MINERALOGY

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Contents

Summary

The central role of mineralogy in the earth sciences is emphasized throughout the article. The importance of minerals for the human society in history, as well as evolution of the fragmentation of mineralogy onto additional scientific disciplines (crystallography, petrography, geochemistry, and experimental petrology), is briefly mentioned. Also discussed are current instrumental methods used in mineralogical research (chemical analytical methods, crystal structure methods, spectroscopic methods, and mineral surfaces methods), including their potential in near future. Systematic classification of minerals (mineralogical system) and examples of important minerals (ores, rock-forming minerals, etc.) are briefly described along with the origin of minerals during various geological processes (magmatic, metamorphic, sedimentary, and hydrothermal ore-forming). Current and near-future tasks in the use and development of new methods in mineralogical research include classical and applied mineralogy, environmental mineralogy, and geomicrobiology. Particular emphasis is made of the importance of the future teaching of mineralogy.

1. Introduction

Minerals are the basic materials of Earth and of the planets, they provide a good proportion of the wealth supporting our society, and they also compose solid parts (e.g., bones, teeth) of living organisms. Consequently, the role of mineralogy—the science dealing with minerals—in natural sciences is crucial. Mineralogy undoubtedly plays a central role in the earth sciences (Figure 1). In igneous, metamorphic, or sedimentary petrology, we always look at the minerals composing the rocks. In geochemistry, the chemical composition of individual minerals gives typical geochemical characteristics. Economic geology deals with both ore and gangue minerals using various petrological and geochemical methods. Geophysics, as well as structural geology, is concerned with physical properties of minerals. Thus, mineralogy is a basic discipline among the earth sciences: the more we know about minerals, the better results the earth sciences may provide (**see *Earth System: Structure, Dynamics, and Materials***). It was recognized that microbes control formation of minerals during many geological processes, hence mineralogy also plays its important role in some biological processes.

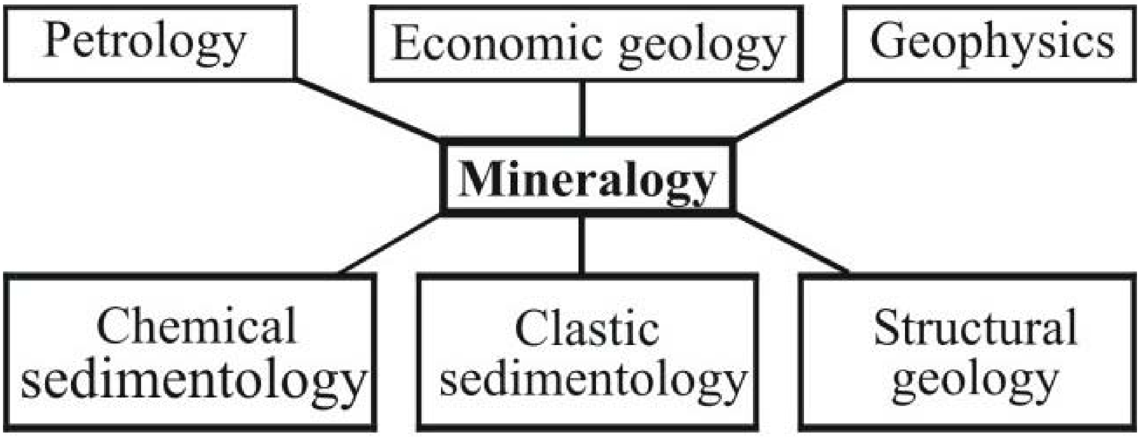

Figure 1. The central role of mineralogy in the earth sciences (from Hawthorne F.C. (1993). Minerals, mineralogy and mineralogists: past, present and future. *Canadian Mineralogist* **31**, 253–296.)

2. Minerals in History

The importance of minerals for human society may be documented in the way we date the prehistory of humankind by the material with which our predecessors made their tools.

2.1. Prehistoric Times

2.1.1. Stone Age

The use of tools, made particularly from flint and obsidian, marks the Stone Age. Our predecessors utilized tools as spear points, knives, and scrapers; and, toward the end of Neolithic period, approximately 40 different rocks and minerals were in common use including naturally occurring poisons such as arsenic oxide.

2.1.2. Bronze Age

The first metals to be used were naturally occurring metals such as copper, gold, and very rare iron from meteorites. Most are too soft for tools, but they can be cold-worked for ornaments and jewelry. Somebody discovered the technique of smelting, and heavy metallic minerals were heated to extract the copper. But a mixture of copper ore and cassiterite (or arsenic) yielded a new and even better material—bronze. The bronze-age technology was spread across Europe and Asia.

2.1.3. Iron Age

The Iron Age is considered to start at ~1400 BC. As iron ores are very common, and iron forms very hard and durable tools relative to bronze, the Iron Age represents a major change in human society. High variability in iron ores, their abundance in nature, and the relatively complex technology of smelting required a more advanced approach to the problem. Therefore, it is not surprising that the earliest descriptions of minerals come from the Iron Age.

Disregarding minerals and other raw materials used to make the tools throughout the Stone, Bronze, and Iron Ages, human beings adorn themselves with minerals and rocks used for other purposes. The firing of clays to make pottery is more for practical than artistic use, but the use of colored minerals—such as amethyst, turquoise, lapis lazuli, jade, malachite, hematite, emerald, Mn-oxides and hydroxides, and gold—to make ornaments has evident religious, superstitious, or artistic character.

2.2. Early Mineral Descriptions

As more and more people dealt with minerals and their properties, the first writings on minerals appeared. The earliest came from India, China, and Greece. Theophrastrus described 16 minerals in his textbook *De Lapidibus* dating from ~300 BC. Pliny (AD 23–79), a famous Roman encyclopedist, produced a work describing minerals, gemstones, and their treatment. He can be considered a true scientist and perhaps the first mineralogist. Several other descriptions, particularly of precious stones, appeared in Egypt, Persia, and Arabia.

The Renaissance was accompanied by a great expansion of economic activity around Europe; particularly extensive mining and smelting gave a new impetus to the geological sciences and mineralogy. Georgius Agricola (George Bauer) published all aspects of minerals and mining in his work *De Re Metallica*. He also defined the properties of minerals—such as color, transparency, luster, hardness, and cleