formation of various *hybrid* rocks. Particularly great changes become, as a rule, apparent in the near-contact parts of the magmatic bodies, since the processes of assimilation there are most turbulent.

The synonym for assimilation is, to a certain extent, *contamination*. In this case the foreign body is usually not wholly processed or assimilated.

All the processes discussed above are responsible for a great variety in the mineral composition of magmatic rocks, which we find in nature.

**The mineral composition of magmatic rocks is extremely various**

Feldspars, quartz, amphiboles, pyroxenes, micas are most widely spread. Olivine, nepheline, leucite, magnetite, apatite and other minerals are less spread. The average per cent content of minerals for 700 magmatic rocks is adduced below:

feldspars	60
quartz	12
amphiboles and pyroxenes	17
micas	4
other silicates	6
the rest of the minerals	1
	<hr/> 100%

Among the minerals, *principal* rock-forming minerals are set apart. They compose the groundmass of the rock. *Minor* minerals are distinguished too. They are either present (in small quantities) or absent altogether. Principal rock-forming minerals are: quartz, orthoclases, plagioclases, leucite, nepheline, pyroxenes, amphiboles, micas, olivine, and some others. *Accessory* minerals are also singled out. They are present (in an inconsiderable amount) in the form of a rare, but characteristic impurity, as is the case with apatite, zircon, sphene, orthite, magnetite, chromite, pyrite, pyrrhotite, etc.

Minerals, rich in Si and Al are called *sialic* (Si, Al); their colour is light. These include feldspar, quartz, muscovite, etc. Minerals containing Mg and Fe, are called *mafic* (Mg, Fe) or *femic*. They are darkly coloured, and are represented by pyroxenes, amphiboles, biotite, and olivine. In the absence of coloured minerals or when their content is inconsiderable, the rock is called *leucocratic*, i.e. of light colour. If, however, the number of coloured minerals is large, the rock is termed *melanocratic*, or dark-coloured.

According to their origin minerals of the magmatic rocks are divided into primary (magmatic) and secondary. Primary minerals are formed as a result of the crystallization of the magma itself. The formation of the secondary, or post-magmatic (epimagmatic) minerals is achieved at the expense of the primary ones in the subsequent stages in the existence of the rock. Thus, for instance, plagioclases (primary) when decomposed yield sericite, zeolites (secondary); pyroxenes and amphiboles (primary) are replaced by chlorite and epidote (secondary). Typical processes of secondary mineral formation are: sericitization, kaolinization, chloritization, serpentization, etc. Secondary minerals also include those that have been formed under the weathering of the rocks.

When magmatic rocks are characterized, the most significant role is allotted to the presence or the absence of such minerals as quartz, feldspars, feldspathoids, and coloured minerals. On the basis of SiO<sub>2</sub> content (weight in %) a tentative division of the magmatic rocks into

the following groups has been accepted:

ultrabasic	<45
basic	from 45 to 52
middle	from 52 to 65
acid	from 65 to 75

A separate group is constituted by *alkaline* rocks, characterized by a substantial content of alkali (up to 20%) and a smaller amount of  $\text{SiO}_2$  (approximately 40–55%), as compared with the acid rocks.

The classification and the most important mineral associations of magmatic rocks are given in Table 7. Thus, for the intrusive rock gabbro and its effusive analogues there is seen a clear-cut mineral association: basic plagioclases (labradorite-bytownite), pyroxenes (diopside, diopside-augite, hypersthene), more seldom olivine, hornblende, and biotite. Of secondary and accessory minerals these rocks are characterized by orthoclase, quartz, apatite, magnetite, titanite, ilmenite, pyrrhotite, pentlandite, as well as sphene, titanomagnetite, rutile, and very seldom platinum. Secondary changes are manifested in the development of albite, chlorite, uralite, talc, and sericite.

In Table 7 the most important mineral associations for the other groups of magmatic rocks are clearly illustrated. Thus, the establishing of mineral associations of magmatic rocks helps to discern them.

Fig. 142 shows three different cases of the crystallization of silicate and ore minerals from the ultrabasic and basic magmas, which leads to the formation of three types of magmatic deposits. They are respectively called early magmatic, when ore minerals are crystallized prior to or synchronically with silicates (the first case), liquation, when the separation of the ore melt from the silicate melt takes place as early as in the liquid stage (the second case), and late magmatic (or hystermagmatic), when the ore melt is separated from the silicate melt and the crystallization of ore minerals takes place later than silicates, as if the ore minerals were cementing the silicates and filling the fissures (the third case).

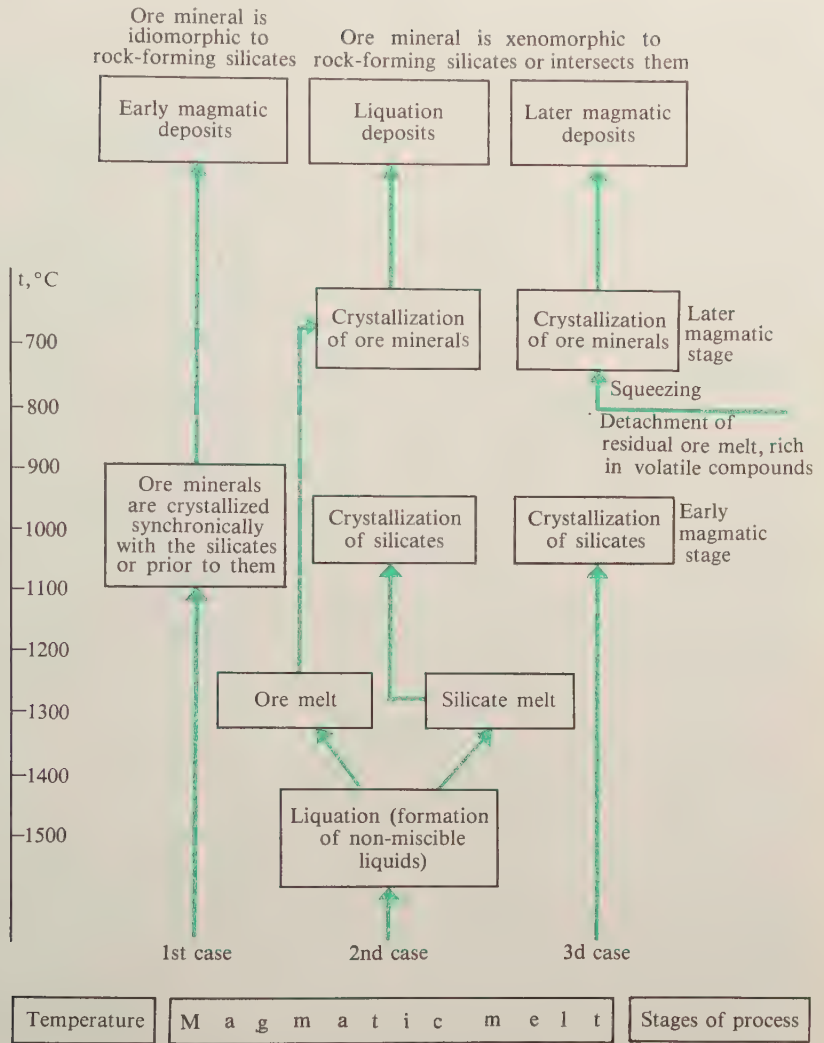
Early magmatic deposits can be exemplified by the chromite ores in Bushveld massif in SAR, the disseminated ores of chromite, the platinoids of the Urals and the diamond-bearing kimberlites of Eastern Siberia. A classical example of liquation deposits is the Norilsk and the Talnakh copper-nickel deposits in the Krasnoyarsk Region, the Monchegorsk deposit in the Kola peninsula, Sudbury in Canada, and others. The later magmatic deposits include the largest in the USSR Donskaya group of chromite deposits in Aktyubinsk Region, Kachkanar, the Pervouralsk and other deposits of titanomagnetite and ilmenite in the Urals, the Khibiny apatite-nepheline deposit in the Kola Peninsula and others.

In discussing mineral associations, connected with the magmatic process, we should dwell upon some of the associations that are of practical importance, such as the mineral associations of the alkaline rocks and genetically related to them carbonatites, the associations of kimberlites, copper-nickel and chromite deposits. Since all igneous processes are also magmatic, the specific mineral associations, e.g. the sublimates occurring during the volcanic activity, will be treated in the present section of this book too.

TABLE 7  
*The Classification of Magmatic Rocks and Their Most Important Mineral Associations*

Group	Intrusive (deep)	Effusive		principal	Primary minerals		Secondary minerals
		with minor changes	considerable changes		minor and accessory		
I. Ultrabasic	dunite peridotite pyroxenite	—	—	olivine (100-85%) pyroxene (0-15%) olivine (70-30%) pyroxene (30-70%) olivine (< 10%) pyroxene (100-90%)	magnetite, ilmenite, chromite, spinel, pyrrhotite (1-3%)	serpentine, uraltite, chlorite, talc	
II. Basic	gabbro	basalt	diabase (or basalt porphyrite)	basic plagioclases (50-70%), pyroxenes (25-50%), less often olivine (5-10%), hornblende and biotite	orthoclase, quartz, apatite magnetite, titanite, ilmenite, pyrrhotite, pentlandite (1-6%)	albite, chlorite, uralite, talc, sericite	
III. Middle (a) with plagioclases	diorite	andesite	porphyrite (or andesite porphyrite)	middle plagioclases (50-70%), hornblende (10-20%), more seldom biotite (10-15%), pyroxenes	quartz (0-15%), orthoclase (0-6%), apatite, titanite, magnetite (1-2%)	sericite, kaolinite, zoisite, chlorite, carbonates	
(b) with orthoclases	syenite	trachyte	orthophyre	orthoclase (50-70%), acid plagioclase (10-30%), hornblende, more seldom biotite (10-20%)	quartz (0-5%), zircon, titanite, apatite, magnetite (1-2%)	sericite, kaolinite, chlorite	
IV. Acid	granite	liparite	quartz porphyry	quartz (25-35%), orthoclase (35-40%), acid plagioclase (15-25%), biotite (5-15%), less often muscovite (0-3%), hornblende	apatite, zircon, magnetite, tourmaline (1-2%)	sericite, kaolinite, chlorite	
V. Alkaline	nepheline syenite	—	—	orthoclase (55-65%), nepheline (15-30%), alkaline pyroxenes and amphiboles (10-25%), more seldom biotite	zircon, titanite, apatite, magnetite (~ 2%)	sericite, kaolinite, chlorite, zeolites	

Fig. 142. Diagram showing the separation of ore components in magma and the formation of various types of magmatic deposits



**Alkaline rocks**

The content of alkaline rocks is characterized by a high concentration of potassium and sodium in relation to aluminium. In their composition there is an insufficient amount of silica for the formation of feldspars; hence alkaline rocks are characterized by the presence of nepheline in their content, while leucite is typical of the effusive varieties (comparatively rare). When the content of silica is markedly low the rocks should be referred to the ultrabasic type, since the content of silicon earth in them reaches 35%, more often, however, 40-50%. But by their mineral composition the rocks are markedly different from the usual ultrabasic rocks of the peridotite and dunite series. This is accounted for by the one-sided classification of rocks solely in terms of one feature, i.e. the content and the quantity of silica.

Alkaline rocks are usually light-coloured and their density is low (2.7-2.8). These rocks are not widely spread (approximately 0.4% of all magmatic rocks). However, their practical significance can hardly be

overestimated since such highly important deposits as apatite, rare-earth minerals, zircon, titanium and other ores are associated with them.

*Nepheline syenites* are the coarse-grained deep rocks representing the extreme varieties of syenites. They differ from syenites in that the content of silica in them is much lower, by a total absence of quartz, the presence of nepheline, and a considerable content of alkaline amphiboles and pyroxenes. The principle minerals are: potassium feldspars (55-65%), nepheline (15-30%), aegirine (10-20%), alkaline amphiboles, and sometimes biotite. It is usual for the nepheline syenites to be characterized by the presence of apatite and various zircon-and-titanium silicates (eudialyte, titanite, etc.), which in some cases function as rock-forming minerals (2-4%).

Nepheline syenites are characterized by an inconstant chemical and mineral composition, as a result of which a number of varieties are distinguished, viz. foyaites, or hornblende or pyroxene nepheline syenites; miaskites, including mica nepheline syenites, khibinites, e.g. coarse-grained nepheline syenites of the pegmatoid texture, etc.

Nepheline syenites form small massifs, sometimes layered intrusions. The largest alkaline province in the world is the Khibiny Mountains in the Kola Peninsula, distinguished by a variety of rocks. There nepheline syenites are responsible for the deposits of apatite and nepheline.

Alkaline rocks are represented not only by nepheline syenites, but by varieties that do not contain feldspars and consist solely of nepheline and aegirine. According to the relationship of these components the rocks are called urtites (up to 15% of aegirine), ijolites (with 15 up to 55% of aegirine), and melteigites (up to 85% of aegirine). Almost all aegirine rocks are called yakupirangites.

The most important associations of alkaline rock minerals (nepheline syenites, khibinites, phonolites, and others) are generalized in Table 8.

### Carbonatites

are rare magmatic (or post-magmatic hydrothermal-and-metasomatic) non-silicate formations, spatially and genetically closely related to the ultrabasic alkaline rocks and consisting of calcite, dolomite, and ankerite. Carbonates account for 50 to 90%, usually more than 80% of all minerals. All other minerals amounting to 150 are more or less rare. The most widespread minerals among them are: alkaline pyroxenes and amphiboles (aegirine, arfvedsonite, riebeckite), phlogopite, diopside, forsterite, magnetite, fluorite, barite and several others.

The association of minerals in carbonatites is unusual. It is characterized by a large number of accessory minerals that are not found in other associations (in other processes) and containing rare earths, niobium, tantalum, uranium, zirconium, strontium, titanium, fluorine, and phosphorus. Some of the carbonatite minerals are of great practical importance. They include pyrochlore, uranium-tantalum pyrochlore-hatchettolite, bastnaesite, parisite, columbite, baddeleyite, and others. Carbonatites are also connected with the deposits of iron ores, from which, apatite, baddeleyite, phlogopite (vermiculite), etc. are recovered as by-products.

Carbonatites form small stocks, ring-dike and radiating dikes, in sharp contrast to the concentrically-zonal alkaline magmatic complexes of



TABLE 8

*Minerals of Alkaline Rocks*

Principal	Minor and accessory	Those of practical importance
Potassium feldspar	titanite	apatite
Nepheline	apatite	nepheline
Arfvedsonite and other alkaline amphiboles	zircon	zircon
Aegirine and other alkaline pyroxenes	eudialite	eudialite
Lepidomelane	astrophyllite	loparite
Leucite	lamprophyllite	
Sanidine	magnetite	
	loparite	
	sodalite*	
	cancrinite*	
	natrolite*	

\* Formed as a result of hydrothermal processing of rocks.

TABLE 9

*Minerals of Carbonatites*

Principal	Minor and accessory	Those of practical importance
Calcite	titanomagnetite	pyrochlore
Dolomite	pyrochlore	magnetite
Ankerite	hatchettolite	columbite
Siderite	aeschnyite	bastnaesite
Diopside	columbite	parisite
Humite	baddeleyite	hatchettolite
Forsterite	bastnaesite	apatite
Phlogopite	parisite	magnetite
Apatite	monacite	phlogopite
Magnetite		fluorite
Aegirine	perovskite	baddeleyite
Arfvedsonite		
Barite		
Fluorite		
Feldspars		

rocks, among which they are deposited and where they compose the central parts. These alkaline zonal complexes are characterized by a rigid correspondence to the platform regions and to the zones of regional fissures. Ring-dikes converging and diverging in the deep regions have been found to be exceptionally characteristic.

Statements on the genesis (origin) of carbonatites are contradictory. We are regarding carbonatites here as magmatic rocks, and the carbonatite magma as a result of the differentiation of alkaline magma. However, it should be pointed out that there are by no means significant assertions substantiating the post-magmatic hydrothermal-metasomatic origin of carbonatites. Thus, the variety of mineral associations with a zonal character of their distribution reflects the multistage process of the formation of carbonatites, often with characteristic features of the metasomatic processes of the replacement of minerals pertaining to the preceding stages by those of the later stages. This is accompanied by the initial stage being formed by coarse-grained calcite rocks with augite-diopside, forsterite, biotite, apatite, and magnetite, together with which perovskite, sphene and others are found. These rocks usually function as the constituents of the peripheral part of the carbonatite massifs. The later stage is related to the development of medium-grained calcite rocks, containing diopside and phlogopite. They are characterized by the minerals, containing TR, Ta, Nb, Zr, U and Th (zirkelite of  $\text{CaZrTi}_2\text{O}_7$ , baddeleyite, hatchettolite, pyrochlore), in addition to the minerals of titanium and zirconium mentioned above. The further stage is associated with the segregation of fine-grained calcite-dolomite accumulations with alkaline amphiboles, serpentine, talc, which associate with pyrochlore, as well as with fersmite, zircon, and aeschnyite. The concluding stage is remarkable for the formation of fine-grained dolomite-ankerite separations with siderite, aegirine, arfvedsonite, and also with epidote, chlorite, albite, bastnaesite, parisite and the sulphides of copper, lead, zinc, etc.

Mineral associations of the concluding stages are usually distributed in the central part of the carbonatite bodies.

The development of diatremes and breccias reveals the explosive

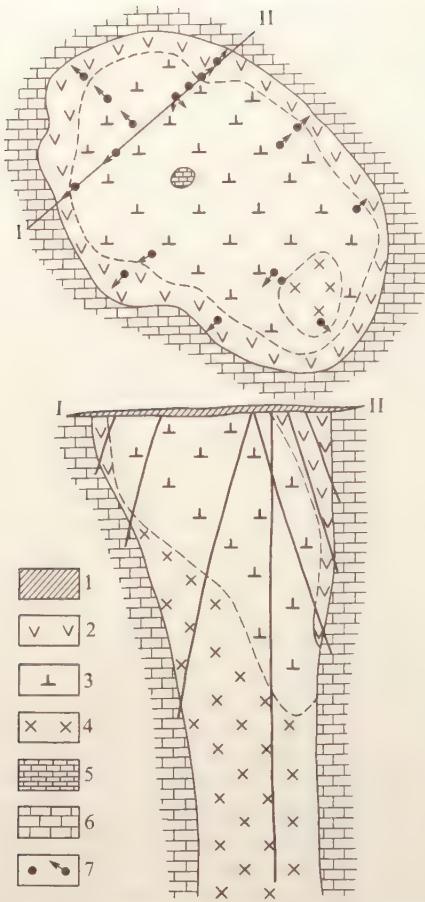


Fig. 143. A survey geological map and profile (I-II) of the kimberlite 'Mir' pipe in the Siberian platform (according to A. P. Bobrievich): 1—the eluvial-and-deluvial layer; 2—altered yellow kimberlite; 3—altered green kimberlite; 4—kimberlite with minor changes; 5—limestone xenolith; 6—limestone of the Lower Ordovician system; 7—caverns

processes in the ultrabasic alkaline magma in its depth, which, to a certain extent, affiliates carbonatites with kimberlites.

In the USSR carbonatites are known in the Kola Peninsula in Eastern Sayan, Tuva, and in the Aldan. In other countries there are deposits of carbonatites in Norway, Sweden, SAR, in Kenya, the USA, and Brazil.

Paragenetic associations of carbonatite minerals are given in Table 9.

*Kimberlites* are a special kind of brecciated rocks, consisting of fragments of ultrabasic and other magmatic rocks, as well as of the fragments of enclosing sedimentary rocks. Kimberlites represent the breccia formed as a result of an explosion (of the pipe explosion, or diatreme) of the ultrabasic (kimberlite) magma and the burst (a funnel in the direction of the surface) of the overlying rocks. The diameter of the kimberlite pipes varies, being in average between 30 and 100 m. In the plan they have either a circular or an oval form (Fig. 143). The fragments of the rocks are cemented by a clay mineral. Among the fragments of various rocks in kimberlites, including those in the cement, the following minerals can be found: diamond, olivine, pyrope, ilmenite, zircon, spinel, celestite, chromite, phlogopite, chrome-diopside, etc.

The content of *diamond* covers the range of 0.00004 to 0.00009% of the kimberlite mass, and is in the form of grains (with crystals weighing

scores and even hundreds of carats).

*Olivine* occurs in the form of spherical disseminations of a green colour, with the average size of 1-2 mm (up to 1.5 cm); it is transparent with a substantial magnesian content.

*Pyrope* is a dark-red magnesian garnet which is found in the form of spherical grains with the size of up to 0.5-1.0 cm. It is very bright, and well discernible mineral in rock and in heavy concentrates. Pyrope is the most characteristic mineral associate of diamonds. The presence of pyrope in heavy concentrates clearly manifests the presence of kimberlite pipes and consequently (possibly) even diamonds.

*Ilmenite* is also an exceptionally characteristic kimberlite mineral. It is noted for its irregularly shaped grains of a black colour and several millimetres in size.

Other minerals, characteristic of kimberlites, are adduced in Table 10. Pyrope and olivine can both be of practical importance as gemstones.

### The copper-and-nickel deposits

of the liquation type (see Fig. 142, the 2nd case) pertain to typically magmatic deposits. The enclosing rocks for them are: gabbro, norites, peridotites. The rock-forming minerals are represented by pyroxene,

TABLE 10 *Kimberlite Minerals*

Principal	Accessory	Those of practical importance
Olivine Diopside	diamond ilmenite magnetite	diamond pyrope olivine (chrysolite)
Phlogopite Pyrope Calcite Serpentine	chromite spinel perovskite zircon celestite	(chrome-di- opside)

TABLE 11 *Minerals of the Copper-and-nickel Deposits*

Principal	Secondary and accessory	Those of practical importance
Pyrrhotite	titanomag- netite	pentlandite
Pentlandite Chalcopyrite Cubanite	ilmenite bornite palladium- platinum	chalcopyrite cubanite bornite
Magnetite	sperrylite	palladium- platinum
Pyrite	sphalerite galena	sperrylite

plagioclase, and olivine. The process of liquation predetermined the emergence of ore melt, rich in sulphur, chalcophile and siderophile elements. Under the crystallization of this melt there emerge substantial accumulations of sulphides of iron, copper, and nickel, entering into the composition of the largest copper-and-nickel deposits in the world, e.g. the Norilsk, Talnakh, and the Pechenga deposits in the USSR, the deposits of Sudbury in Canada and those in South Africa.

The mineral association of ore minerals is extremely characteristic: pyrrhotite-pentlandite-chalcopyrite. It can be assumed that if two of these minerals are found, the third one will be found too. Pyrrhotite is the principle, and the most widespread mineral: it forms granular aggregates with grains of the size up to 1 cm, and intergrows with pentlandite and chalcopyrite. Pentlandite forms idiomorphic, coarse, with grains sometimes up to several centimetres in size. Pentlandite is intersected by pyrrhotite and chalcopyrite. Chalcopyrite is the latest of the sulphides mentioned above. It often contains fine inclusions of bornite, cubanite, sphalerite, and galena.

The presence of platinoids in ores, e.g. palladium-platinum (Pt, Pd) and sperrylite is extremely characteristic. The associations of ore minerals of copper-and-nickel deposits are given in Table 11.

**Chromium deposits**

are genetically related with ultrabasites. As a rule, they are located among serpentinitous dunites and dunite-and-harzburgite rocks and have the form of lenses or veins, thus forming massive or disseminated ores.

In the USSR the largest deposits are those in the Aktyubinsk Region: the Almaz-Zhemchuzhina, Millionnoe, the 40 years of Kazakh SSR, and others, connected with the Kempirсай ultrabasic massif. The ores are composed of chrome-spinellide and have a characteristic nodular structure (disseminations of chromite in serpentinite, Fig. 144) and a specific composition (Table 12).

As a result of serpentinization process and subsequent oxidation the following minerals emerge: serpentine (antigorite, chrysolite), magnesite, magnetite, brucite, chalcedony, chlorites, including kaemmerite and kotschubeite, nontronite, aragonite, gypsum, hydrosilicates of nickel, hydroxides of iron, and opal.

**Minerals of volcanic sublimates**

During the eruption of volcanoes, in the process of the crystallization of magma, the separation of gases takes place. In large quantities they enter the atmosphere through volcano funnels and fissures.

Fig. 144. Chromite in serpentinite (the Southern Urals). Natural size

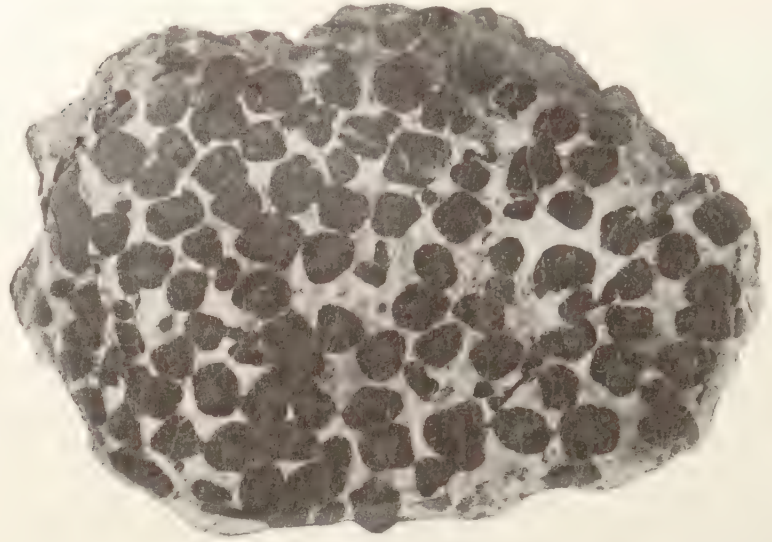


TABLE 12 *Minerals of Chromite Deposits*

Principal	Accessory	Those of practical importance
Olivine Pyroxene	uvarovite sulphides of Fe, Ni, Cu	chromite platinum
Chromite Chromediopside	platinum, etc.	

TABLE 13 *Minerals of Volcanic Sublimates*

Principal	Minor	Those of practical importance
Sulphur Ammonium-chloride Sassoline	pyrite covellite  realgar orpiment cinnabar hematite halite sylvite	sulphur sassoline

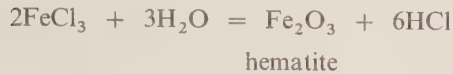
The main gases during the eruptions are: water vapours, HCl, H<sub>2</sub>S, SO<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>, CO, O<sub>2</sub>, chlorous and sulphate compounds of sodium, potassium, calcium, and aluminium. The chlorine compounds of Fe, Cu, Mn, Pb, the compound of boron, fluorine, bromine, phosphorus, arsenic, antimony, mercury, etc. are also found in gases.

The quantity of emanated volcanic gases is very great. In the valley of Ten Thousand Smokes in Alaska within the period of one year the fumaroles has emitted 1 250 000 tons of HCl and 200 000 tons of HF. One of the side cones of the Etna volcano in the Island of Sicily during its eruptions emitted the quantity of water steam, which, if condensed, would amount to 20 million litres of water a day.

The sublimates in the fissures of lava coverings and volcanic craters are responsible for the extraction of minerals. Predominantly they are chlorides and sulphates, the minerals that are easily soluble, and, consequently, not found in large quantities. Minerals formed during the volcanic activity usually have the form of coatings, microcrystalline crusts, and yield earthy aggregates.

The process of mineral formation from the gaseous phase is called pneumatolysis process (from the Greek word 'pneumat', meaning 'gas'). The formation of minerals from gases,

can be exemplified by the following reactions:



In the fumarole fissures of the Mendelejev volcano in Kunashir (the Kuril Islands) we have the extraction of native sulphur.

The industrial value of minerals of volcanic origin is extremely restricted. First and foremost, it is native sulphur (sometimes containing selenium), small deposits of which are known in Kamchatka and the Kuril Islands, Japan, Chile, and Italy. In Italy native boric acid, sassoline is also recovered. Minerals of volcanic sublimates are presented in Table 13.

## The Pegmatitic Process and the Association of Minerals in Pegmatites

*Pegmatites* are coarse- and gigantic granular veined bodies, close in the composition to those intrusions, with which they are spatially connected and from which they are distinguished by their form, structure, and sometimes the presence of rare-metal and rare-earth minerals.

The form of pegmatites is predominantly veined, and lens-like. They are sometimes found as irregular, and not infrequently as branching formations and stocks. Pegmatites are deposited both in the intrusive rocks and in the roof rocks, i.e. in gneisses and crystalline schists. The close spatial link between pegmatites and intrusive rocks proves their genetic affiliation. Pegmatites are usually at a distance of more than 1-2 kilometres from the intrusive rocks.

Most of the pegmatites are related to granites (granite pegmatites), more seldom pegmatites are found to be connected with alkaline magmatic rocks (alkaline pegmatites) and the basic rocks (gabbro-pegmatites).

The mineral composition of granite pegmatites is similar to the mineral composition of granites. The principal minerals are the feldspars (microcline, plagioclases), quartz and micas (muscovite, biotite); tourmaline is often found. Pegmatites are characterized by beryl, cassiterite, spodumene, tantalite, columbite, the minerals of rare earths, etc.

Pegmatitic veins can reach several kilometres in length and have thickness equal to some scores of metres. Pegmatitic minerals can also be of great dimensions. Thus, for instance, in the pegmatites of the basins of the Bolshaya Chuya and Mama Rivers (Eastern Siberia) muscovite crystals were found weighing one ton. Plates of biotite can reach 7 m<sup>2</sup> (Norway); spodumene crystals are sometimes as long as several metres (South Dakota, the USA). In Karelia, where pegmatites are being developed as ceramic raw material, there are crystals of feldspar weighing 100 tons. In the pegmatites of Volyn the crystals of topaz have been mined. They are the largest in the world, and the

weight of the heaviest of them is 117 kilograms. A classical summary of the granite pegmatites is the work of Academician A. Ye. Fersman ('Pegmatites', vol. 1, Moscow-Leningrad, 1940, 712 pp., in Russian), in which all the basic questions pertaining to the origin of pegmatites, their mineralogy, geochemistry and practical application, have been brought to light.

A. Ye. Fersman's conceptual approach is based on the theoretical scheme elaborated by Voght and Niggli, according to which the segregation of a special residual pegmatitic melt-solution (the fluid phase) was introduced as an assumption. In A. Ye. Fersman's opinion, when the crystallization of granite magma takes place, there is a residual silicate melt rich in the compounds of rare and rare-earth elements and other volatile substances, or mineralizers (the compounds of chlorine, fluorine, and boron). This residual melt, as a result of the difference in pressures, is pressed out on to the overlying rocks and fills in their fissures and cavities. The composition of this silicate melt is also granite; hence, the main rock-forming minerals of pegmatites (feldspars, quartz, micas) are the same as those in the parental intrusion.

During the crystallization of quartz and feldspar there appear characteristic formations which are called graphic granite, or jewish stone (Fig. 145). Regular ingrowths of quartz in feldspar resemble oriental letters, or hieroglyphs, which are mainly responsible for the name itself.

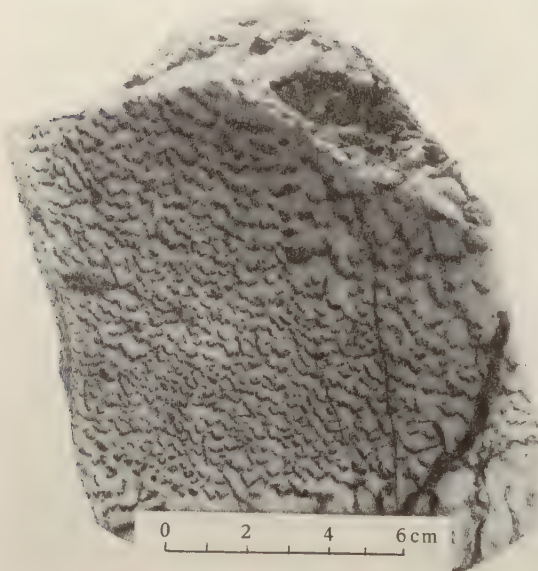
The term 'pegmatite' was originally, in 1801, suggested by the French scientist R. J. Haüy for the specimens of graphic granite from the Urals ('pieces of material inserted into another material'), and it was some time later that the term was applied to all coarse-grained and macro-block veined bodies connected with them.

A. Ye. Fersman gives the following geochemical and genetic definition of pegmatites: 'What we call granite pegmatites is a veined body basically connected with a magmatically granite residue, the main crystallization part of which is within the limits of 700-350°, and which is characterized by a considerable value of crystalline individuals, by a greater or smaller synchronism of crystallization, a higher content of some particular volatile and mobile components, as well as the accumulation of scattered elements of the residual melt'.

A. Ye. Fersman subjected the process of pegmatite formation to an elaborate analysis (from the crystallization of magma to hypergene changes), and singled out 5 stages and 11 geophases. Among the stages he singled out magmatic, epimagmatic, pneumatolytic, hydrothermal, and hypergene. A. Ye. Fersman designated the geophases by the letters from A to L. They reflect the temperature, depth (pressure), physicochemical conditions of the environment and are 'the total paragenetic and geochemical scheme'.

A. Ye. Fersman contrived a temperature scale applicable to the process of pegmatite

Fig. 145. Graphic granite (Biryusa, Eastern Sayan)



*The Scheme of Pegmatitic Process According to A. Ye. Fersman*

Stages	Magmatic	Epimagmatic	Pneumatolitic	Hydrothermal	Hypergene
Geophases	magmat. A	epimag. B	pegmatoidal D	the hydrothermal H I K	the hypergene L
Temperature, °C	900	800	600 575	400 375	50
Processes		premagmatic from the melt	pegmatitic from the fluid melt	postpegmatitic from the hydrothermal melt	hypergene
Means of crystallization		the formation of aplites and contact fringes	the main stage of pegmatite-forma- tion feldspars, quartz, muscovite, shorl, beryl, topaz	green micas, fluorites, carbonates sulphides and zeolites	hypergene minerals
Characterization of geophases	solidifica- tion of granite massif	pegmatite of graphical structure	musco- vitiization, albi- tization, the formation of minerals of lithium, and other rare metals		
Types of pegmatites		I, II	III, IV	VIII, IX, X	
			V, VI, VII		

formation, with only two points on it being fixed. The first refers to the boundary between geophases C and D, and characterizes the polymorphic transitions of quartz ( $t = 573^{\circ}\text{C}$  at normal pressure). The second coincides with the boundary of geophases of G and H and corresponds to the critical point of water ( $t = 374^{\circ}\text{C}$ ). The pegmatitic process proper is characterized by geophases C-G. The pegmatitic process in its diagram form, according to A. Ye. Fersman, is given on page 267.

For granite pegmatites of the pure line A. Ye. Fersman devised 10 types, which characterize the process of pegmatite formation in a sequential order. Each type has a certain paragenetic association of minerals distinguishing it from others.

		Geophases
<i>Type I.</i>	Common and cerium pegmatites. Plagioclase, microcline, quartz, biotite laths, monazite, orthite, garnet.	B-C
<i>Type II.</i>	Pegmatites with rare elements. Plagioclase, microcline, quartz, biotite, samarskite, columbite, uraninite.	C-D
<i>Type III.</i>	Boron-fluorine (shorl-muscovite). Microcline, plagioclase, quartz, shorl, muscovite, apatite.	D-E
<i>Type IV.</i>	Fluorine-beryl (topaz-beryl). Orthoclase, amazonite, smoky quartz, beryl, topaz, black-blue tourmaline.	D-E
<i>Type V.</i>	Natrolithium. Albite, lepidolite, coloured tourmaline, topaz, pink beryl, green muscovite, columbite, spodumene, cassiterite, etc.	F-G
<i>Type VI.</i>	Lithium-manganese-phosphate. Albite, quartz, caesium beryl, polychromatic tourmaline, pollucite, petalite, amblygonite, triphylite and other phosphates.	F-G
<i>Type VII.</i>	Fluorine-aluminium. The characteristic mineral is cryolite.	H-I-K
<i>Type VIII.</i>	Fluorine-carbonate. The characteristic minerals are: carbonates, fluorite, parisite.	H-I-K
<i>Type IX.</i>	Sulphide (less common)	H-I-K
<i>Type X.</i>	Alkaline (with zeolites)	H-I-K

The most widespread types are I, III, and V, VI, the latter being hard to distinguish. Type II is rare, while type IV mainly refers to pegmatites with voids (cavities), which are characterized by tabular albite and morion. Types VIII and X are tentative and refer to the hydrothermal process.

The typomorphic features of minerals characterizing their position in the process of pegmatite formation are: colour, appearance, size, crystalline forms and the elements-impurities.

If minerals of the pegmatitic veins with characteristic typomorphic features were distributed into geophases, it would be possible to receive a fairly reliable information concerning their associations (see Fig. 139). Hence, judging by the location of some of the minerals it is possible to assume what other minerals, including those of practical value, can be

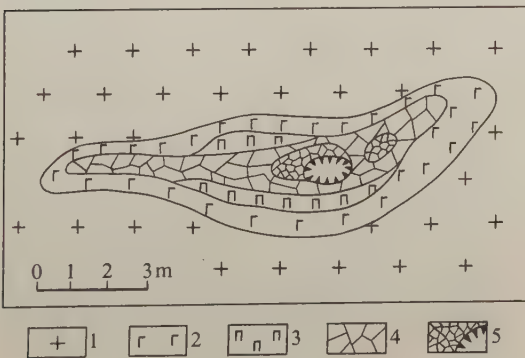


found. Thus, the association of minerals characteristic of soda-lithium type V is: albite (cleavelandite), lepidolite, rubellite, spodumene, pollucite, columbite-tantalite, and others. Consequently, if lepidolite or pink tourmaline has been discovered in the pegmatite, there is every reason to expect other finds of minerals paragenetically related to them. It means that the exploratory work must proceed, and this pegmatite presents interest as to Li, Ta-Nb, and Cs. In Figure 139 the order of segregation and the typomorphic features of minerals of one of the pegmatitic fields in Central Asia is illustrated.

In 1952 K. A. Vlasov suggested a structural-paragenetic classification of pegmatites. According to structural features, and taking into account the paragenetic associations of minerals, he singled out the following types of pegmatites (Fig. 147):

1. *The uniformly granular type*, e. g. simple pegmatites, including those of the graphic texture.
2. *The block type*, consisting of blocks of microcline and quartz, separated from the enclosing rocks by a graphic or aplitic fringes.
3. *The fully differentiated type* is exemplified by microcline blocks containing a quartz nucleus, and the presence of similar fringes.
4. *The rare-metal replacement type* is connected with the development of replacement processes (albitization) and the formation of minerals of Li, Cs, Be, Ta-Nb, etc.
5. *The albite-spodumene type* illustrates the more fully replaced pegmatites.

Fig. 146. Pegmatitic vein of a chamber type in granite:  
 1 - granite; 2 - pegmatite of the graphic structure ('graphic granite');  
 3 - pegmatite of the pegmatoidal structure (block aggregate of quartz and potassium feldspar); 4 - monomineral feldspar zone; 5 - the quartz nucleus with the cavity (chamber), in which the crystals of smoky quartz, topaz and beryl are located



K. A. Vlasov, as well as A. Ye. Fersman, assumes the formation of pegmatites from a particular melt-solution in the conditions of a closed system. At the same time it is characteristic of pegmatites to have an intensive manifestation of replacement processes. Replacement processes can be exemplified by the development of albite-spodumene paragenetic association in rare-metal pegmatites and the quartz-muscovite association in mica-bearing pegmatites at the expense of potassium feldspar. D. S. Korzhinsky, studying the mica-bearing pegmatites of Eastern Siberia, came to the conclusion that they were formed metasomatically and outside any fluid pegmatitic melt.

The American geologists R. Jones, E. Cameron and others are of the opinion that in the formation of pegmatites two stages are to be singled out. The first stage (the half-closed and closed system) is connected with the crystallization from the melt and the formation of simple pegmatites. The second stage, on the open system, is related to the intensive metasomatic processing of pegmatites by gaseous-like solutions, emitted from the depths.

In A. N. Zavaritsky's opinion pegmatites are being crystallized in the conditions of the open system. This is substantiated by the fact that pegmatites contain replacement textures. He made it clear that the theoretical concept based on the non-restrictive character of solubility of volatile substances in the melt (J. Voght and P. Niggli) is groundless, and arrived at the conclusion that the separation of gaseous solutions at the lowering of temperature of the magmatic melt is inevitable. The sum and substance of A. N. Zavaritsky's research can be

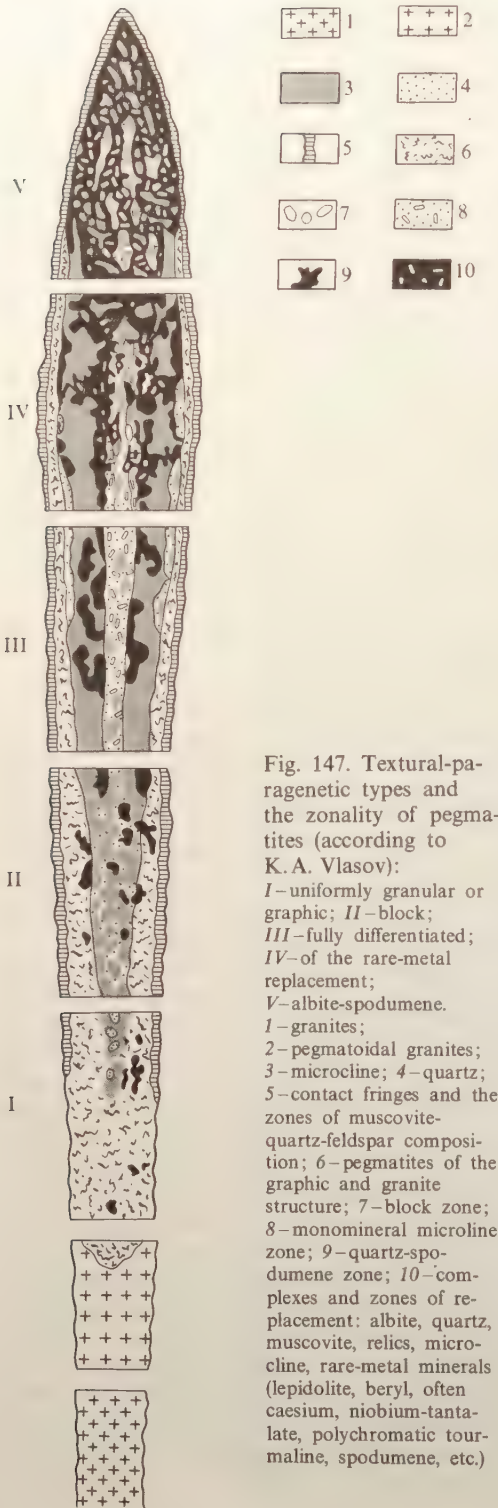


Fig. 147. Textural-petrographic types and the zonality of pegmatites (according to K. A. Vlasov):  
 I—uniformly granular or graphic; II—block;  
 III—fully differentiated;  
 IV—of the rare-metal replacement;  
 V—albite-spodumene.  
 1—granites;  
 2—pegmatoidal granites;  
 3—microcline; 4—quartz;  
 5—contact fringes and the zones of muscovite-quartz-feldspar composition; 6—pegmatites of the graphic and granite structure; 7—block zone; 8—monomineral microcline zone; 9—quartz-spodumene zone; 10—complexes and zones of replacement: albite, quartz, muscovite, relics, microcline, rare-metal minerals (lepidolite, beryl, often caesium, niobium-tantalate, polychromatic tourmaline, spodumene, etc.)

formulated thus: there is no particular pegmatitic magma and residual pegmatitic melt. Pegmatites are formed as a result of the recrystallization of rocks under the action of gaseous solutions, separated from the magma at a certain stage. Gaseous solutions, during the subsequent cooling can yield hydrothermal solutions.

A detailed study of pegmatites of Karelia and the Kola peninsula gave V. D. Nikitin a substantial amount of evidence to furnish to the following explanation of their origin: 'Pegmatites, with all the immanent features of their structure, originated in the veined bodies of common magmatic rocks (granites, granite-aplites), through the recrystallization of these rocks and their metasomatic transformation...'. The processes of replacement in pegmatites studied by V. D. Nikitin prove that the process of pegmatite formation characterizes an open system.

The metamorphogenic concept of pegmatite formation is based on the bond between their textural and chemical characteristic features with the degree of regional metamorphism and the granitization of enclosing strata. In accordance with this, there are metasomatic, anatexite, and intrusive pegmatites. For instance, the formation of most of the muscovite pegmatites (type III, according to Fersman) is connected with the granitization of enclosing strata, while that of the rare-metal pegmatites (type V, according to Fersman) is related to intrusive granites.

Granite pegmatites are characterized by the following features:

- (1) veined, lens-like, irregular, often branched form of depositing;
- (2) depositing among granites and deep metamorphosed strata, close spatial bond with the granitized rocks;
- (3) mineral composition, corresponding to the composition of granites and granitized rocks;
- (4) gigantic or large dimensions of mineral individuals, and their light colour;
- (5) the presence of rare-metal and rare-earth minerals, including a large number of such mineral species as aluminosilicates, zircon silicates, and niobium tantalates; in other formations they are practically not found.

TABLE 14

*Pegmatite Minerals*

Principal	Minor and accessory	Those of practical importance	Principal	Minor and accessory	Those of practical importance
<i>I. Granite pegmatites (ceramic and muscovite)</i>			<i>IV. Miaskite pegmatites of the Ilmen Mountains</i>		
Plagioclase (oligoclase, oligoclase-albite)	garnet orthite beryl	feldspar and quartz muscovite	Orthoclase Plagioclase Nepheline	lepidomelane biotite hastingsite calcite cancrinite ilmenite natrolite sodalite apatite zircon pyrochlore sphene muscovite magnetite	
Microcline-perthite	monazite	beryl			
Quartz	xenotime				
Muscovite	zircon				
Biotite					
Apatite					
Schorl					
<i>II. Granite pegmatites (rare-metal)</i>			<i>V. Syenite pegmatites of the Urals</i>		
Albite (cleavelandite)	muscovite rubellite	spodumene tantalite-columbite	Microcline	zircon aeschynite	
Quartz	polychromatic tourmaline	pollucite	Orthoclase	orthite	
Microcline	beryl	beryl	Oligoclase	monazite	
Spodumene	amblygonite	lepidolite	Muscovite	pyrochlore	
Lepidolite	triphylite columbite-tantalite pollucite cassiterite	amblygonite cassiterite tourmaline	Biotite	corundum	
			Sphene	ilmenite	
			Aegirine-augite	ilmenorutile	
			Hornblende	fluorite	
<i>III. Granite pegmatites (crystal-bearing)</i>			<i>VI. Nepheline-syenite pegmatites of the Kola peninsula</i>		
Quartz	muscovite	mountain crystal	Microcline	sphene	loparite
Mountain crystal	phenacite	smoky quartz	Nepheline	ilmenite	pyrochlore
Smoky quartz (rauchtopaz)	biotite	topaz beryl	Aegirine	zircon	
Morion		phenacite	Arfvedsonite	eudialyte	
Potassium feldspar			Lepidomelane	astrophylite lamprophylite aenigmatite pyrochlore lovchorrite rinkolite loparite	
Albite (pectinal)					
Topaz					
Beryl					

Granite pegmatites are divided into ceramic (large blocks of microcline and quartz), mica-bearing (muscovite), rare-metal (lithium, beryllium, tantalum-niobium, caesium) and rock-crystal-bearing (rock crystal, topaz, beryl). The latter are usually deposited among granites or granite gneisses and form cavities, or chambers; hence they are also called chamber pegmatites. In these cavities (bags) there is a growth of large crystals of rock crystal, smoky quartz, morion, topaz, beryl, phenacite, and other minerals (Fig. 146).

Everything that has been said above concerns the granite pegmatites, genetically related to granite or granitized rocks.

Besides granite pegmatites connected with the granite magma there are also pegmatites connected with syenite, alkaline rocks, and gabbro. The paragenetic associations of minerals characteristic of granite pegmatites, pegmatites of the 'intersection line', syenite and the miaskite pegmatites of the Urals, the nepheline-syenite pegmatites of the Kola Peninsula are illustrated in Table 14.

The composition of the comparatively rare gabbro-pegmatites corresponds to gabbro (basic plagioclase and pyroxene). Ilmenite and magnetite enter into their composition too. The veins of gabbro-pegmatites are characterized by a coarse-grained structure.

Pegmatitic veins are remarkable for the concentration of valuable mineral resources. For instance, in Karelia ceramic pegmatites (feldspar, quartz) are widely spread. In Irkutsk Region, Mama and Chuya river basins there are vast fields of muscovite pegmatites. The latter have also been found in the Kola peninsula, Karelia, eastern Sayan (Biryusa river) and on the Enisei ridge. Rare-metal pegmatites are known in eastern Kazakhstan, in the Kola Peninsula, Eastern Sayan in Central Asia, the Transbaikal Region, and elsewhere. Rock-crystal-bearing and other pegmatites of the chamber type are found in the Ukraine (Volyn), Kazakhstan, in the Urals and Aldan. Pegmatites are known in India, Afghanistan, Brazil, Canada, the USA, Zaire, and other countries of Africa.

## Postmagmatic Metasomatic Processes of Mineral Formation and the Mineral Associations in Skarns, Albitites, and Greisens

Metasomatic phenomena connected with metamorphism, the magmatic and postmagmatic activity, including the metasomatic formation of ore minerals, are extremely widespread in nature.

Academician D.S. Korzhinsky's contribution to the development of the theory of metasomatic processes can hardly be overestimated, since his research in this field of geology is by right considered to be fundamental. According to D.S. Korzhinsky what we mean by *metasomatism*, at present, 'Is any replacement of the rock with a change in its chemical composition, under which the solution of the old minerals and the depositing of the new ones is practically synchronic, so that during the process of replacement the rocks continue to retain its solid state all the time'. The concept 'metasomatism' is applicable both to the endogene and the exogenetic processes. It was for the

latter that it was initially suggested. However, we shall regard metasomatic processes as applied to those of the endogene postmagmatic type.

The processes of metasomatism are widely spread in the formation of pegmatitic and hydrothermal ore veins.

In what comes next we shall dwell on some of the practically important postmagmatic, metasomatic processes with which quite a few ore deposits are associated: (1) the contact-metasomatic, or skarn, process; (2) the near-contact leaching, leading to the formation of apogranites, greisens, and secondary quartzites. It should be pointed out that mineralization, as is the case with gold, can also be connected with a low-temperature periveined metasomatism (beresitization, listwenzitization, chloritization).

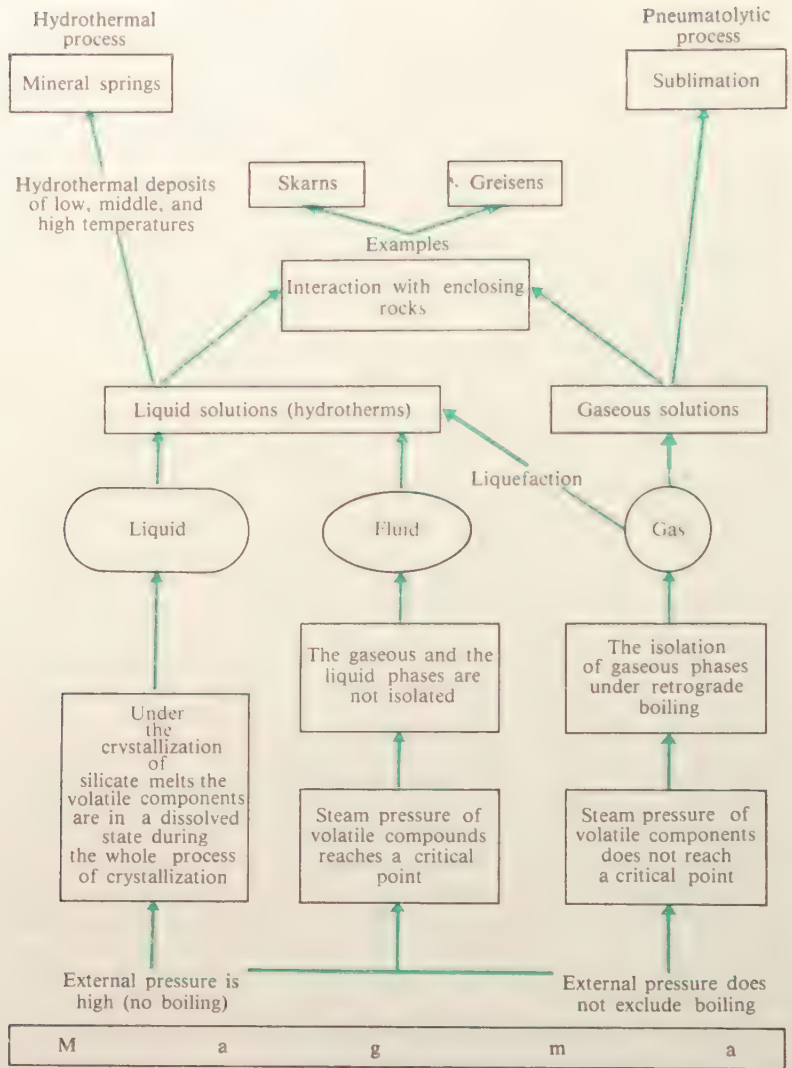
Metasomatic processes cannot possibly be divorced from the participation of liquid and gaseous solutions that are responsible for the admission of some of the components and the departure of others, thus causing a metasomatic replacement. These solutions are usually referred to as porous, since they can permeate through the smallest pores in the rocks. The source of these solutions is the magmatic chamber in the state of solidification, from which, depending on the circumstances, gaseous and liquid phases, not always independent of each other, can be separated (Fig. 148). Postmagmatic solutions emit from the magmatic chamber a whole range of volatile compounds and compounds of metals, that usually move upwards, in the direction of the least pressure. The solutions move along the fissures, tectonically weakened zones, rock contacts, or penetrate, as a result of diffusions. Well-grounded statements have recently been made substantiating the idea that these solutions need not necessarily be of magmatogenic origin, they can also occur under the ultrametamorphosis of sediments. However, this does not alter the fact that metasomatic processes do lead to the replacement of some of the minerals by others.

Solutions serve as a medium through which the components are migrated in the rocks. The mechanism of this kind of migration, according to D. S. Korzhinsky, can take place in two extreme cases: (1) the components are diffused through immobile porous solutions in the direction of the fall in their concentration, i. e. the migration occurs by means of diffusion. This is called *diffusive metasomatism*; (2) the components are involved in the movement of the solution, permeated through rocks, i. e. the migration process takes place by means of infiltration (*infiltrational metasomatism*). Between these two extreme cases it is possible to have variants of metasomatic replacement. There is also enough ground to single out *bimetasomatism*, when the migration of components takes place in both directions from the contact of heterogeneous rocks, by means of a reactionary exchange. In the replacement process, the composition and the character of postmagmatic solutions undergo changes that lead to the emergence of various contact zones, with their own chemical and mineral compositions or metasomatic zonality. The latter is more or less characteristic of all metasomatic formations.

The phenomena of diffusive metasomatism are confined within the limits of several metres, while the infiltrational elements of the solution can be transferred at greater distances.

By studying metasomatic processes it is essential that we should

Fig. 148. Diagram showing the separation of gaseous and liquid solutions from the magma and their connection with postmagmatic processes



bear in mind the fact that they are inseparable from the magmatic and metamorphic processes and lead to the formation of the mineral resources.

### The Skarn Process and the Association of Minerals in Skarns

Skarns\* are metasomatic rocks composed of limestone-ferriferous and magnesian silicates, formed as a result of the reactionary interaction of carbonate and the aluminosilicate rocks in conjunction with

\* The term of the Swedish miners, was earlier used for a void rock, enclosing magnetitic ore.

TABLE 15

*Minerals of  
Magnesium Skarns*

Principal	Minor	Those of practical importance
Forsterite Diopside Calcite	quartz plagioclases spinel	phlogopite magnetite ludwigite and other borates
Phlogopite	ludwigite and other borates	borates
Magnetite Scapolite	apatite titanite actinolite (tremolite) chondrodite periclas humite lazarite	lazarite

postmagmatic solutions. Thus, skarns are formed as a result of interaction of three media: two enclosing rocks, different in their composition, and the postmagmatic solutions. It is the latter that cause the phenomenon known as metasomatism. Skarns originate in the zone of the high-temperature contact aureole of intrusions, hence skarn deposits are not infrequently called contact-metasomatic too. Before skarn deposits were also called contact-metamorphic, and pyrometasomatic. In the USA, the term 'tektite' was employed to denote the mineralized skarns.

Skarns are formed at the contact of aluminosilicate (granitoids) and carbonate (limestone, dolomites) rocks as a result of their metasomatic replacement. Skarns, that have emerged as a result of the replacement of the aluminosilicate rocks are called *endoskarns*, while the replacing carbonates have acquired the term *exoskarns* (endo- and exo- in relationship to intrusion). However, the replacement of such chemically active rocks as carbonates, takes place at a considerably greater pace as compared with aluminosilicates, which accounts for the fact that exoskarns are practically always more developed than endoskarns, the latter being occasionally represented by a narrow zone of periskarn rocks.

The gnosiological process of skarn-formation is reflected in the outstanding works of D. S. Korzhinsky.

According to the mechanism of metasomatic replacement skarns are distinguished as *diffusive* and *infiltrational*. The predominant part of skarns are developed bimetasomatically; however, the formation of most of the ore skarn bodies is connected with the infiltrational and reactional interaction of postmagmatic solutions in the contacts of carbonate and aluminosilicate rocks. Skarns of this kind are called *contact-infiltrational*. Under intensive bimetasomatism endo- and exoskarns are difficult to distinguish.

Owing to the diffusive interaction of contact rocks there appear, in the process of skarn formation, a number of zones ranging from granitoid to limestone. The metasomatic zonation for skarns is a characteristic feature that is quite clear. Skarn zones are different as far as their mineral and chemical compositions are concerned; their emergence corresponds to the change of the chemical potentials of the

TABLE 16

*Minerals of the  
Limestone Skarns*

Principal	Minor	Those of practical importance
Grossular-andradite	plagioclases	magnetite
Diopside-hedenbergite	tremolite	scheelite
Idocrase	scheelite	molybdenite
Epidote	molybdenite	cobaltite
Scapolite	datolite	glaucodot
Magnetite	danburite	smaltite
Wollastonite	axinite	safflorite
Quartz	helvite	galenite
	ilvaite	sphalerite
	fluorite	datolite
	cassiterite	danburite
	pyrite	helvite
	chalcopyrite	chalcopyrite
	cobaltite	gold
	galenite	cassiterite
	sphalerite	
	glaucodot	
	gold	
	safflorite	
	bismuthine	
	bismuth	
	smaltite	

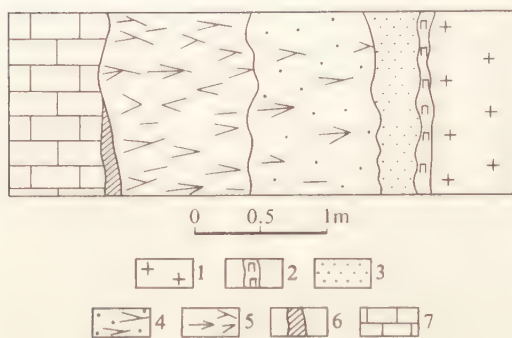


Fig. 149. Skarn zone at one of the deposits in Central Asia:

1 - granite; 2 - pyroxene-plagioclase rock; 3 - fine-grained pyroxene-garnet skarn; 4 - medium- and coarse-grained garnet-pyroxene skarn; 5 - pyroxene (hedenbergite) skarn; 6 - wollastonite fringe; 7 - marbled limestone

components entering into the solution, the change of temperature, the transportation from the source of contact, and depends on a host of other factors. Thus, for instance, for the skarns of Ingichke (Central Asia) the zonalinity, in its general form, from the intrusion to limestones, is presented in Fig. 149.

Depending on the composition of the replaced carbonate rocks, two groups of skarns are distinguished. They are: *magnesian skarns*, developed after dolomites, and *limestone skarns*, developed after limestones. Their mineral associations are various. Magnesian skarns are characterized by such minerals, as forsterite, spinel, diopside, phlogopite, and ludwigite. The characteristic minerals of limestone skarns are: diopside-hedenbergite, grossular, andradite, as well as wollastonite, vesuvianite, scheelite, and other calcium minerals. Mineral associations of magnesian and limestone skarns are given in Tables 15 and 16.

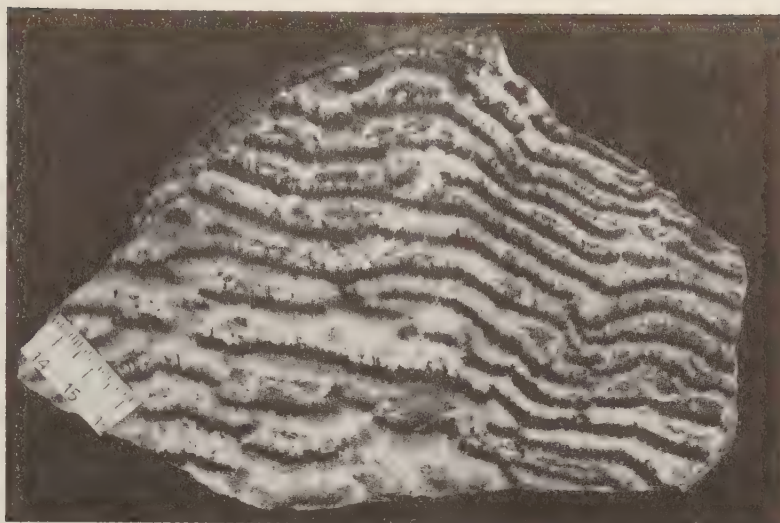
Skarns are an extremely important genetic type of the deposits of metallic mineral resources and phlogopite-mica. Mineralization, as a rule is of a superimposed type in respect to skarn minerals. Magnesian skarns are characterized by the following ore formations and typical of the USSR:

Ludwigite-magnetite	- Tayozhnoye, Eastern Siberia
Phlogopite	- Slyudyanka in the Baikal region; the Aldan group of deposits
The following formations are of practical value to limestone skarns:	
Scheelite	- Ingichke, Koitash in Central Asia
Molybdenite-scheelite	- Tyrnyauz in the Northern Caucasus
Magnetite	- Vysokogorsk and others in the Urals; Sokolovsk and Sarbai in the Kustanai Region; Temir-Tau, Tashtagol in Western Siberia, Abakan in Khakassiya.
Polymetallic	- Altyn-Topkan and others in Central Asia, as well as in the Primorski Krai, and Kazakhstan
Cassiterite	- Kitelya in the near Ladoga district, Maikhura and the Takfon deposit in Tadzhikistan
Chalcopyrite and magnetite-chalcopyrite	- Turyinsk in the Urals, Sayak in Kazakhstan
Cobaltite-magnetite	- Dashkesan in the Transcaucasus region
Safflorite-glaucodot	- Khovuaktsy in Tuva
Helvite-magnetite	- the deposits in Kazakhstan
Boron-silicate	- The Primorski Krai
(Fig. 150)	

Scheelite skarn deposits are known in China, South Korea, Australia; magnetite deposits are found in Sweden and the USA; polymetallic deposits - in Mexico, Argentine, etc.



Fig. 150. Rhythmically-striped structure of skarns (Primorskii Krai). Hedenbergite (dark stripes); wollastonite and datolite (light parts)



Besides, skarns are remarkable for the cases of gold and bismuth mineralization. The practical value of skarn deposits consists in that they yield the whole of mica-phlogopite output, approximately 50% of tungsten, about 30% of lead and zinc, a considerable amount of molybdenum, iron, copper and other metals.

### Albitization and Mineral Associations in Albitites

*Albitites* are metasomatic rocks formed as a result of processing granitoids by postmagmatic solutions bringing forth a substantial change in their content and structure. The action of these solutions results in an intensive development in the apical parts of granitoids of albite, lithium micas and other minerals of practical value, e.g. columbite, pyrochlore, zircon, beryl, and rare-earth minerals. The process of albitization is typical of postmagmatic sodium metasomatism, which is manifested in various rocks. Thus, when pegmatites were discussed earlier, we distinguished V—the soda-lithium type of pegmatites, according to A. Ye. Fersman, or IV—the rare-metal replaced type, according to K. A. Vlasov; the intensive development of albite in them, in some cases, leads to that the rocks can be called *albitites*.

Substantially albiticized granites are called *apogranites*. According to A. A. Beus, it is possible to single out apogranites of the normal, subalkaline, and alkaline series, the mineral associations and mineralization in them being varied. In Table 17 minerals of apogranites that are, in principle, secondary and those of practical importance, are adduced.

Apogranites have a vertical metasomatic zonality. The general diagram of zonality, determined by the structure of the metasomatic column within the limits of parental intrusive rocks, is the following (in ascending order, according to A. A. Beus):

- (1) intrusive rock;

TABLE 17

Minerals of Apogranites

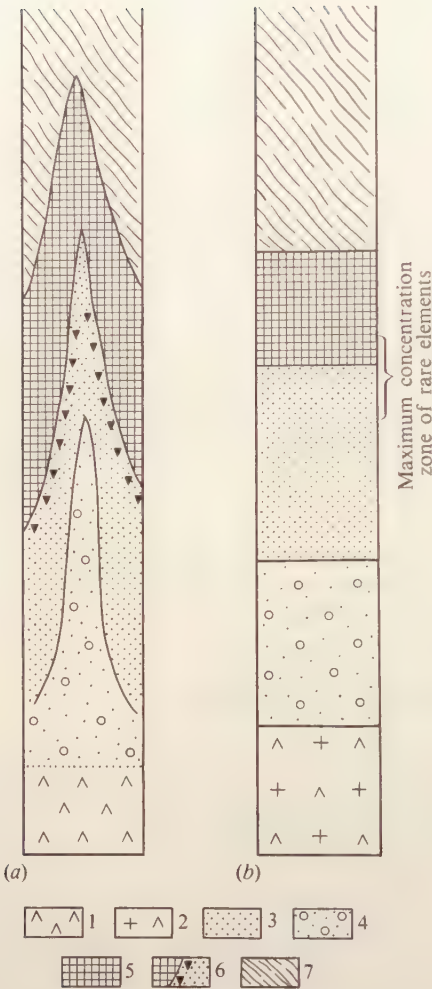


Fig. 151. The zonalities of albitites:

*a*—a typical column of albitized alkaline rocks with niobium and zircon mineralization (according to I. P. Tikhononkov), and *b*—a generalized metasomatic column of the deposits of albitite formation (according to A. A. Beus): 1—alkaline rocks; 2—acid and alkaline intrusive rocks; 3—albitite; 4—quartz albitite; 5—microclinization, quartz microclinites, microclinites; 6—concentration of

dark-coloured and rare-metal minerals in albitite; 7—metamorphic schists

- (2) intrusive rock with an apparent manifestation of processes pertaining to the high-temperature postmagmatic metasomatism;
- (3) the zone of development of high-temperature silicification;
- (4) the zone of predominant albitization;
- (5) the zone of predominant microclinization.

The metasomatic columns of apogranites, in a generalized form, are shown in Fig. 151. The deposits of rare metals in albitites are known in the Transbaikal region and in Kazakhstan. Rich deposits of niobium and tantalum are connected with columbite-bearing albiticized granites of Northern Nigeria.

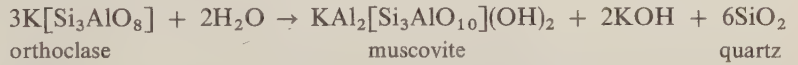
Principal	Minor	Those of practical importance
<i>Apogranites of the normal series</i>		
Albite	muscovite	beryl
Quartz	beryl	phenacite
Microcline	phenacite	
	bertrandite	
	wolframite	
	molybdenite	
<i>Apogranites of the subalkaline series</i>		
Albite	lepidolite	columbite-tantalite
Amazonite	zinnwaldite	pyrochlore
Quartz	topaz	
	columbite-tantalite	
	pyrochlore-microlite	
	spodumene	
	amblygonite	
	cassiterite	
<i>Apogranites of the alkaline series</i>		
Albite	biotite	columbite-tantalite
Microcline	riebeckite	pyrochlore
Quartz	aegirine	
	zinnwaldite	
	pyrochlore	
	zircon	
	columbite	
	xenotime	
	gagarinite	
	monazite	
	bastnäsite	

The process of albitization is genetically closely related to another postmagmatic metasomatic process, viz. greisenization.

### Greisenization and Mineral Associations in Greisens

*Greisens\** are metasomatic rocks formed as a result of the processing the main specimens of granites by postmagmatic gaseous and water solutions. Same can be said of the effusive and some sedimentary metamorphic rocks, rich in silica and alumina. As a rule, greisens are formed in dome-like protrusions of granite intrusions, in their exocontact zones and along ore veins. By their mineral composition greisens are substantially quartz-muscovite rocks, often with lithium micas, topaz, tourmaline, fluorite and such valuable minerals, as cassiterite, wolframite, molybdenite, and beryl. In the greisens of the Transbaikal region we can find the transparent variety of beryl of the aquamarine colour, which in itself is a precious stone, viz. aquamarine.

Greisens and albitites emerge as a result of postmagmatic metasomatic processes. They are developed in the same kind of rocks, mainly in the apical parts of granitoids, and in pegmatites; spatially they are brought together, and, in their essence correspond to one and only one metasomatic process, which finds a different expression depending on the change of acidity in solutions. The process of greisenization is of a comparatively later period than that of albitization, and is connected with the formation of quartz-muscovite rocks, that takes place under the hydrolysis of feldspars:



Gaseous and water solutions, causing greisenization, contain a large number of volatile components: F, Cl, B, etc. in composition with which there occurs a transportation of rare metals. Thus, the more probable form of tin transportation (according to V.L. Barsukov) becomes compound  $Na_2[Sn(OH, F)_6]$ , in which the migration of tin at a considerable distance takes place, and which serves to explain the characteristic paragenesis of cassiterite with topaz, fluorite, and micas.

\* An old term of the German origin for quartz-mica periveined rocks containing a cassiterite.

Fig. 152. Diagram showing the structure of the periveined greisen bodies in the granites of the Transbaikal region (according to I. F. Grigoriev):

- 1 - biotite granites;
- 2 - bimicaceous granites;
- 3 - muscovite granites;
- 4 - muscovite-quartz-greisen;
- 5 - quartz-muscovite greisen;
- 6 - muscovite greisen;
- 7 - topaz greisen;
- 8 - quartz greisen;
- 9 - ore veins: cassiterite-quartz, cassiterite-quartz-topaz, cassiterite-wolframite-quartz.

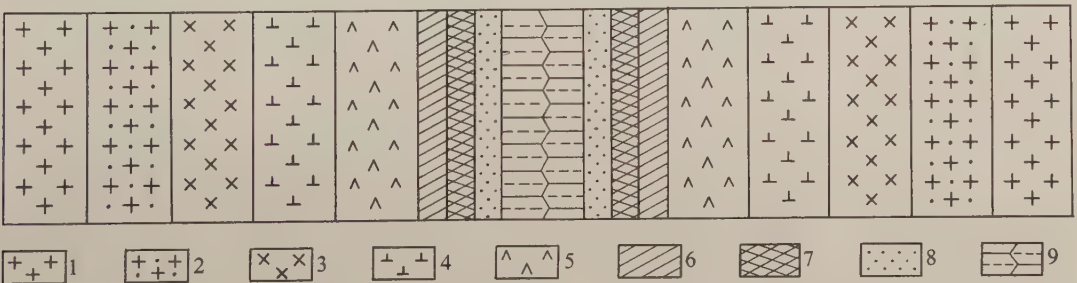


TABLE 18

*Greisen Minerals*

Principal	Minor	Those of practical importance
Quartz	cassiterite	cassiterite
Muscovite	tourmaline	wolframite
Zinnwaldite	beryl (aquamarine)	scheelite
Topaz	wolframite	beryl
Fluorite	scheelite arsenopyrite molybdenite pyrrhotite chalcopyrite pyrite bismuthine cosalite	

In those cases when greisenization occurs along the fissures and ore veins, greisens of zonal structure are formed (Fig. 152).

Rare-metal veined deposits, e.g. the wolframite deposits of the Eastern Transbaikal region, and the accompanying them greisen zones have identical mineral composition. It has been established that all the principal minerals of ore veins, including those of the ore type, e.g. wolframite, scheelite, pyrite, cassiterite, are formed at the place of the rock-forming minerals of granitoids and other rocks, enclosing ore veins.

In the apical parts of granitoids the number of fissures and veins, along which greisenization takes place, can be very large. The parts of granitoids intensely greisenized or containing an abundance of variously oriented veined greisen bodies are called *stockworks*.

Thus, the characteristic features of greisens

are:

(1) geological position: the development in the apical parts of granitoids, in pegmatites and along ore veins.

(2) mineral composition: quartz, muscovite, or quartz and zinnwaldite, as well as the development of topaz, beryl, cassiterite, wolframite, arsenopyrite, molybdenite, tourmaline, and fluorite.

Greizen deposits are known in the Transbaikal region, Kazakhstan (USSR), in South America, Malaysia, China, Burma, Czechoslovakia, etc. The most important minerals of greisens are given in Table 18.

### **Silicification, Sericitization and Other Low-Temperature Metasomatic Processes, and Their Mineral Associations**

Besides the metasomatic processes discussed above, such as skarn formation, albitization, and greisenization, it is necessary to touch upon silicification, sericitization, and some others.

#### **Silicification**

is a metasomatic replacement of rocks by quartz as a result of an intensive acid leaching, which is sometimes extremely great (depending on the composition of rocks). *Secondary quartzites* are particularly characteristic. They are formed under the hydrothermal-metasomatic processing of acid and medium, mainly volcanic rocks.

The principal and the minor minerals of secondary quartzites are shown in Table 19.

#### **Sericitization**

is a metasomatic replacement of aluminosilicates (mainly plagioclases) by a fine-scaly, sometimes fibrous mica (sericite). The process of sericitization is widely spread in rocks and is particularly characteristic of pyrite, copper-molybdenum (copper-porphyrific), and quartz-gold-bearing deposits. Sericitization in latter cases is manifested intensively, and the quartz-sericitic rocks are formed which often contain pyrite. The quartz-sericitic rocks with pyrite developed in the Berezovskii

TABLE 19

*Minerals of Secondary Quartzites*

Principal	Minor	Those of practical importance
Quartz	dickite	corundum
Sericite	tourmaline	diaspore
Alunite	rutile	alunite
Kaolinite	dumortierite	pyrophyllite
Andalusite	pyrite	chalcopyrite
Diaspore	chalcopyrite	
Pyrophyllite	molybdenite	
Corundum	hematite	

gold-bearing deposit in the Urals were called *beresite* by G. Rose. A. P. Karpinsky determined their metasomatic origin and has proved that they emerge at the expense of hydrothermal-metasomatic periveined change of granite-porphyrries. The formation of sericite and quartz at the expense of the decomposition of feldspars is synchronic with the pyritization of rocks. Beresites are connected with gold-bearing quartz veins. *Listvenites* are the products of the hydrothermal change of the basic rocks and serpentinites. They represent granular rocks of a light- or bright-green colour, consisting of quartz, carbonate, bright-green fuchsite (a chrome-containing variety of

muscovite), and chlorite. Beresites and listvenites are being developed in the Berezovskii gold-bearing deposit in the Urals and in some other gold deposits.

Metasomatic rocks with sericite are characterized by the following minerals:

<i>principal</i>	<i>minor</i>
quartz	tourmaline
sericite	rutile
chlorite	fluorite
dolomite	barite
calcite	sulphides of Fe,
ankerite	Cu, Pb, and Zn
siderite	
pyrite	

**Propylitization,**

a greenstone metasomatic change of volcanic strata under the impact of ascending postmagmatic solutions, is included into regional metasomatic processes.

This process occurs at inconsiderable depths. Propylitization corresponds to the fields of the distribution of igneous rocks (andesites, basalts, etc.) in tectonically weakened zones and accompanies some of the ore veins. Propylites are characterized by the following minerals:

albite	ankerite
chlorite	calcite
epidote	pyrite
actinolite	adular
sericite	quartz

Low-temperature periveined metasomatic processes comprise *epidotization*, *chloritization*, *carbonatization*, *zeolitization*, and some other processes, occasionally accompanying the hydrothermal ore veins.

**The Hydrothermal Process and the Association of Minerals in Ore Veins**

*Hydrothermal solutions* are hot water solutions, separated from the magma or formed as a result of the liquefaction of gases (see Fig. 148). Hydrothermal solutions are responsible for the flowing out of the

magmatic chamber of a whole range of metallic compounds. Besides, hydrotherma can acquire various substances from the lateral rocks along which their movement takes place. It is assumed that most of the metals in solutions are in the form of highly complex compounds (with haloids).

The movement of hydrotherma is caused by various degrees of pressure. When the inner pressure of the solutions is greater than the external, the solutions move in the direction of the least pressure, which is usually ascending to the earth's surface. When in motion, they make use of various tectonic distortions, fissures, and contact zones.

The more the solutions depart from the magma chamber, the lower their temperature becomes. There are various reasons for the fallout of minerals from the hydrothermal solutions, for example, the drop in temperature and pressure, the change of the chemical environment, as can be the case when the said process becomes associated with underground waters and the reaction of the enclosing rocks. As a result of all or some of the conditioned reasons, that have just been mentioned, hydrothermal springs deposit their load in the form of minerals. The segregation of minerals from water solutions (occasionally colloidal) is, in fact, the sum and substance of the hydrothermal process.

Since hydrothermal springs usually move along the fissures, the form of most of the hydrothermal mineral bodies is veined. The most important veined mineral is quartz (quartz veins, Fig. 153).

Hydrotherma can be of high-, mid-, and low-temperature varieties, and it is by the temperature of their formation that we tentatively single out the following hydrothermal deposits: high-temperature deposits (450-300°), mid-temperature deposits (300-200°), and low-temperature deposits (below 200°).

As a rule, the high-temperature hydrothermal mineral bodies are situated close to the parental magma chamber, while those of the low-temperature variety are removed farther. To a certain extent this leads to the zonal localization of the products of the hydrothermal process in relation to the magma chamber, to which they are connected by their origin. Thus, closer to the granite intrusions and in the intrusions themselves there are hydrothermal veins with wolframite, cassiterite, and molybdenite. Farther on there are veins with the sulphides of copper, gold, lead, zinc, silver, and then antimony and mercury. However, this kind of zonality is not rigidly concentric, in the sense that it is not always found and is characteristic of a comparatively small (up to 10 kilometres in cross-section) granite stocks.

The hydrothermal process is by no means confined to the depositing of minerals in the fissures with the formation of various veined

Fig. 153. Molybdenite in the selvages of a quartz vein



bodies. Hydrothermal springs, as is the case with gases, permeate through the lateral rocks, enter into chemical reactions with them, replacing them and bringing forth new compounds. This is the way metasomatic bodies are formed. They often have a pipe-like or irregular form, and, in most cases, are deposited among carbonate rocks.

Under the hydrothermal processing of enclosing rocks the latter can undergo marked changes. In this way some of the talc schists are formed. When hydrothermal solutions act upon ultrabasic rocks and dolomites, rich in magnesium, asbestos, talc, and magnesite are formed, while under the activity of low-temperature sulphate hydrotherma on the rocks rich in alkaline, alunite is formed.

Hydrothermal origin is shared by most of the ore nonferrous, rare and radioactive metals, gold, as well as various nonmetallic minerals resources.

At present, it is assumed that hydrothermal solutions, bearing mineralization, need not necessarily be magmatogenic. This assumption rests upon the following. Together with sedimentary rocks into the deep horizons of the lithosphere there enters a vast quantity of water and gases, both in their free state (underground, pellicular, and capillary waters), and in their bound state (crystallization and colloidal water). The whole of the lithosphere seems to be permeated with water and gases. It is known that the weakly mineralized underground water near the surface are transformed into brines with mineralization reaching 300 g/l and more at the depth. The temperature of these waters at the depth of 4-5 kilometres increases up to 150°. Many waters are enriched (at the expense of leaching from the enclosing rocks) by the typical elements of ore deposits, e.g. Cu, Pb, Zn, volatile compounds S, F, B, Cl, As, and a large number of others. These highly concentrated thermal water solutions can, in essence, be the solutions which we call hydrothermal. They can transmit elements in their ionic and colloidal forms, in the form of various compound complexes and under certain changes in the conditions, deposit them in the form of hardly soluble compounds, or minerals. These very solutions can also cause metasomatic changes in rocks and ores.

As far as hydrothermal deposits are concerned, it was revealed by V.I. Smirnov (1976) that the features pertaining to the temperature and the depth of formation could not possibly form the basis of their genetic classification. Among hydrothermal deposits he singled out the following three classes: plutogenic, volcanogenic, and amagmatogenic, or telethermal (stratiformal). This classification is simple and convenient for the hydrothermal deposits, and, hence, for ore mineral associations.

### **Plutogenic**

hydrothermal mineral associations are connected with acid and moderately acid magmatic rocks. They are situated in the covering of the intrusives or at an inconsiderable distance from them, in sedimentary metamorphic rocks, and are formed as a result of the fallout of minerals from the postmagmatic hydrothermal solutions. The temperature of the process is between 450 and 50°C. The form of mineral bodies is varied, mainly veined.

Quartz veins and the associations of ore minerals with quartz are characteristic. Sometimes they are together with an abundance of sul-

TABLE 20

*Minerals of Plutogenic Hydrothermal Ore Veins*

Veined	Ore	Those of practical importance	Veined	Ore	Those of practical importance
<i>Lead, tungsten, and molybdenum veins</i>			<i>grey ore</i> chalcopyrite		
Quartz	cassiterite	cassiterite	Periveined changes: chloritization, carbonatization		
Adular	wolframite	wolframite	<i>Cobalt-nickel-silver-bismuth-uranium veins</i> ( <i>pentaelement formation</i> )		
Muscovite	bismuthine	molybdenite	Quartz	cobaltite	arsenides of nickel and cobalt
Zinnwaldite	arsenopyrite	beryl	Calcite	smaltite	
Topaz	molybdenite	bismuthine	Ankerite	niccolite	
Fluorite	beryl	gold	Barite	rammelsbergite	pitchblende
Ankerite	pyrite			safflorite	bismuth
Rhodochrosite	pyrrhotite			gersdorffite	proustite
Calcite	chalcopyrite			pyrargyrite	pyrargyrite
	scheelite			proustite	silver
	gold			silver	
	magnetite			grey ores	
Periveined changes: greisenization				pitchblende	
<i>Gold-quartz veins</i>				hematite	
Quartz	pyrite	gold		bismuth	
Ankerite	chalcopyrite		Periveined changes: carbonatization, hematization, chloritization		
Barite	arsenopyrite		<i>Polymetallic and lead-zinc veins</i>		
	galena		Quartz	chalcopyrite	chalcopyrite
	gold		Calcite	sphalerite	sphalerite
	grey ores		Barite	galena	galena
	scheelite		Siderite	pyrite	gold
	aikinite		Ankerite	pyrrhotite	grey ores
Periveined changes: beresitization, listwanization			Fluorite	gold	bornite
<i>Cobalt-nickel-arsenic veins</i>				arsenopyrite	
Calcite	niccolite	arsenides of nickel and cobalt		grey ores	
Dolomite	rammelsbergite			bornite	
Quartz	smaltite		Periveined changes: sericitization, chloritization, carbonatization		
	safflorite				
	löllingite				
	skutterudite				

phides, and at times with carbonates without quartz. Plutogenic hydrothermal paragenesis includes mineral associations of tin and tin-tungsten veins, gold-quartz, cobalt-nickel-arsenic, polymetallic (lead-zinc), cobalt-nickel-silver-bismuth-uranium veins, etc. These mineral associations are given in Table 20.

Deposits of the ore mineral associations listed above, the main veined mineral of which is quartz, can be exemplified by the Ononsk



cassiterite, the Chikoi molybdenite, and the Bukuka wolframite deposits of the Transbaikal region, the Berezovsk gold with pyrite and the Kochkar gold with arsenopyrite deposits of the Urals, the chalcopyrite deposits of Almalyk in Uzbekistan and Kadzharan in Armenia, the bismuth deposit of Andrasman in Uzbekistan, the Sadonsk group (Sadon, Zgid, and Kholst) of polymetallic deposits of the Northern Caucasus, the cobalt-nickel-arsenic deposit of Kho-uaksy in Tuva, the gold deposits of the North-East of the USSR, and many others.

### Volcanogenic

hydrothermal mineral associations are genetically connected mainly with the terrestrial andesite-dacite volcanism. The deposits are located either among the volcanoes themselves, or in the rocks overlapping them, and sometimes correspond to the vent funnels of the volcanoes. The depth of the formation of volcanic associations is much smaller than those of plutogenic type, which is usually not more than 1-2 kilometres. Volcanogenic ore mineral associations include gold-silver, sulphide-cassiterite, polymetallic copper (chalcopyrite-enargite-chalcocite), copper-molybdenum (veinlet-disseminated) ores with mercury and arsenic, and some others. Examples of volcanogenic hydrothermal mineral associations are given in Table 21.

Underwater volcanic eruptions of the basic, medium, and acid magma (basalts, andesites, and liparites) are genetically bound to pyrite deposits, composed mainly of pyrite, sometimes of chalcopyrite, sphalerite, galena and more seldom of other sulphides. Pyrite deposits are formed on the routes of ascending postmagmatic solutions, i.e. their connection with volcanism is established accurately enough. Sometimes pyrite deposits are referred to volcanic-sedimentary formations, laying particular stress on the fact that ore minerals could have originated at the bottom of the sea, but necessarily in the genetic association with the volcanic activity. Mineral associations of pyrite deposits are given in Table 21.

### Amagmatogenic

(nonmagmatogenic) hydrothermal associations do not have any perceptible bond with the plutonic (deep) or volcanic rocks. The connection can test only upon an assumption, as was the case before, and these deposits were called telethermal. Later, it turned out, that a large number of lead-zinc and copper deposits, referred to this group, have a rigid stratigraphical control, in other words, correspond to particular stratigraphical horizons, and are stratiformed themselves.

Amagmatogenic deposits comprise the largest copper deposits of the cupreous sandstone type (Dzhezkazgan in Kazakhstan, Udokan in the Chita Region). In other countries deposits of this type are in Zambia and Zaire, and the lead-zinc deposits of the Karatau Mountain Range in Kazakhstan (Mirgalimsai, and others), Zhairam in Central Kazakhstan and the Three State deposits in the USA. Copper mineralization corresponds to sandstone, while that of the lead-zinc type corresponds to carbonate rocks.

The mineral substance of ores probably has a primarily-sedimentary origin, and later undergoes various transformations, including those pertaining to the impact of solutions, not connected with magmatic activity.

TABLE 21

*Minerals of Volcanogenic Hydrothermal Ore Veins*

Veined	Ore	Those of practical importance	Veined	Ore	Those of practical importance
<i>Gold-quartz and gold-silver veins</i>			<i>Copper-molybdenum (copper-porphyrific ores)</i>		
Quartz (opalescent)	gold altaite	gold tellurides of gold pyrargyrite	Enclosing rocks:	pyrite	chalcopyrite
Chalcedony	pyrite		quartz-sericitic,	chalcopyrite	enargite
Adular	marcasite		secondary quartzites	molybdenite	bornite
Fluorite	chalcopyrite		after grano-diorite-porphyrites	enargite	molybdenite
Barite	sphalerite pyrargyrite antimonite			bornite grey ore galena sphalerite	
<i>Antimonite-ferberite veins</i>			<i>Pyrite deposits</i>		
Quartz	antimonite	ferberite	Quartz	pyrite	chalcopyrite
Chalcedony	ferberite arsenopyrite realgar cinnabar (orpiment)		Barite	chalcopyrite	galena
<i>Quartz-cassiterite and sulphide-cassiterite veins</i>			Carbonates	sphalerite	sphalerite
Quartz	cassiterite	cassiterite		grey ores	grey ores
Topaz	wood tin	wood tin		bornite	gold
Chlorite	pyrrhotite			chalcocite	
Tourmaline	pyrite chalcopyrite arsenopyrite			gold	
			Periveined changes: sericitization, chloritization, propylitization, alunization		

The mineral composition of copper and lead-zinc deposits is remarkably simple (Table 22).

If no tangible connection with magmatism has been established for the copper and lead-zinc deposits discussed above, there seems to be much more ground to speak of this kind of bond in relation to amagmatic antimony and mercury. This assumption rests upon the fact that the compounds of mercury, antimony, and arsenic are extremely volatile and are sublimated from very low depths, and, besides, the minerals of arsenic and mercury often occur among igneous rocks and are found during the present volcanic activity (e. g. cinnabar in the sublimates of the Mendeleyev volcano in the Kunashir Island).

The source of ore substance of antimony-mercury deposits are, probably, deep chambers. This is substantiated by the correspondence of mineralization to fissures at the depths.

Deposits of antimony and mercury are of great practical value. Among them the following mercury deposits can be mentioned: the Khaidarkan deposit in Southern Fergana, Aktash in Altai, Nikitovka

TABLE 22

*Minerals of Amagmatogenic Hydrothermal Ore Bodies*

Veined	Ore	Those of practical importance	Veined	Ore	Those of practical importance
<i>Deposits of the cupreous sandstone type</i>			Calcite		
Mineralization corresponds to sandstones with carbonaceous cement	bornite chalcocite chalcopyrite galena pyrite sphalerite grey ores	bornite chalcocite chalcopyrite galena grey ores	Fluorite		
<i>Lead-zinc deposits (stratiformed)</i>			<i>Antimony deposits</i>		
Mineralization corresponds to carbonaceous rocks	galena sphalerite chalcopyrite pyrite marcasite	galena sphalerite	Quartz	antimonite	antimonite
Barite			Carbonates		
Chalcedony			Barite		
Quartz			<i>Mercury-antimony deposits</i>		
<i>Mercury deposits</i>			Carbonates	cinnabar	cinnabar
Calcite	cinnabar	cinnabar	Quartz	antimonite	antimonite
Dolomite			Chalcedony	marcasite	
Quartz			Fluorite		
Opal			Barite		
Dickite			<i>Mercury-arsenic deposits</i>		
Barite			Calcite	cinnabar	cinnabar
<i>Barite deposits</i>			Dolomite	antimonite	antimonite
Quartz	barite	barite	Quartz	marcasite	
			Opal	realgar	
			Fluorite	orpiment	
			Barite		
			<i>Fluorite deposits</i>		
			Quartz	fluorite	fluorite
			Chalcedony		
			Calcite		
			Opal		
			Barite		

in Donbass, Almaden in Spain, and others. Antimony deposits are: the Kadamdzhai deposit at the foot of the Alai Range, Abshir and others in Central Asia, the Turgai deposit in Kazakhstan and in China, etc.

Telethermal deposits yield more than 95% of mercury and about 80% of antimony output. Telethermal deposits also include the large deposits of fluorite in Takob and Aurakhmat (Central Asia), Amderma on the coast of the Kara Sea, etc. The deposits of barite can be exemplified by the Kutaisi in Georgia, the Arpaklen group of deposits in Turkmenia, and others; the optical raw material (Iceland spar, fluorite, barite), and a comparatively small deposits of tin-tungsten and gold-silver ores. As a rule, telethermal deposits are composed of an inconsiderable number of both the ore and the veined minerals. This phenomenon finds its explanation in a high degree of separability of

the ore-forming solutions, that have covered a fairly large distance to their places of localization.

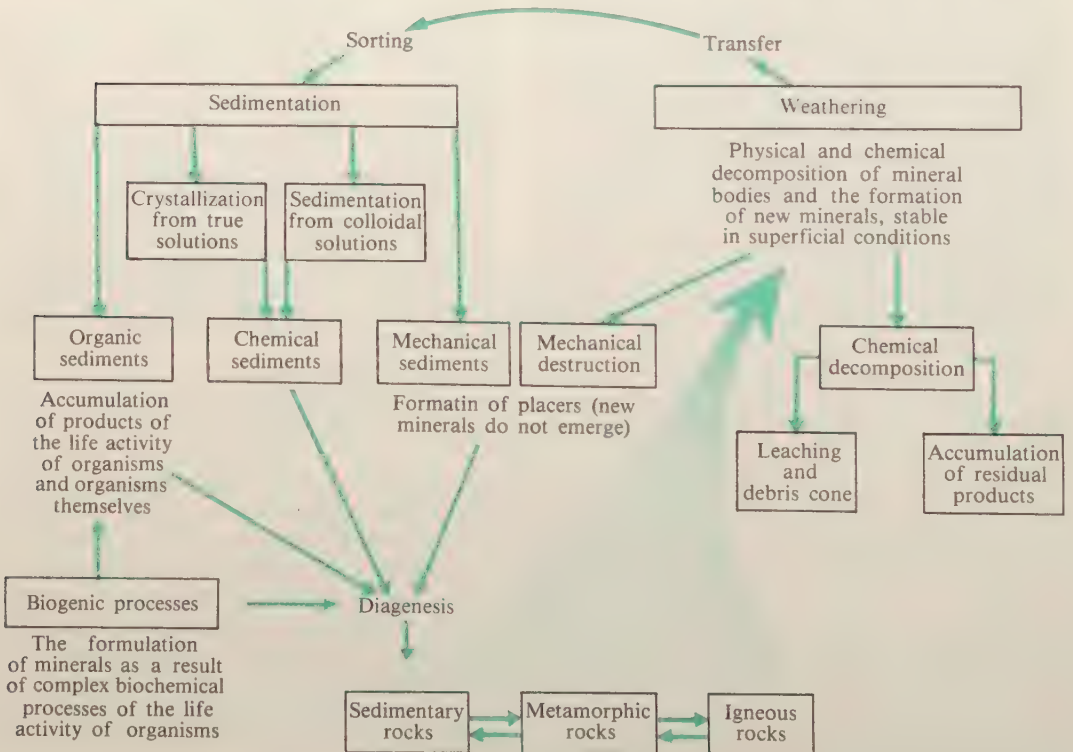
Mineral associations of amagmatogenic deposits are given in Table 22.

## The Weathering Processes and Mineral Associations in the Weathering Crusts

At first glance, it could be assumed, that the geochemistry of hypergene processes presents no difficulties at all. The formation of weathering crusts, sediments, and then sedimentary minerals and rocks at the surface of the earth is obvious. Everything seems to be fairly clear. It is quite the opposite with the process of mineral formation in endogenous conditions, where nothing is perceptible, everything hardly lends itself to interpretation, and we are thus confronted with the necessity of applying hypotheses, some experimental data and thermodynamic equations to explain the origin of rocks and ores. However, this is not exactly so. It is the processes of weathering and sedimentation that present a greater variety of factors and complexity, since only at the surface of the earth we can observe the maximum of all possible quantitative and qualitative varieties in the combination of chemical elements, and, consequently, rocks, ores, and minerals.

Exogenic processes are indebted to solar energy. All their varieties can be reduced to the weathering of rocks and ores, and se-

Fig. 154. Diagram of exogenous processes



dimentation, the two main processes that are closely connected with each other (Fig. 154).

## Weathering

is the sum total of processes, leading to mechanical destruction and chemical disintegration of rocks and minerals, that are not stable in superficial conditions. The agents of weathering are water and wind, fluctuations in temperature, oxygen and the carbon dioxide of air, and the living organisms. The intensity of weathering depends on the climate and the relief of the locality, the chemical composition of rocks, and hydrochemical conditions. When certain weathering agents predominate, physical (or mechanical), chemical, and biochemical types of weathering are distinguished. The first consists in the mechanical splitting of rocks, and their disintegration. The second type is exemplified by the chemical decomposition of minerals (diffusion, oxidation, carbonatization, hydration), and the formation of new products that are stable in the weathering zone. The plants and living organisms (e.g. bacteria) take part in the biochemical weathering. The processes of physical, chemical, and biochemical weathering are interconnected, and take place synchronously, but, depending on the physico-geographical conditions, one of the types of weathering can be the predominant one. The processes of weathering are not confined to land, but can occur in the hydrosphere, e.g. at the bottom of seas and oceans. In these cases, as a result of the saltiness of sea water, its temperature, pressure, and the gas regime, the disintegration of minerals and rocks also takes place. The sum total of all these highly complicated processes of decomposition and change is called underwater weathering or *halmyrolysis*.

The stability of the main rock-forming minerals to weathering varies, and is approximately reverse to the sequence at which these minerals are segregated from the melt. Thus, the more stable mineral is quartz, and the less stable ones are microcline, plagioclases, muscovite, with biotite, amphiboles, pyroxenes, and olivine completing the descending scale of stability. The basic plagioclases are much more susceptible to weathering as compared with the acid varieties. Same can be said of ultrabasic and basic rocks, when compared, for example, with granites. Other highly weathering resistant minerals are those of the oxide group and include spinel, rutile, anatase, and corundum. Silicates are exemplified by tourmaline, topaz, and zircon. The native minerals are represented by diamond and platinoids. Many minerals of the metamorphic strata, e.g. garnets, disthene, sillimanite, sphene, and others also share the stability of those mentioned previously. Hence, weathering resistant minerals are the oxygen-containing ones. This calls for no special comment since their origin is closely related to oxygenous medium. Sulphides are the unstable minerals in the weathering crust; they are easily decomposed and form numerous secondary minerals.

Under chemical weathering there occurs a chemical disintegration of minerals and new minerals are formed. The latter are found to be remarkable for their stability in superficial conditions. Chemical decomposition of rocks and minerals is greatly indebted to the amalgamated activity of a large number of chemical reactions, the most important of which is hydrolysis, oxidation (restoration, in some cases), carbonatization, and hydration.

**Hydrolysis**

consists in the reactions of  $H^+$  and  $OH^-$  ions of water with the ions of minerals. Here the silicates are slowly dissolved and form secondary products. For instance, the hydrolysis of potassium feldspar results in the formation of kaolinite (hydrolysis is often accompanied by the action of carbon dioxide):

**Oxidation**

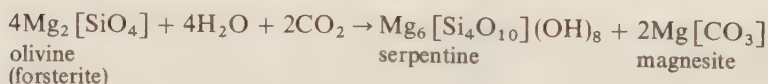
occurs in aqueous and air media with the presence of free oxygen and is primarily connected with such a widespread element as iron. The decomposition of ferrous minerals and the bivalent-trivalent transition of iron are usually in combination with the process of hydration, a characteristic process of the hypergene zone. At the weathered surfaces of rocks and ores concentrations of brown hydroxides of iron are apparent in all places. In ore sulphide deposits they form substantial 'iron caps' which are a reliable exploratory feature of ore.

**Restoration**

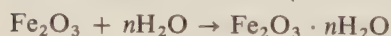
is a process opposite to oxidation, and is motivated by the buried organic substance ( $C_{org}$ ) and the activity of microorganisms in soil horizons and some reservoirs with the total absence of free oxygen. An example illustrating the formation of minerals in the regenerated conditions is the formation of siderite during the restoration of iron hydroxides by an organic substance:

**Carbonatization**

is a process occurring in an aqueous medium and involving the interaction of carbonates and bicarbonate ions with rock minerals, as a result of which the latter are disintegrated and carbonates are formed. Carbonatization is usually accompanied by the hydrolytic decomposition of silicates (for the reaction of kaolinite formation, or the process of kaolinization, see above). A similar activity of hydrolysis and carbonatization is applicable to ultrabasic rocks and results in their serpentinization:

**Hydration**

is an addition of water (in various quantities). For example,



The formation of iron hydroxides and manganese, gypsum, opal and many other hydrated minerals is very characteristic of the weathering crust.

All the processes discussed above often accompany one another and are widely spread in the zone of hypergenesis. They are directly connected with an increase in the volume of substance. In characterizing the weathering processes a considerable role should be attributed to microorganisms, which enhance and sometimes change the redox conditions of mineral existence. Their function is so great that questions pertaining to biological enrichment of mineral resources

are being raised. As a result of mechanical, chemical, and biochemical weathering, silicates and aluminosilicates, the main rock-forming minerals of the earth's crust, are decomposed. This is accompanied by the subtraction of soluble products of reaction, e.g. the salts of K, Na, Ca, Mg,  $\text{Fe}^{2+}$ , and the accumulation of hardly soluble products, such as  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{SiO}_2$ . Soluble products are evaluated from the weathering zone and can migrate at considerable distances, some of which reach oceans and seas. Under favourable conditions of the medium the soluble products are falling out in the form of minerals.

Hardly soluble products of weathering remain at the place where rocks and ores are destroyed, or move at inconsiderable distances. This is the way the *weathering crusts* are formed. They acquire the shape of mantles covering, sometimes, vast areas or find themselves in correspondence to the linear zones of tectonic breaks along which the mechanical destruction of rocks takes place. This promotes the penetration of waters and gases, which equally refers to weathering as well.

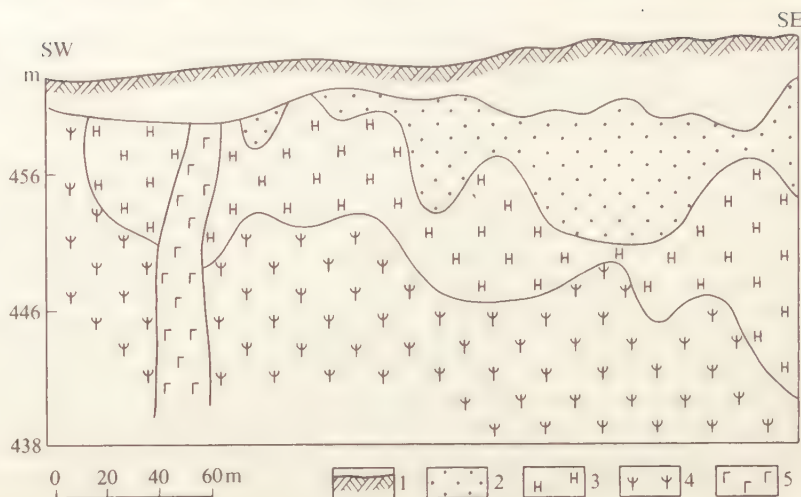
In the composition of the weathering crusts, depending on the intensity of the process, it is possible to single out secondary hypergene minerals, originally related to weathering, and the preserved remains of the primary non-weathered minerals. The number of the former and the latter can be varied. The transitions between the weathering crust and the primary rocks, are, as a rule, gradual.

The study of weathering and mineral resources related to them has been the concern of many Russian and Soviet geologists: P.A. Zemyatchensky, K.D. Glinka, V.I. Vernadsky, I.I. Ginsburg, I.D. Sedletsky, B.P. Krotov, and G.I. Bushinsky.

The physicochemical conditions in which the weathering crusts are formed, stages of weathering, zonality, and the migration of elements have received a thorough investigation. The direction of weathering and the composition of hypergene minerals depend on numerous factors, such as the mineral composition and the structure of rocks, climatic, morphological and hydrochemical conditions of the regions. Several types of weathering crusts are distinguished: the lateritic type being the most important of them. The said type of weathering of aluminosilicate magmatic rocks takes place in the conditions of hot and humid climate, and what is particularly characteristic, during the alternation of dry and rainy seasons (Africa, South America, South-East Asia). These conditions are necessary for a substantial chemical decomposition of magmatic rocks. The chemical character of lateritization process consists in evaluating silica and alkaline elements and the formation of hydrated oxides of aluminium and iron.

Laterites are residual (eluvial) formations resulting from the weathering of acid, alkaline and ultrabasic rocks. They are rich in alumina and are mainly composed of diaspore, boehmite, hydrargillite, and hydroxides of iron, which are represented both as amorphous and crystalline varieties. The colour of laterites is red (from the hydroxides of iron, hence the term which has its Latin word '*later*', meaning '*brick*', as its origin). Laterites can be either soft or compact (with hardness between 2 and 6), they are usually earthy, and often have a leguminous structure. Their thickness sometimes reaches more than 100 metres. The study of laterites and the vertical zonality of rocks

Fig. 155. Nickel-bearing nontronites, emerged under the weathering of ultrabasites. The deposits of Novaya Buranovka in the Aktyubinsk Region (Western Kazakhstan): 1—soil layer; 2—ochre zone; 3—nickel-bearing nontronites; 4—serpentinites; 5—dikes of gabbro-diabases



and laterite weathering has an immense significance for the exploration of bauxites.

Bauxites are the sedimentary or residual rocks, which are an ore of aluminium. They consist of aluminium hydroxides, i.e. diaspore, boehmite, hydrargillite, with the mixture of ferric hydroxide, ferrous chlorites, kaolinite,  $\text{SiO}_2$  and  $\text{TiO}_2$ . According to mineral composition the following types of bauxites are distinguished: diaspore, boehmite (monohydrated), and hydrargillite (trihydrated).

Macroscopic bauxites represent fine dispersed soft or compact rock. Their hardness is usually 2-4; the density is about 2.5. The colour is white, grey, yellow, red, white and red are particularly characteristic (depending on the content of iron). Bauxites often have a clear-cut oölitic structure; they often resemble clay rocks. They are hardly hygroscopic, and very thin, as compared with kaoline.

Bauxites are of great practical importance as an ore of aluminium. The content of  $\text{Al}_2\text{O}_3$  in them must not be less than 45%. The content of iron oxide does not play any considerable role and can be up to 20-25%. The main harmful impurity is silica. The silicic modulus  $\frac{\text{Al}_2\text{O}_3}{\text{SiO}_2}$  in industrial ores must not be lower than 2.6.

Under metamorphism of bauxite ores corundum rocks and emeries are formed.

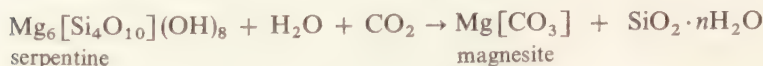
The weathering of serpentinous ultrabasites is conducive for the emergence of nontronite, a mineral of an irregular chemical composition (sometimes containing nickel, isomorphically replacing magnesium), montmorillonite, halloysite, of iron hydroxides and manganese (occasionally with cobalt), chalcedony, opal, magnesite, calcite, and quartz. Nickel-bearing nontronites of the Southern Urals and Western Kazakhstan are a good ore of nickel (Buruktau, Novaya Buranovka, Chuguevskoye, and others; Fig. 155). Besides silicate nickel ores the weathering of serpentinites is responsible for the concentration of iron, manganese and cobalt, which leads to the formation of the deposits of brown iron ore, or naturally alloyed ores. Magnesite also proves to be a valuable mineral raw material under the weathering of serpentinites. It is formed during the hydrolytic action of



TABLE 23 *Minerals of Weathering Core Rocks*

Types of weathering	Principal and minor	Those of practical importance
<i>A. Bauxite deposits</i>		
Lateritic weathering of ultrabasic, alkaline, and acid rocks (alkaline medium) in hot and humid climate conditions	diaspore boehmite hydrargillite Fe hydroxides kaolinite	diaspore boehmite hydrargillite } bauxites
<i>B. Silicate-nickel deposits (occasionally nickel-cobalt)</i>		
	serpentine (chrysotile, antigorite) nontronite nickel nontronite halloysite nickel-bearing ferriferous montmorillonite and beidellite hydrohematite goethite hydrogoethite Mn and Co hydroxides garnierite revdinskite magnetite magnesite calcite chromite chlorite chalcedony opal gypsum	Ni-bearing nontronite revdinskite garnierite Co hydroxides iron and other ochres as mineral paints
<i>C. Brown iron-ore deposits</i>		
	hydrohematite goethite hydrogoethite and other Fe hydroxides Mn, Co and Ni hydroxides Al hydroxides nontronite kaolinite Ni silicates chlorite	Fe hydroxides (as well as Mn, Ni, Co hydroxides, or nature-alloyed ores)
Kaolinite weathering of acid rocks in moderate climatic conditions (subacid or neutral medium)	kaolinite halloysite montmorillonite chalcedony opal Fe hydroxides allophane hydromicas	kaolinite

water, rich in carbon dioxide, upon serpentinites. Solutions containing magnesium deposit magnesite in deeper horizons (slightly altered serpentinites):



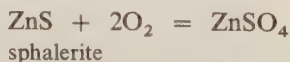
Minerals of residual bauxite deposits, formed under the lateritic weathering of ultrabasic and alkaline rocks in hot and humid climate conditions, as well as minerals of the silicate-nickel deposits after serpentinous ultrabasic rocks are presented in Table 23.

If hot tropical climate and alkaline medium are relevant for the lateritic weathering with the formation of hydrated oxides of aluminium (bauxites), it is in the moderate climate in the subacid or the neutral medium that the weathering of granites and gneisses take place with the formation of kaolinite. The mineralogy of these formations is by no means complicated: the principal mineral here is kaolinite, sometimes in a mixture with halloysite and chalcedony. Relict mineral rocks are also found (see Table 23). Residual kaolinite deposits are known in the Ukraine. They correspond to the long formed weathering crust of the Pre-Cambrian granites and gneisses (the Glukhovetsk and Turbinsk deposits in the Kiev Region, the Prosyansk deposit in the Dnepropetrovsk Region, and others, as well as in the other regions of the Urals, Western Siberia, and elsewhere).

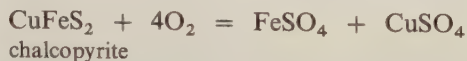
Specific weathering crusts emerge at ore, and particularly at sulphide deposits. In textbooks and scientific literature they are treated as the oxidation zones of ore deposits. In ore veins recovered by erosion the primary (hydrothermal and other) ore minerals, particularly, sulphides, are easily destroyed and are transferred into numerous, sometimes very bright, secondary oxidized minerals, e.g. sulphates, oxides, carbonates, phosphates and other compounds. This results in the formation of oxidation zones of sulphide deposits, or the 'iron caps'. These zones were given this name because of the brown oxides of iron, which are concentrated in the upper, oxidized part of the deposit. 'Iron caps' are of great prospecting value. They help to locate at a certain depth the presence of sulphide deposits.

Oxidized sulphide deposits often have a zonal structure (Fig. 156). According to S. S. Smirnov, the upper part is occupied by the oxidation zone, or the zone of the 'iron cap', which, in its turn, is subdivided into the upper leached zone and the lower zone that is richly oxidized.

In the uppermost part of the oxidation zone, rich in oxygen, sulphides are oxidized into sulphates, e.g.



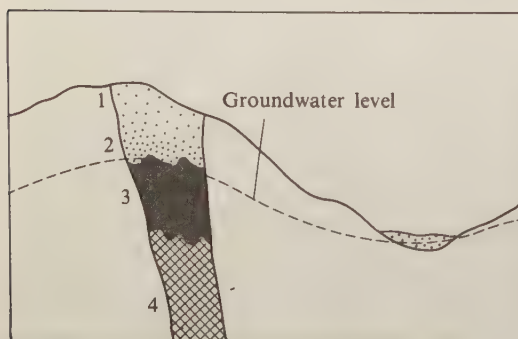
or



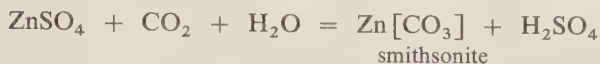
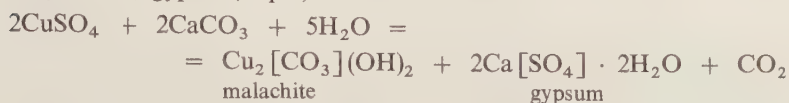
Sulphates are easily soluble: they permeate into the lower part of the oxidation zone where

Fig. 156. The structure of oxidation zone of sulphide deposits (diagram):

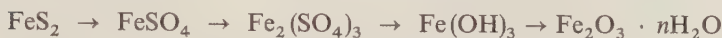
- 1—leached zone; 2—richly oxidized zone;
- 3—cementation zone (zone of secondary sulphidic enrichment); 4—zone of primary (nonoxidized) ores



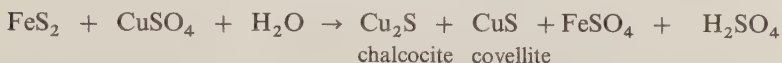
new minerals are formed, e. g. malachite, azurite, smithsonite, cerussite, chrysocolla, gypsum, opal, etc:



The oxidation zone is mainly composed of limonite or brown iron ore. The transformations of compounds of iron in the oxidation zone of sulphides, according to S. S. Smirnov, can be represented in the following way:



Below the level of groundwaters there comes the cementation zone, or that of the secondary sulphide enrichment, followed, in descending order, by primary nonoxidized ores. In the cementation zone the newly formed minerals seem to cement the ore deposit, thus filling up the fissures and pores. Waters, here, contain hydrogen sulphide and sulphuric acid. Free oxygen is totally absent from them. Sulphates of metals (mainly those of copper) react to primary ores, as a result of which secondary sulphides are formed:



In the cementation zone the ores of copper, silver, gold, lead, and zinc are formed. The thickest cementation zones are formed in those cases when the primary ores are represented by pyrite and chalcopyrite, hence, this zone is of particular importance to copper deposits, where chalcocite, covellite and bornite, sometimes form considerable accumulations. Mineral associations of the oxidation zone of copper and polymetallic deposits are given in Table 24.

The oxidation of arsenopyrite leads to the emergence of iron hydroxides and scorodite. The arsenides of nickel and cobalt in the oxidation zone form bright annabergite and erythrite. Cobalt is characterized by its bound with the hydroxides of manganese, or asbolan ores. There appears a wide group of minerals that are difficult to diagnose when the process of oxidation of antimonite  $\text{Sb}_2\text{S}_3$  and other minerals of antimony, e. g. valentinite, senarmontite, stibiconite, etc. takes place. They are often referred to by such a generalized term as 'antimonial ochre'. The oxidation of bismuthine is responsible for bismuth ochre, or bismite. The oxidation of molybdenite is responsible for the appearance of a bright-yellow molybdenum ochre, ferromolybdate. Powellite is also characteristic of the molybdenite zone of oxidation. In the oxidation zone proustite and pyrargyrite are transformed into native silver, electrum, cerargyrite, and argentite. All of them, in mass accumulations, can have practical value.

The zone of the iron cap is characterized by the accumulation of gold not only at gold-bearing deposits, but also at the deposits of other types, such as those of pyrite. Numerous secondary minerals emerge in the oxidation zone of the uranium deposits. They are: uranophane, kasolite,

TABLE 24

*Minerals of the  
Oxidation Zone of  
Sulphide Deposits*

Principal	Minor	Those of practical importance
<i>Copper deposits</i>		
Gypsum	melanterite	bornite
Aragonite	chalcantinite	chalcocite
Fe hydroxides	brochantite	covellite
	diopside	gold
Chalcedony	libethenite	malachite
Jarosite	tenorite	native copper
Chrysocolla	phosphates,	cuprite
Malachite	arsenates	
Azurite		
Native copper		
Cuprite		
Gold		
Covellite		
Bornite		
Chalcocite		
<i>Lead-zinc deposits</i>		
Gypsum	pyromorphite	cerussite
Aragonite	mimetesite	anglesite
Fe hydroxides	vanadinite	smithsonite
Cerussite	crocoite	calamine
Anglesite	ferriferous smithsonite	
Plumbo- jarosite		
Wulfenite	willemite	
Smithsonite	hydrozincite	
Calamine	aurichalcite	

autunite, torbernite, zeunerite, sulphates, and the carbonates of uranium.

It is obvious that in the weathering crust (oxidation zone) of sulphide deposits many new secondary minerals are formed. They reflect the chemical and mineral composition of primary ores, and serve as a reliable guide to mineralization processes which occur at the depth and are in themselves sometimes highly important as far as their practical implementation is concerned (ores of copper, gold, etc.).

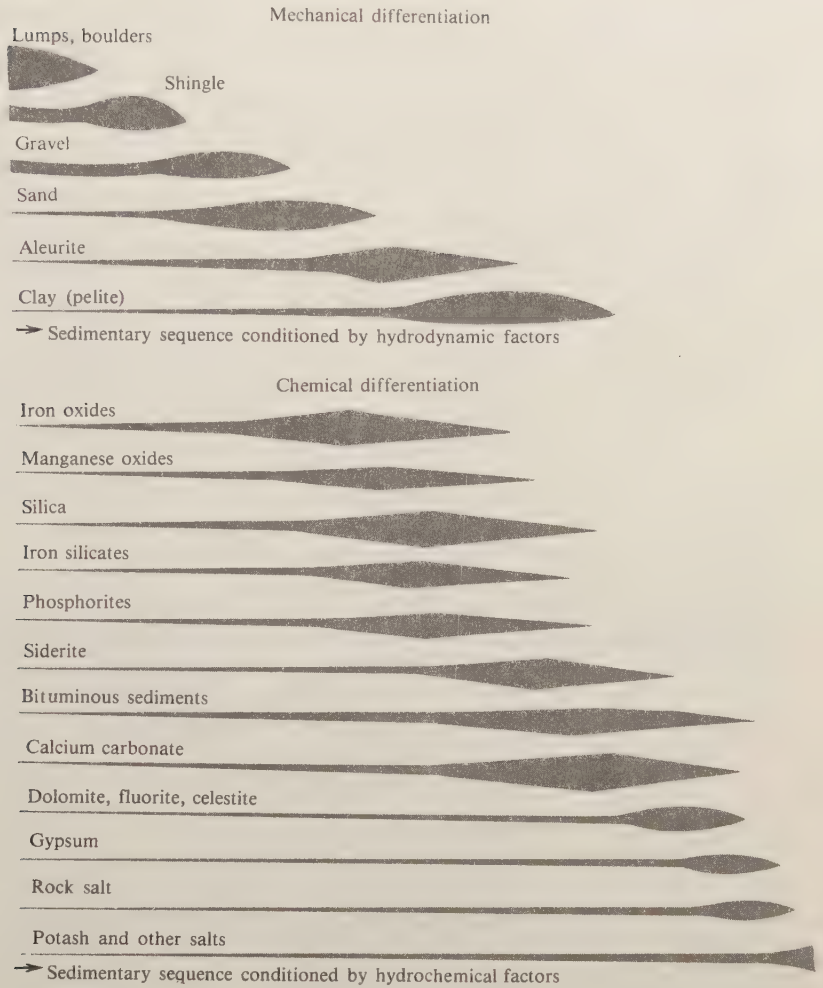
Accumulations of black oxides and hydroxides of manganese (psilomelane, etc.), which are formed as a result of the weathering of sedimentary and carbonate manganese ores, are transformed, at the depth, into manganese-bearing rocks. This process is similar to that occurring in the oxidation zone, or the zone of the iron cap of sulphide deposits. The said accumulations have acquired the term of manganese caps. Besides gypsum caps are existing; under the weathering of salt deposits, the chlorides and sulphates of Na, K, and Mg, as easily soluble salts, are washed out, while gypsum and anhydrite, possessing the reverse properties as far as solubility is concerned, remain, and thus form gypsum and gypsum-anhydrite caps. Some of the latter are characterized by a concentration of hardly soluble borates, e.g. hydroboracite, inyoite, colemanite, pandermite, ulexite, and others that sometimes have practical significance (West Kazakhstan).

## Sedimentation and Mineral Associations of Some Sedimentary Rocks and Ores

The products of weathering can remain at the place of disintegration or be migrated at various distances. If the weathering products remain at the place where rocks and ores underwent the process of collapse, there appear weathering crusts (eluvium, resulting from the physical and residual formations conditioned by the chemical type of weathering). However, an inconsiderable part of the weathering products remains at the place of disintegration; their main mass is transported by flowing waters, wind, ice, and living organisms. The transporting function of water streams in carrying a vast amount of material is of particular importance in this respect.

The weathering products are migrated by water streams either in the form of hard particles (when they are deposited, mechanical sediments

Fig. 157. Diagrams illustrating sedimentary differentiation (according to L. V. Pustovalov)



are formed), or in a dissolved state (chemical and biochemical sediments). This is the way numerous and various sedimentary associations of minerals are formed.

The fall out of mechanical particles and dissolved substances in the process of sedimentation is of gradual order; a certain sedimentary differentiation of weathering products takes place. Two types of sedimentary differentiation are distinguished. They are: mechanical and chemical.

Mechanical differentiation is the segmentation and the gradual fall out of the particles from the disintegrated rocks in the process of sedimentation by the size of the particles, their form, and density.

Chemical differentiation is the gradual fall out of substances that are in a dissolved state. The regularity of the fall out depends on the degree of the solubility of substances in physicochemical conditions of the solutions (concentration, temperature, pressure, acidity or alkaline character of the medium, and so on).

Mechanical and chemical differentiations are closely interrelated, as

can be seen from Fig. 157. It is usual for the mechanical differentiation to start a bit earlier, before the two types of differentiation become synchronic. At present, biogenic differentiation is also being distinguished, i. e. the transformation of dissolved components and gases into mineral skeletal formations or organic tissues conditioned by the living activity of organisms (accumulation of organogenic limestone and phosphorites).

Sediments thus formed can be mechanical, chemical, biochemical, and organogenic. They undergo the stage of compactness and cementation, or diagenesis, which is conditioned by a change in the physicochemical equilibrium between the sediment and the environment, and between various parts of the sediment itself. Diagenesis finds its expression in the recrystallization of the sediment, the formation of concretions, and the stable polymorphic modification. Sediments that have undergone the stage of diagenesis are transformed into sedimentary rocks.

According to their genetic features, i. e. the conditions of their formation, all sedimentary rocks can be divided into three groups:

- (1) fragmental (clastic) rocks;
- (2) chemical (chemogenic) rocks;
- (3) organogenic rocks.

### Fragmental rocks

are formed from mechanical sediments; pebble, gravel, sand are such kind of material. No new minerals appear under the mechanical disintegration of rocks and ores. However, as a result of rock segmentation, the transfer of fragmental material by water streams, and their further sedimentation there emerge various fragmental rocks and *placers* of a large number of valuable minerals.

Such placers abundantly yield diamonds, gold, platinum, cassiterite, scheelite, zircon, monazite, garnet, ruby, sapphire, rutile, ilmenite, and magnetite.

Since the mineral genesis of placers is of various kind, it is practically impossible to find them all together. Thus, placers, containing diamond, are characterized by pyrope, ilmenite, olivine, diopside, and grossular with gold-bearing placers the minerals are: magnetite, ilmenite, zircon, apatite, sphene, garnet, cordierite, and other common minerals of the acid and medium intrusive, as well as metamorphic rocks, etc. It is quite natural that the platinum-bearing placers are characterized by quite a different inventory of minerals than the one that is typical of placers with cassiterite, monazite, etc.

It is quite obvious that together with heavy minerals of practical importance placers contain a number of widespread weather-resistant highly important rock-forming and accessory minerals of magmatic, sedimentary, and metamorphic rocks (quartz, feldspars, garnets, titanite, tourmaline, andalusite, sillimanite, disthene, pyroxenes, amphiboles, spinel, epidote, fluorite, apatite, and many others). It is these minerals that constitute the placer itself. Table 25 furnishes a list of characteristic mineral placers.

Placer is an industrial concentration of minerals in sands. Placer deposits can be much more rich than the primary deposits and serve as the main source of output for a vast number of minerals.

Sands can originate in rivers, seas, lakes, and dunes. The degree of roundness with grains is varied. It covers the range of those that are

TABLE 25

*Minerals of Placers*

Those of practical importance

Others

Gold

quartz, garnets, feldspars, magnetite, tourmaline, titanite, ilmenite, rutile, zircon

Platinum  
Iridosmium

magnetite, ilmenite, chlorite, spinel, olivine, pyroxenes

Polyxene

Diamond

pyrope, ilmenite, titanomagnetite, olivine, diopside, grossular, perovskite

Monazite

Zircon

Magnetite

Ilmenite

Rutile

Cassiterite

Wolframite

Scheelite

Ruby and

sapphire

Topaz

Spinel

Garnet

(precious

stones,

abrasives)

Quartz (quartz

sands)

various weathering-resistant minerals of the enclosing magmatic and metamorphic rocks, pegmatites, and ore veins

angular to perfectly rounded ones (sea sands). Depending on the number of minerals that enter into the composition of sand, the following kinds of sand are distinguished: monomineral sands, comprising only one mineral; oligomictic sands, consisting of two minerals; polymictic sands, with several minerals entering into their composition. The most widespread mineral of sands is quartz. It should be mentioned here that it is not infrequently that pure quartz sands are found. Sands, containing feldspar are called *arkosic sands*. In various quantities, sands can be found to include glauconite, mica, carbonates, and other minerals.

**Chemical rocks**

are formed from the chemical sediments of the true or colloidal solution. The fall out of the sediment from the solutions primarily depends on the concentration of dissolved salts and the temperature of the solution. Chemical rocks include salts, several types of limestone, dolomite, bauxites, and siliceous rocks.

Salts represent typical chemical sediments that fall out of the true water solutions. The fall out takes place in enclosed water basins, shallow bays, and salty lagoons, where intensive evaporation results in the formation of saturated solutions, which leads to a gradual crystallization of salts. Saline deposits are characteristic of the world's arid regions, where evaporation exceeds the inflow, the concentrated solutions do not have any exit from the concentration basin. This process is called *halogenesis*.

A characteristic feature pertaining to all the territories where the process of salt deposit takes place, is an intensive, and usually irregular warping. In the region where warping is most intensive, there is a run-off of the most concentrated brines, where they are later evaporated, as a result of which salts are deposited in the order corresponding to the lowering of the temperature of their crystallization.

At certain periods in the development of our planet salt-bearing basins reached immense proportions. Thus, for instance, in the Permian period the salt-bearing basin covered a vast region from the Northern Urals to the Caspian Sea, and included the eastern part of the East-European platform. In Europe the salt-bearing basin covered a vast territory, too. There was an immense salt-bearing basin in the lower Cambrian system in Eastern Siberia.

Continental halogenesis, though more varied in its composition, is smaller, as far as its range is concerned. It is confined to lakes, and only occasionally to lagoons. Usually the saline sediments are represented by

TABLE 26

*Minerals of Chemical Sediments*  
*Continental sediments*

Principal	Minor	Those of practical importance
Mirabilite	thenardite	mirabilite
Trona	astrakhanite	trona
Halite	epsomite	halite
Gypsum	bishofite	gypsum
	berkeyite	
	tachyhydrite	
	glauberite	
<i>Sea sediments</i>		
Bishofite	leonite	halite
Carnallite	schoenite	gypsum
Sylvite	astrakhanite	bishofite
Kainite	löweite	carnallite
Laugbeinite	vanthoffite	sylvite
Kieserite	glaserite	kainite
Halite	epsomite	langbeinite
Gypsum	polyhalite	polyhalite
Anhydride	glauberite	glauberite
Ca and Mg carbonates	syngenite	
	görgeyite	

*Boron-containing sediments*

Borates of halogen strata	Borates of the weathering core of halogen strata	Those of practical importance
Boracite	hydroboracite	boracite
Preobrazhenskite	ascharite	preobrazhenskite
Kaliborite	colemanite	kaliborite
Ascharite	inoite	ascharite
Sulphoborite	pandermite	hydroboracite
Pinnoite	ulexite	colemanite
Hydroboracite	borax	inoite
	kernite	pandermite
		ulexite
		borax
		kernite

gypsum, anhydride, halite, sylvite, and carnallite. Chemical sediments that are of practical importance are also mirabilite, bishofite, and borates.

The composition of saline rocks is determined by the composition of the outcome solution. Hence, to understand the conditions in which salts are formed, it is necessary to know the physicochemical equilibria, which become apparent in saline solutions within the process of their evaporation, cooling, and so on. The interpretation of paragenetic associations of minerals in saline deposits became possible only when the physicochemical conditions of salt formation were studied in the laboratories in complex equilibrium systems.

The order in which the salts fall out depends exclusively on physicochemical conditions, viz. the solubility of salts, their concentration, the presence of other salts, the temperature of the solution, and the time of crystallization. The first to fall out into the sediment are the hardly soluble calcium and magnesium carbonate: calcite and dolomite, sulphates: gypsum and anhydrite, followed by rock salt, and when the concentration of solutions is furthered, there come the easily soluble halide and sulphates of potassium and magnesium; e.g. polyhalite, kieserite, astrakhanite, epsomite, sylvite, kainite, carnallite, and bishofite. The final stage of halogenesis is characterized by the fall out of borates. Minerals falling out as chemical sea sediments are presented in Table 26.

The following types of salt lakes are distinguished: soda lakes (sodium carbonate, trona, thermonatrite), sulphate lakes (epsomite, mirabilite, thenardite), chloride lakes (halite and other minerals), boric lakes (borax, ulexite, colemanite, pandermite).

### Organogenic rocks

are formed as a result of the life activity of organisms, e.g. chalk, limestone, diatomite, and caustobioliths (coal and petroleum).

Chemical sediments often fall out with the direct or indirect participation of organisms. Many organic sediments are connected with the chemical properties of the environment and are independent of them. Thus, a vast group of

sediments, and rocks as well is connected with chemical and biochemical processes at the same time. Such rocks are called *biochemical*.



Among the sedimentary rocks of chemical and biochemical origin carbonate rocks are most widely spread. They are represented by limestones, dolomites, and marls. Limestones consist of only one mineral, calcite. In their pure form they contain 56% of CaO and 44% of CO<sub>2</sub>. Dolomite is a widespread sedimentary rock, composed of dolomite mineral. Dolomites often comprise the impurity of calcite and clay material; sometimes gypsum, fluorite, celestite and opal are found. There are intermediate varieties between dolomites and limestones. They are usually referred to as dolomitized limestones.

Rocks of chemical, or to be more exact, of biochemical origin that have practical implementation are the ferriferous and manganese rocks of the sedimentary type. Ferriferous rocks are formed in sea and lake basins at the expense of the transfer and sedimentation of ferriferous compounds. The sedimentation originates in the colloidal solutions in connection with the change of physicochemical conditions, as is the case when continental river waters get in contact with the brakish sea waters, or due to the activity of humic acid and the vitality of bacteria.

The oxygenous regime of the environment plays a considerable role in the sedimentation of ferriferous rocks and ores. The quantity of free oxygen is directly connected with the formation of oxidized (hydrogoethite, hematite), carbonate (siderite), and silicate (ferriferous chlorites) ores. Various limonites are most widely spread. They represent a mechanical blend of iron hydroxides with clay, and partly sandy (arenaceous) material.

By their outer appearance ferriferous rocks and ores are of various kind. Their colour is usually brown of variegated shades. They often have an oölitic structure (leguminous ores). They are also ochreous, cellular, sometimes in sintered forms and concretions. Siderites form block fine-grained masses or nodules and concretions in clay rocks. Ferriferous rocks and ores are deposited in the form of layers and lenses. The latter correspond to the synclinal warps and troughs. According to the place of their origin ferriferous rocks and ores are divided into two types: continental (lacustrine, boggy) and pelagic.

Sedimentary iron deposits account for nearly 30% of the world's iron ore output. In the USSR this can be exemplified by the Kerch deposit in the Crimea, Ayait and Lisakov in the Kustanai Region. There are large deposits in Lotharingia (France, FRG, Luxemburg). Deposits are also known in Canada, the USA, and China.

Sedimentary ores contain 30-40% of iron, the impurity of manganese, very small amount of phosphorus, vanadium, and arsenic. Under metamorphism the sedimentary iron ores become dehydrated and are transformed into hematite and magnetite. Such richly ferriferous metamorphic rocks are particularly spread in the Pre-Cambrian system (Krivoi Rog, and KMA deposits), India, Brazil, and the USA can also serve as examples.

Manganese sedimentary rocks are less widely spread as compared with the ferriferous rocks but are nevertheless highly important for industrial purposes.

Manganese is transported in the form of colloidal compounds which are sedimental at very low depths in comparison with the colloidal compounds of iron. It could be supposed that in the formation of manganese rocks and ores microorganisms or bacteria take part. The ores of manganese are represented either by black pyrolusite and other

TABLE 27

*Minerals of  
Sedimentary  
Iron and Manganese  
Ores*

Principal	Minor	Those of practical importance
<i>Sedimentary iron ores</i>		
Hydrogoethite	pyrite	hydrogoethite
Goethite	vivianite	goethite
Chamoisite	barite	chamoisite
Thuringite	hydrotroilite	thuringite
Glaucosite	psilomelane	siderite
Siderite	Rhodochrosite	
	apatite	
	hematite	
	chalcedony	
<i>Sedimentary manganese ores</i>		
Psilomelane	glaucosite	psilomelane
Pyrolusite	chamoisite	pyrolusite
Manganite	barite	manganite
Rhodochrosite	marcasite	rhodochrosite
Manganocalcicite	pyrite	
Opal	apatite	
Hydrogoethite		

oxidized compounds of manganese, or by grey-pink rhodochrosite. They often have an oölitic structure, and are soft and sooty. They are deposited in block layers or in the form of lenses and concretions.

In the USSR the most important manganese deposits include the Chiatura in Georgia, and the Nikopol in the Ukraine.

The accumulation of rocks, containing manganese, are widely spread in the deep ocean sediments. The concentration of manganese takes place as a result of coagulation of colloidal compounds of manganese, brought from the continent. In this way manganese concretions and crusts are formed. Sometimes they have enhanced content of cobalt, nickel and other elements, and can function as a special kind of ore of these elements in the future.

Characteristic minerals of the sedimentary ores of iron and manganese are given in Table 27.

Biochemical sedimentary rocks include phosphorites, in the composition of which carbonate-apatite is predominant.

As far as their outer form is concerned, phosphorites are highly variegated. Their colour is grey to black. Solid layered phosphorites are found resembling limestone, sandstone, silicon and flint. The nodular type is in the form of concretions (Fig. 35).

There are several hypotheses as to the origin of phosphorites (biolitic, chemical), in accordance with which one thing is quite clear: phosphorites are the sediments of comparatively shallow seas with normal salinity, and phosphorus is of organic origin. Together with phosphorites the following minerals are found: glaucosite, hydroxides of iron, carbonates, clay minerals, chalcedony, and marcasite. In the concretions of some phosphorites in the Ukraine galena and sphalerite are sometimes found too. The deposits of phosphorites are known in south and west Kazakhstan, Algeria, Tunisia, Morocco, and the USA.

The life activity of anaerobic bacteria serves as a biochemical factor in promoting the formation of native sulphur. The bacteria decompose the organic substances, as well as sulphates and sulphides. Hydrogen sulphide thus formed is migrated to the top and, entering into the oxygenous medium, undergoes oxidation itself, which results in the formation of sulphur



In paragenesis with sulphur the following minerals occur: gypsum, calcite, celestite, and bitumens.

The biochemical process is also responsible for the formation of the sedimentary deposits of vanadium, uranium, and some sulphides of

Mo, Pb, and Zn. The deposits are confined to the carbonaceous interlayers in rocks, the carbonaceous (black) schists, and bituminous rocks. An organic substance possesses adsorptional properties and selectively accumulates vanadium and uranium, as a result of which large industrial deposits of these ores are formed. The most important ore minerals are roscoelite, carnotite, and tyuyamunitite.

In conclusion, to all that has been said of the minerals of sedimentary rocks, it should be added that carbonate rocks (limestones, dolomites, and marls) are, to a great extent, characterized by the following minerals: chalcedony (and silicon), sphaeroiderite, Fe hydroxides, psilomelane, and ratofkite, with gypsum-bearing strata it is gypsum, palygorskite, celestite, barite, sulphur, aragonite, and calcite. Glauconite, phosphorite, vivianite, and others are found to be typical of clay and sandy rocks.

## Metamorphic Processes of Mineral Formation and the Associations of Minerals in Metamorphic Rocks

The influence of high temperature and pressure, gaseous and water solutions, experienced by sedimentary and magmatic rocks is caused by the movement of the Earth's crust. The fact that the rocks undergo changes calls for no special comment. All the processes leading to such changes are brought together by the term *metamorphism*.

The sources of heat are: (1) radioactive processes of the disintegration of elements; (2) high temperatures in connection with the geothermal gradient; (3) proximity of the melted rocks. It can be assumed that the second and the third sources of heat are also the results of radioactive disintegration. The pressure is caused by the weight of the overlying rocks and the mountain making processes. The metamorphic processes are mainly expressed in dehydration and recrystallization of rocks.

The quantity of H<sub>2</sub>O and CO<sub>2</sub> can undergo substantial changes in the process of metamorphism. If the content of other rock components does not experience any change here, the metamorphism is called isochemical, i.e. there is nothing but dehydration and simple recrystallization of rocks. If, however, the content of chemical elements in the process of metamorphism is changed, the phenomenon is referred to as metasomatic with the addition of some of the elements and the loss of others. The latter becomes exceptionally manifest when contact-metasomatic skarns are formed, as well as under ultrametamorphism, particularly during the granitization of rocks.

Metamorphic rocks are extremely widespread. They compose practically the whole of the platform bases and their part that is exposed, i.e. the shields. The function of metamorphic rocks as constituents of the earth's crust on the continents can hardly be overestimated.

### Types of metamorphism

Several types of metamorphism are distinguished according to the prevalence of certain factors.

*Thermal metamorphism* is connected with the change of rocks under the influence of temperature (roasting, hardening, partial change in the composition and structure of minerals, or recrystallization).

*Dynamometamorphism*, or the dislocational metamorphism, which occurs when rocks are submerged to considerable depths and during the processes of folding. In the former case it is related to the general hydrostatic pressure of the overlying rocks, in the latter case it is connected with the directional pressure, or stress. As a result of dynamomorphism there is a change in the structure, and, partly, in the mineral composition of rocks.

*Contact metamorphism* is connected with the impact of the interpenetrating magmatic masses in the enclosing rocks (temperature, solutions). If gaseous and water solutions function not only within the contact zone, but also outside of it, it is sometimes said that the metamorphism in question is either pneumatolithic or hydrothermal. In this case the metamorphic phenomena consist in the metasomatic processing of rocks accompanied by a change in their chemical and mineral composition. If the solutions function along the fissures and veins, the directions that are most relaxed and convenient for penetration, the metamorphism is called parafissured or paraveined.

*Regional, or dynamothermal, metamorphism* occurs at low depths and is the result of the joint activity of temperature and pressure upon rocks. Regional metamorphism covers vast territories of the earth's crust and is particularly spread in ancient and most deeply submerged rocks. Thus, deep-metamorphized rocks are known among the ancient continental shields (Aldan, the Ukrainian platform, Canada, India, Australia, Central Africa, South America, etc.). The axial parts of the more recently developed mountain ranges (e.g. the Paleozoic ones) where the deepest zones of the Earth's crust are observed, are also subjected to regional metamorphism.

Deep-metamorphized rocks are represented by gneisses and migmatites. The structure of the latter is conditioned by in layers implementation of granitic or pegmatitic material, or injection. The said process is called *injectional metamorphism*, or *migmatization*.

The extreme case of metamorphism consists in a partial or complete melting of rocks with the formation of secondary magma. The terms that are applied to designate these processes are: *anatexis*, or *palingenesis*.

Among the processes of deep metamorphic processing the ascending gaseous and liquid solutions are of no minor significance. They bring forth alkali and silica, thus causing metasomatism and recrystallization. In the long run the totality of all these processes leads to the formation of rocks of the granite type and is called *granitization*.

### The mineralogical characterization of metamorphic rocks

The original material for the formation of metamorphic rocks is the sedimentary and magmatic rocks. Hence, the forms of the depositing of metamorphic rocks resemble those that are typical of the deposits of these rocks.

The chemical composition of metamorphic rocks is different and primarily depends on the composition of the origin of rocks itself. However, the composition of a metamorphic rock can undergo substantial changes as compared with the original rock under the impact of substances introduced by solutions and the metasomatic processes.

The mineral composition of metamorphic rocks is also variegated.



Rhodonite. Black  
hydroxides of manganese  
by fissures (Ural Mts.)



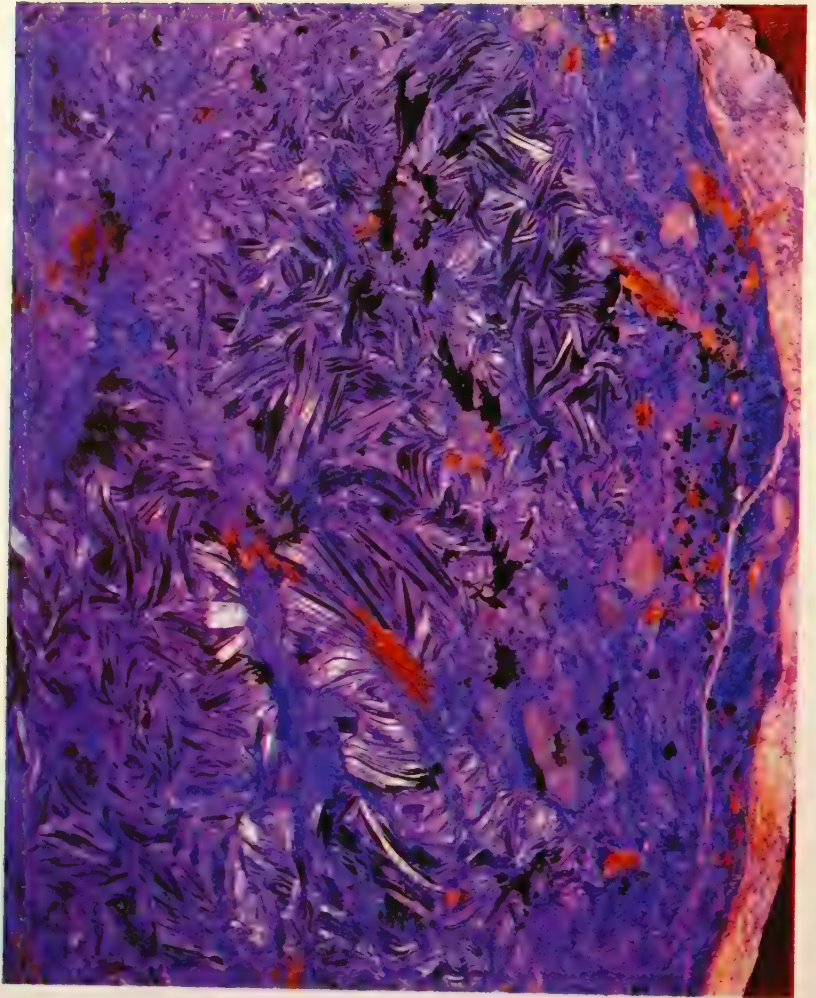
Lazurite—blue veins  
(southern Baikal region)



Eudialyte  
(Khibiny Mts.,  
Kola Peninsula)

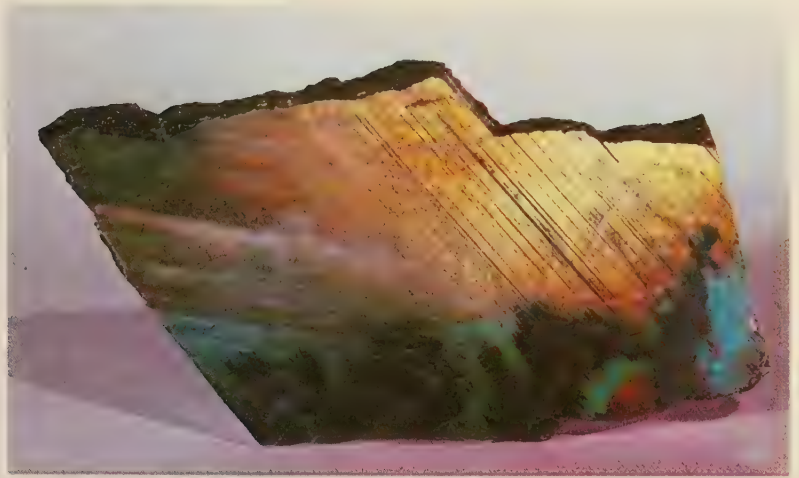
Cyanite  
(the Murmansk region)





Charoite (Chara river,  
eastern Siberia)





Iridescence on cleavage  
plane of labradorite  
(Zhitomir region, the  
Ukraine)

Amazonite  
(the Murmansk region)





Beryl  
(Volyn, the Ukraine)



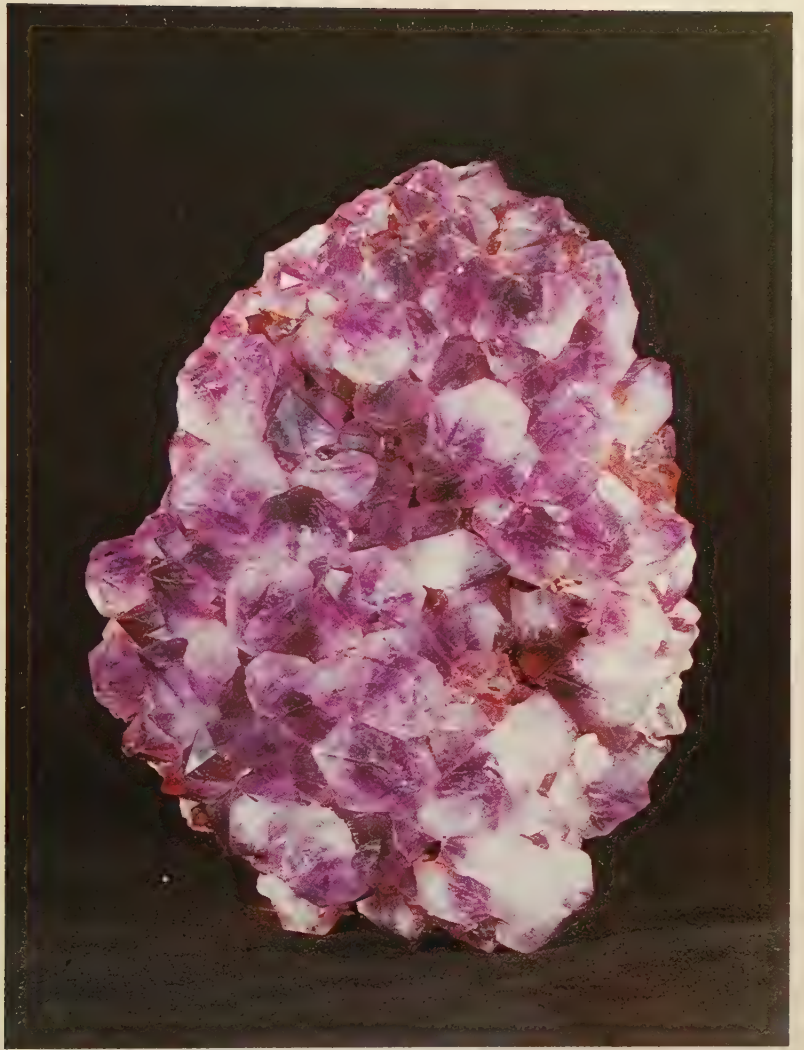
Topaz—blue (Ural Mts.)  
and light-brown  
(the Pamirs)

Beryls—yellow heliodor  
(the Ukraine), green  
emerald (Ural Mts.)  
and blue aquamarine  
(Transbaikal region)





Rock crystal with  
acicular rutile  
(Ural Mts.)



Amethyst (Ural Mts.)



Reniform aggregates of malachite (on the right) and a polished specimen (on the left)

Hemimorphite (Italy)



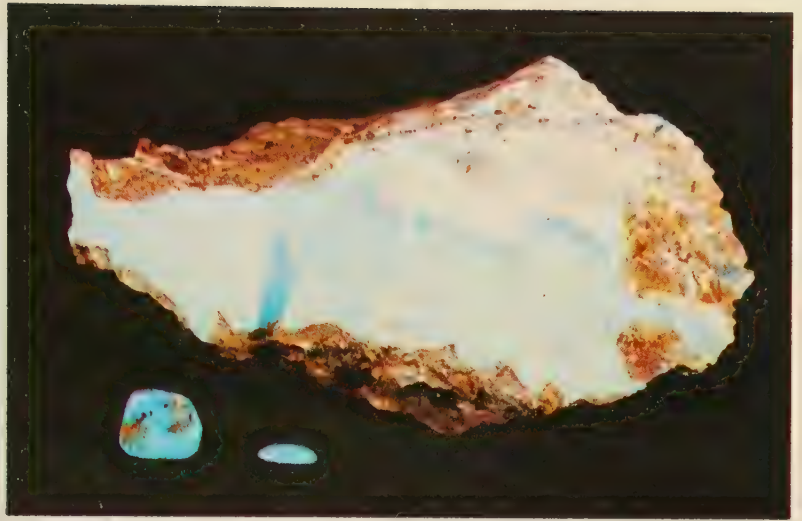


Azurite from the zone  
of oxidation of copper ores  
(Kazakhstan)



Apatite crystals  
(Slyudyanka, the Baikal  
region)





Turquoise (Central Asia)

Scheelite crystal on  
the quartz  
(Chukotka Peninsula)



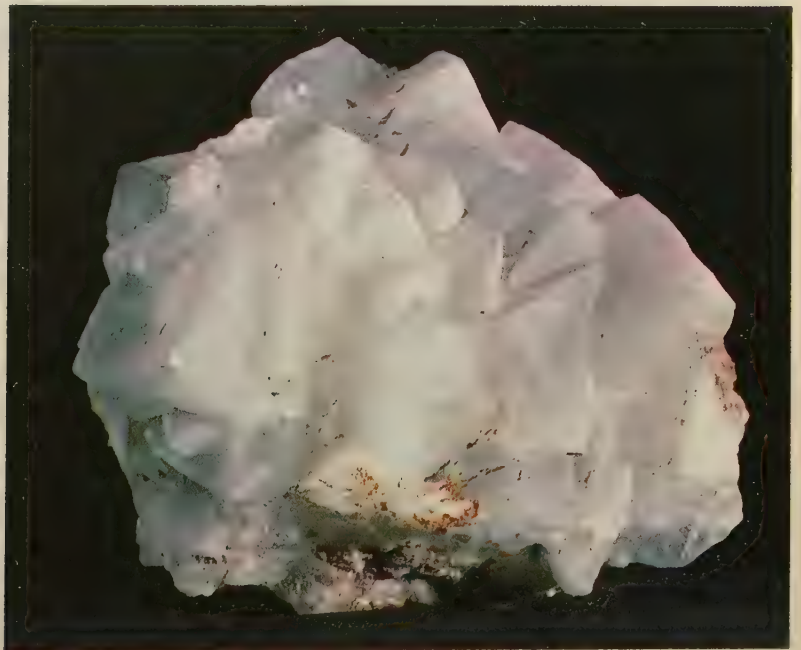


Native sulphur  
(Kuibyshev region)



Fluorite (a polished specimen, the Pamirs)

The druse of fluorite crystals – cubic habit (the Pamirs)





The druse of chalcopyrite  
crystals. Galena is  
shown in dark  
(Primorski Krai)

These rocks can consist of one mineral, e.g. quartz (quartzite), calcite (marble), or of a large number of complex silicates. The most important rock-forming minerals are represented by quartz, feldspars, micas, pyroxenes, and amphiboles. Typically metamorphic minerals are present together with them, e.g. garnets, andalusite, disthen, sillimanite, cordierite, scapolite, and several others. Talc, chlorites, actinolite, epidote, zoisite, and carbonates are found to be characteristic, particularly of the weakly metamorphic rocks.

Most of the minerals pertaining to metamorphic rocks do not have crystallographic forms of their own, though some minerals are idiomorphic, as is the case with garnet, tourmaline, and some others.

Foliated, imbricate, and platy minerals are exceptionally widespread. This is connected with their accommodation to the conditions of crystallization, when the pressure is high, the fact which finds its expression, first and foremost, in the development of the schistosity of metamorphic rocks. The foliated structure is characterized by the fact that rocks are split into thin tiles and plates. This structure can well be regarded as the result of the parallel arrangement of the flat surfaces of minerals.

In the process of regional metamorphism the rocks acquire the feature which is known as *striation*. The latter finds its expression in the alternation of interlayers or bands of rocks, distinguished by the content of the main rock-forming minerals. The other feature that is pertinent to metamorphic rocks obtained in the regional process is *crystallizing schistosity*. It is conditioned by a regular and parallel orientation of micas, e.g. biotite and muscovite, and more seldom by other minerals.

The products of metamorphism can be singled out by their forms, thus distinguishing the rocks of thermal, dislocational, contact, and regional metamorphism.

Thermal metamorphism, as a certain change undergone by rocks only under the influence of high temperature, is confined to local manifestation. In intrusive contact it causes the marbleization of limestones, the formation of hornfelses of sandy-argillaceous rocks, as well as a change in the xenoliths within the intrusive bodies.

The products of thermal metamorphism, in their essence, coincide with the products of contact metamorphism without the introduction of any new substance. This is mainly called *hornfelses*, i.e. the rocks representing clay schists that have undergone changes in contact with intrusion, and have been transferred into compact fine-grained rocks of the hornfelsic structure. The recrystallization of rocks takes place in solid state. Hornfelses are distinguished by the proximity in which they find themselves with magmatic rocks (which accounts for the fact that they are often referred to as contact hornfelses), and by their transitional departure from contact into spotted and knotted schists. The latter represent partially recrystallizing clay rocks, in which the carbonaceous substance and some minerals are accumulated in various places, thus forming spots. The widespread varieties of hornfels are those of the biotite, andalusite, andalusite-plagioclase-cordierite types, etc.

The original rocks can include not only clay rocks, but those of the quartz-feldspar, and carbonate types, basic and magnesium rocks, and others.

TABLE 28

*Minerals of  
Contact Hornblendes  
(in relation to  
original rock content)*

	Original rocks	
	Carbonate	Basic and magnesian
Clay		
Andalusite	calcite	basic plagioclase
Cordierite	wollastonite	diopside
Biotite	grossular	hypersthene
Plagioclase	vesuvianite	cordierite
Orthoclase	scapolite	biotite
Microcline	quartz	epidote
Quartz	tremolite	actinolite
Corundum	diopside	anthophyllite
Spinel	In contact with dolomites: dolomite diopside hedenbergite forsterite actinolite brucite talc spinel periclase	forsterite spinel

TABLE 29

*Minerals of the  
Alpine Type Veins*

Principal	Minor	Those of practical importance
Quartz	anatase	rock crystal
Rock crystal	sphene	adular
Carbonates	tourmaline	
Chlorites	actinolite	
Adular	talc	
Albite	axinite	
Rutile	danburite	
Brookite	datolite	
Hematite	apatite	
Epidote	pyrite	
Zeolites		
Prehnite		

Table 28 presents mineral association of contact hornfels in their relationship to the content of original rocks.

Products of dynamometamorphism or dislocational metamorphism are responsible for the emergence of cataclasites, and mylonites, when the grinding of rocks is complete. These rocks appear in the zones of tectonic dislocations and crushing. Cataclasites are crushed as the result of rock stress. Crushing and deformation are characteristic not only of certain parts of the rock, but also of the minerals that are its constituents. Under the process of dislocation with a break in continuity rocks undergo crushing, and are also subjected to grinding and become more compact when they are dislocated along the breaks. This results in the emergence of mylonites, or fine-grounded compact rocks. As distinct from cataclasites, mylonites are characterized by a greater degree of crushing of the material. Mylonites are found in the zones of fractures, faults, thrusts, and other disjunctive breaks. The zones of colour blending, i.e. the crushed mixed rocks, are exceptionally typical of ultrabasic contacts (e.g. in the South Urals). The crushed rocks are not infrequently healed by the newly formed minerals, and other changes, including the silification of rocks, take place.

Dislocational metamorphism is connected with the formation of the break in the veins of the Alpine type, which in themselves are mainly composed of quartz, the break occurring in the fissures transversal to schistosity. The term by which these veins are designated originated in the Alps where they were first described. The veins of the Alpine type are distinguished by beautiful crystals of various minerals, found in druses. Mountain crystals are of particular interest and present practical value. The acicular and hairlike crystals of rutile in rock crystal (maidenhair) are pleasantly conspicuous.

The composition of veins is uniform of different regions. The main minerals are: quartz, calcite, adular, albite, rutile, brookite, chlorite, epidote, hematite, zeolites. The complete absence of sulphides, chalcophile elements, gold, tin minerals, tungsten, and many other minerals typical of ore veins is found to be characteristic feature.

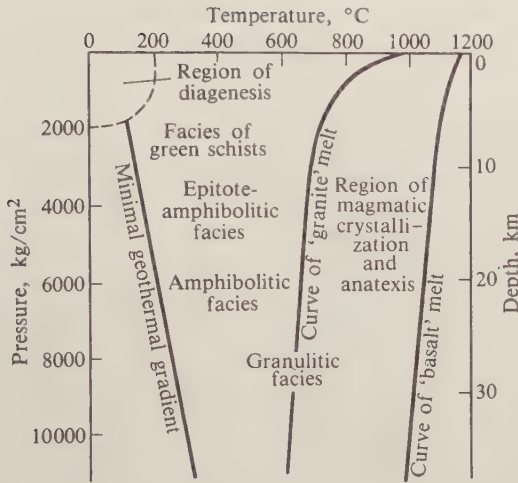


Fig. 158. Basic metamorphic facies in relationship of temperature and pressure (according to B. Mason)

interest as a source of piezoquartz (rock crystal), and sometimes even adular, which is used in jewellery. The deposits of rock crystal in the formations of the type of Alpine veins are known in the South and Polar Urals.

The products of simple contact metamorphism are the hornfels mentioned above. As a result of more complex contact-metasomatic processes skarns, greisens and other rocks discussed in the earlier parts of this work, are formed.

Rocks formed as a result of regional metamorphism are most widely spread. They are represented by clay schists, phyllites, various crystalline schists, amphibolites, quartzites, marbles, gneisses, migmatites, and many others.

At present, most of the geologists adhere to the classification of metamorphic rocks according to metamorphic facies. Research in this field has been conducted by P. Escola, D. S. Korzhinsky, V. S. Sobolev, A. A. Marakushev, and other scientists. Metamorphic facies are singled out on the basis of the study of mineral paragenesis, which represents systems, which have come into equilibrium under certain  $P$ - $T$  conditions. Thus, *metamorphic facies* is a group of rocks, the mineral paragenesis of which reflects more or less similar  $P$ - $T$  conditions of metamorphism (Fig. 158).

With the change of  $P$ - $T$  conditions the following main facies are distinguished: (1) green schists; (2) epidote-amphibole; (3) amphibole; (4) granulitic.

Facies are distinguished by the location of 'critical' minerals, or mineral associations, which are possible only in one particular facies and not characteristic of others. Thus, the facies of green schists cover the low-temperature part of the regional metamorphism. The following paragenesis are typical of it: chlorite-calcite-quartz; quartz-albite-muscovite-chlorite; muscovite-chlorite-actinolite, etc. The most typical rocks are: various green schists, metasandstones, metaeffusives, and others. The rocks of the green schist facies are widely spread in the Phanerozoic folds of the Caucasus, the Carpathians, Tien Shan, the Urals, and other districts.

The epidote-amphibole facies is confined to higher temperatures of

On the other hand, the similarity of the mineral composition of Alpine veins and the rocks enclosing them, usually gneisses or crystalline schists, is being determined. It is assumed that the formation of veins of the Alpine type is connected with the impact of water that is released under metamorphism and the occurrence of metamorphic hydrothermal solutions, which deposit minerals in the fissures of the breaks, the composition of minerals being identical to the minerals of the enclosing rocks. Consequently, the veins of the Alpine type are metamorphogenetic formations, which are genetically not connected with any of the deep magma chamber.

Mineral associations of veins of the Alpine type are characteristic in themselves (Table 29). In a practical sense they present considerable

which chlorite is a 'forbidden' mineral. This is where biotite appears. The usual minerals of this facies are: hornblende, epidote, biotite, muscovite, quartz, staurolite, chloritoid. The lower limit of the epidote-amphibole facies is probably confined to the temperature of approximately 400 C (the formation of biotite). The typical rocks are: andalusite, micaceous, micaceous-garnet, staurolitic schists and numerous gneisses. They are characteristic of the same regions as the rocks of the green schists facies, but are widely associated with the rocks of the amphibole facies as well.

The amphibole facies covers a wide range of temperature and pressure and is characterized by such critical minerals as: hornblende and plagioclase. The usual minerals are biotite, amphibole, plagioclases, almandine, sillimanite, orthoclase, and quartz.

The rocks of the amphibole facies are widely spread in the anticlinal zones and the uplift of folded regions and the median masses of the Paleozoic structures as well as in all ancient shields. The typical rocks here are: various gneisses (biotite, sillimanite, etc.), amphibolites, quartzites including ferriferous quartzites (Fig. 159), and marbles.

The granulitic facies is confined to higher pressures and temperatures. It is a 'dry' facies (among the rocks of this facies there are no hydroxyl-bearing minerals, such as hornblende, muscovite, and biotite). The usual minerals are: orthorhombic and monoclinic pyroxenes, garnet, plagioclase, orthoclase, quartz, and sillimanite. Besides hornblende and micas, 'forbidden' minerals also include epidote, andalusite, and staurolite. The typical rocks are: pyroxene and bipyroxene gneisses, and granulites. Such rocks are spread in the regions of the Pre-Cambrian shields (Ukrainian, Baltic, Aldan, and Anabar), and in the basement of the East-European platform.

The paragenetic associations of minerals pertaining to various facies of metamorphic rocks are given in Table 30. Among metamorphic rocks subfacies are also singled out (the latter are not discussed in the present manual).

Besides facies characteristic of regional metamorphism mentioned above metamorphic facies of high pressures have also been singled out. They include, for example, the facies of disthene gneisses and schists and the facies of eclogites. The former forms both the narrow zones, connected with deep breaks and the wide fields of high-temperature metamorphism, composed of disthene schists and gneisses (for instance, along the south fringe of the Siberian platform). The eclogite facies is characterized by the paragenesis of garnet, pyroxene (and rutile) and is confined to the region of higher temperatures and pressures. The eclogite rocks are typical of the deeper zones of metamorphism and are known in the north and south Urals, Kazakhstan, and Yakutia. It

Fig. 159. Ferriferous quartzite (hematite spreading over the darker region). Krivoi Rog. Half the natural size

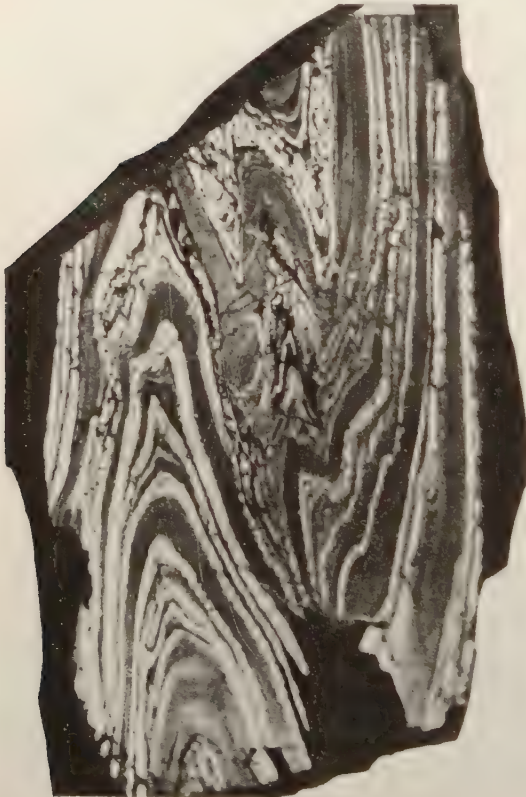




TABLE 30 *Paragenetic Associations of Minerals of Various Facies of the Regional-metamorphosed Rocks*

Green-schist facies	Epidote-amphibolite facies	Amphibolite facies	Granulite facies
Chlorite	hornblende	hornblende	rhombic and
Calcite	epidote	medium	monoclinic pyroxenes (diopside, hypersthene)
Quartz	biotite	plagioclases	garnet
Albite	muscovite	biotite	basic plagioclases
Muscovite	quartz	quartz	
Sericite	acid plagioclases	garnet	
Actinolite	staurolite	(almandine)	
Tremolite	chloritoid	sillimanite	orthoclase
Glauco-phane	garnet	cyanite	quartz
Talc	andalusite		
Serpentine	anthophyllite	magnetite	sillimanite
Magnetite	magnetite		forsterite
Hematite			rutile
Graphite			
Asbestos			

Accessory minerals: magnetite, hematite, ilmenite, graphite, tourmaline, zircon, rutile, sphene, pyrite, apatite. Minerals that have practical importance: magnetite and hematite (ferriferous quartzites), graphite, talc, asbestos, andalusite, disthene, sillimanite, garnets, rutile, marble, and quartzites (as rocks), etc.

is assumed that eclogitic rocks, or the eclogitic layer, are characteristic of the coating underlying the Earth's crust (for the upper regions of the mantle).

The mineral composition of metamorphic rocks depends, as has been made abundantly clear, not only on the degree of metamorphism, but also on the composition of original rocks, a fact reflected in Table 31. Graphite, formed under the metamorphism of an organic substance ( $C_{org}$ ) should be included into the table as the most important mineral. Graphite-bearing schists, gneisses, quartzites, and marbles are widely spread. The content of graphite can reach practically significant values (the Zavalyevsk deposit in the gneisses along the Bug River in the Ukraine). Graphite originates at the expense of the metamorphism of organic matter found in sedimentary rocks, a fact which is substantiated by the isotopic research of graphitic carbon dioxide.

In conclusion it should be pointed out that the determining of the mineral paragenesis of metamorphic rocks on a strictly physico-chemical basis is the most important task of petrology, a special branch of geological sciences.

TABLE 31

*Principal Minerals of Metamorphic Rocks*

(in relation to original rock content, according to A. A. Marakushev)

Original rocks	Metamorphic rocks	Principal minerals
Clays	hornblendes	quartz, feldspars, andalusite, cordierite, magnetite, biotite
	gneisses	quartz, feldspars, biotite, muscovite, staurolite, sillimanite, andalusite, cordierite, garnet
	micaceous schists	quartz, muscovite, biotite, chlorite, andalusite, sillimanite, disthene, staurolite, almandine, chloritoid, albite
	phyllites and clay schists	quartz, mica, chlorite, chloritoid, almandine, pyrophyllite, stilpnomelane
Marbles, limestone tuffs, greywackes, basic effusives, and their tuffs, gabbroids	pyroxene hornblendes	feldspars, pyroxenes, quartz, amphiboles
	amphiboles, pyroxene-plagioclase basic and crystalline schists	plagioclase, hornblende, diopside (hypersthene), garnet
	epidote amphiboles	plagioclase, epidote, hornblende, quartz
	chlorite (green) schists, porphyritoids, spilites	albite, epidote, chlorite, actinolite, quartz, prehnite, pumpellyite, calcite
	glaucofane (light-blue) schists, jadeite metagreywackes	glaucofane, chlormelanite, aegirine, riebeckite, almandine, epidote, chlorite, albite, lawsonite, jadeite, aragonite, quartz
	eclogites	garnet, pyroxenes, amphiboles, plagioclase, disthene, zoisite
Acid effusives, granitoids, arkosic sandstones	cericitic schists, porphyroids, albitophyres	cerisite, albite, quartz, chlorite
	gneisses	quartz, feldspars, biotite
Quartz sandstones	quartzites	quartz and accessories: micas, feldspars, sillimanite, disthene, Mn-andalusite, spessartine, diopside, tremolite, apatite, etc.
Sandstones, dolomites, magnesites	marbles	calcite, dolomite, magnesite, diopside, forsterite, spinel, phlogopite, tremolite, talc, hydrotalcite
Peridotites	amphibole, chlorite, talc schists, talcites, serpentinites	olivine, pyroxenes, amphiboles, chlorite, magnetite, talc, brucite, magnesite, dolomite, serpentine
Ferriferous and manganese siliceous sediments	magnetite, hematite, and manganese-ore quartzites, gondites	quartz, magnetite, hematite, manganese oxides, spessartine, piedmontite, amphiboles
Bauxites, laterites	emery	corundum, diaspore, spinel, hematite, magnetite

## Minerals of Lunar Rocks and Meteorites

The characterization of lunar minerals and meteorites has a great scientific importance. Hence, a brief acquaintance with these concepts is found to be desirable. In what follows we have an inventory of the most widely spread lunar minerals and meteorites, as well

as some of these that are rare and characteristic only of these celestial bodies. The 'Apollo' (USA) and 'Luna-16, -17, and -20' (USSR) space research projects have provided data concerning the chemical and mineral compositions of lunar rocks.

The Moon is a solid body, consisting of silicates and deprived of both the atmosphere and the hydrosphere. There is no life on the Moon, and a total absence of oxidized forms of metals, e. g.  $\text{Fe}^{3+}$ . It is possible to distinguish lowered dark surfaces, or lunar 'seas', as well as the lightly coloured elevations, or mountains. There can be no doubt that the lunar 'seas' contain no water. It has become merely customary to apply this term to them since it was first introduced by Galileo himself. On the visible side of the lunar 'seas' and continents share almost an equal amount of space, while the reverse side of the lunar has very few 'seas' but abounds in mountains. The lunar's surface is covered with friable material called regolite, the thickness of which ranges from several centimetres to many metres. Regolite is a kind of loose grounds, a nonhomogenous blend of rock and mineral fragments, various in their form and composition, with most of the grains being 0.1 mm. As far as its composition is concerned regolite is somewhat different from the crystalline lunar rocks upon which it is deposited.

TABLE 32 *Minerals of Lunar Rocks*

Principal (> 10%)	Minor (1-10%)	Accessory (< 1%)	Those that are of practical importance
Pyroxene Plagioclase Ilmenite	olivine cristobalite pyroxferroite* tridymite	iron copper nickel iron** cohenite** shreibersite** troilite chromite spinel ulvite perovskite rutile baddeleyite zircon apatite tranquillityite* armalcolite* orthoclase quartz	none at present

\* Minerals discovered in lunar rocks:

pyroxferroite  $\text{CaFe}_6[\text{SiO}_3]_7$ ,

armalcolite  $(\text{Fe}, \text{Mg})\text{Ti}_2\text{O}_3$ ,

tranquillityite  $(\text{Fe}, \text{Y}, \text{Ca}, \text{Mn})(\text{Ti}, \text{Si}, \text{Vn}, \text{Cr})\text{O}_3$ .

\*\* Minerals discovered in meteorites earlier:

cohenite  $\text{Fe}_3\text{C}$ ,

shreibersite  $(\text{Fe}, \text{Ni}, \text{Co})_3\text{P}$ ,

nickel iron  $(\text{Ni}, \text{Fe})$ .

Lunar 'seas' are composed of magmatic rocks of the type similar to earthy basalts, while mountains on the Moon resemble such rocks as gabbro-anorthosites. The mineral composition of sea basalts on the Moon is the following: pyroxene, rich in iron, ~50%, basic plagioclase (anorthite), ~30%, ilmenite up to 18%, olivine, cristobalite, tridymite are in a subservient quantity (from 1 to 10%); orthoclase, apatite, zircon, spinel, chromite, as well as native iron and copper, troilite (FeS), and such 'non-terrestrial' minerals as cohenite  $\text{Fe}_3\text{C}$  and shreibersite  $(\text{Fe}, \text{Ni}, \text{Co})_3\text{P}$  (Table 32) are known to exist in quantities of less than 1%.

As compared with the basalts of the Earth, the lunar rocks are enriched with iron, nickel, titanium, vanadium, zirconium, hafnium, yttrium, scandium, though depleted of alkaline, particularly of sodium, potassium, rubidium, and caesium. In lunar rocks there is a relatively low content of europium element, as compared with other rare earths; same can be said if the comparison is drawn between lunar rocks and the Earth's basalts containing uranium, in which case the lowering of the said content equals one unit.

Meteorites are fragments of cosmic bodies that fall upon the Earth. There is substantial evidence that they represent fragments of cosmic bodies of our solar system and are by no means 'intruders' from far-away worlds. Their size varies, covering the range of fractions of a millimetre to several metres in cross-section. It is seldom that large meteorites fall upon the Earth. Meteorites are characterized by an angular form in which the protruded parts seem to be smoothed, and depressions that are the result of their existence in cosmos and their melting in entering the atmosphere. According to their chemical and mineral compositions, all meteorites can be divided into three classes: (1) iron meteorites (siderites), (2) stony-iron meteorites (siderolites), and (3) stony meteorites (aerolites). According to D. Wood the frequency with which the meteorites of various classes fall is the following (%):

iron meteorites	5.7
stony-iron meteorites	1.5
stony meteorites:	
(a) chondrite	85.7
(b) achondrite	7.1

In other words, more than 90% of meteorites are stony and only 7.2% are iron and stony-iron.

In the substance of meteorites a number of phases are singled out, the most important of which are the metallic, or the nickel-iron stage, the sulphide, or the troilite stage, and the stony, or the silicate stage. All the meteorites represent a combination of the nickel-iron and the silicate phases, to which the sulphide stage is variably related.

### Iron meteorites

consist almost completely of nickel iron (Ni, Fe) with rare accessory minerals, e.g. troilite  $\text{FeS}$ , shreibersite  $(\text{Fe}, \text{Ni}, \text{Co})_3\text{P}$ , cohenite  $\text{Fe}_3\text{C}$ , graphite, daubreelite  $\text{FeCr}_2\text{S}_4$ , oldhamite  $\text{CaS}$ , lawrensite  $\text{FeCl}_2$ , etc. Content of nickel in (Ni, Fe) is usually between 4 and 20% and rarely more. The etching of a polished surface of nickel-iron with an alcohol solution  $\text{HNO}_3$  brings forth widmanstätten figures. The latter represent a disintegrating structure of solidified plessite alloy and consist of tabular kamacite (~6% of Ni), surrounded by a strongly

reflective taenite (~30-40% of Ni). By the etching figures, iron meteorites, composed of kamacite, are called hexahedrites; those composed of kamacite and taenite are known as octahedrites, while the term 'ataxite' is used in reference to those iron meteorites the composition of which includes only taenite. Shreibersite has a variable ratio of Fe: (Ni + Co), and is a magnetic mineral. Lawrensite comprises not only 20-50% of Fe, but also and often, 15-35% of Ni, 30-40% of chlorine. Daubreelite is usually present in association with troilite. Cohenite is a characteristic rare mineral of iron meteorites.

### Stony-iron meteorites

represent spongy formations of plessite cemented by silicates. The quantity of plessite and silicates is nearly the same. Troilite can also be present here. *Pallasites* consist of plessite with olivine disseminated into it (up to 40%); *mesosiderites* comprises the mixture of plessite, anorthite, orthopyroxene, and olivine (1.5-2.5%).

### Stony meteorites

are divided, according to their structure, into two groups. They are: chondrites and achondrites. Chondrules are small (the diameter is 1 mm or less), rounded or drop-like bodies, consisting of olivine and rhombic pyroxene. By the presence of chondrules these minerals are called *chondrites*. They consist of olivine (40-50%), orthorhombic pyroxene (30%), plessite (10-15%), plagioclase (10%), and troilite (5-6%). *Achondrites* do not have any chondrules (the latter are recrystallized); they are more coarse-grained; their content of plessite is markedly lower. They consist of olivine (12-13%), orthorhombic pyroxene (~50%), diopside (12%), plagioclase (25%), and plessite (~1%). Chondrites, in their turn, fall into several types: enstatite chondrites, common chondrites, rich, deplete, and extremely deplete of iron, and carbonaceous chondrites. The latter are rarely found, but are unique, since they are more oxidized, all the iron in them being part and parcel of oxides and silicates. They consist of serpentine or chlorite, and contain up to 10% of complex organic compounds and a large amount of sulphur in the form of sulphates.

Table 33 includes principal and some minor minerals of three basic classes of meteorites. The composition of meteorites (excluding the carbonaceous chondrites) shows excessively recovering conditions of their formation, iron being in a metallic state. The minerals of meteorites, as compared with terrestrial minerals, are characterized by native elements, such as kamacite, taenite, awaruite ( $\text{Ni}_3\text{Fe}$ ), lonsdaleite, diamond, graphite, gold, copper, sulphur, as well as carbides, silicides, nitrides, phosphides, and chlorides. The latter are represented by cohenite  $\text{Fe}_3\text{C}$ , chexonite  $(\text{Fe}, \text{Ni})_{23}\text{C}_6$ , perrierite  $(\text{Ni}, \text{Fe})_n(\text{Si}, \text{P})_m$ , carlsbergite  $\text{CrNi}$ , osbornite  $\text{TiN}$ , barringerite  $(\text{Fe}, \text{Ni})_2\text{P}$ , and the mentioned above shreibersite  $(\text{Fe}, \text{Ni}, \text{Co})_3\text{P}$  and laurenseite  $\text{FeCl}_2$ . All of them have been discovered only in meteorites. Many sulphides, rarely found on the Earth, are common to meteorites. They are: troilite  $\text{FeS}$ , alabandine  $\text{MnS}$ , but it is the sulphides of calcium, chromium and the sulphides containing alkaline metals, unknown in terrestrial conditions, that present particular interest. They are: oldhamite  $\text{CaS}$ , brezinaite  $\text{Cr}_3\text{S}_4$ , daubreelite  $\text{FeCr}_2\text{S}_4$ , djerfisherite  $\text{K}_3(\text{Na}, \text{Cu})(\text{Fe}, \text{Ni})_{12}\text{S}_{11}$  etc. From the class of minerals belonging to oxides in meteorites the following are found: tridymite, cristobalite,

TABLE 33

*Minerals of Meteorites*

	Iron		Stony-iron		Stony	
	principal	minor	principal	minor	principal	minor
kamacite	shreibersite	plessite	shreibersite		<i>Chondrites</i>	
taenite	troilite	olivine	troilite	olivine	anorthite	
	cohenite	pyroxene	cohenite	enstatite	orthoclase	
	graphite	(orthopyroxene)	chromite	bronzite	troilite	
	daubreelite	plagioclase	daubreelite	hypersthene	chromite	
	oldhamite	(anorthite)		plessite	apatite	
	lawrensite			albite		
				<i>Carbonaceous chondrites</i>		
				serpentine	pyroxene	
				chlorite	astrakhanite	
				olivine	gypsum	
				organic matter	jarosite	
					epsomite	
				<i>Achondrites</i>		
				enstatite	orthoclase	
				hypersthene	plessite	
				olivine	shreibersite	
				diopside	augite	
				anorthite	chromite	
				albite	diamond	

rutile, spinel, chromite, ilmenite, magnetite, perovskite, and other terrestrial minerals. A large number of phosphates unknown on the Earth, e. g. farringtonite  $Mg_3[PO_4]_2$ , brianite  $Na_2CaMg[PO_4]_2$  and others have been found in meteorites. Among the silicates those of chromium, e. g. juriite  $NaCr[Si_2O_6]$ , krinovite  $NaMg_2[Si_3CrO_{10}]$  and several others, also unusual for the Earth's crust, have been found.

Minerals of cosmic origin (or, to be more exact, of mixed origin, including both the cosmic and the terrestrial varieties) should include formations that have resulted from the shock impact of meteorites on the terrestrial rocks. First and foremost, this can be said of special kind of glasses, small in size and rich in silica, containing on the average 70-75% of  $SiO_2$ . They are called *tektites*. They are found in the form of small stones, weighing up to 200-300 grammes. Their composition and structure do not resemble any of the minerals and rocks found on the Earth, including the obsidians. Nature provides tektites in the form of aureoles, sometimes scattered over vast territory. Earlier it was assumed that they were of cosmic, or meteoritic origin, though no one has actually witnessed their fall. Places where they were found suggested the terms applied to them now, e. g. moldavites, tasmanites, australites, philippinites, and so on.

Since at present their shock origin has been proved, and since the formations emerging as a result of shock impact of meteorite on terrestrial rocks are called *impactites*, these glasses should also be referred to as impactites. The large meteoritic crater Zhamanshin, recently discovered in west Kazakhstan, contains vitreous formations, or tektites, which, by the place of their find, near the Irgyz River have acquired the term of *irgyzites*.

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**Studies of  
Mineral Deposits**

by V. I. Smirnov (Ed.)

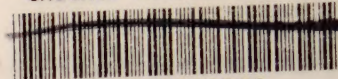
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The purpose of this volume is to introduce the student majoring in geological aspects of mineral deposits to industrial development of ferrous and nonferrous ore deposits of rare earths, precious and radioactive metals, and scattered elements. For each metal and its most important geological deposits in the USSR and other countries, the book presents data on its historical and economical background and describes its geochemistry, mineralogy, and metallogenic properties. The book is intended as a college text but will be also of interest to industrial geologists.

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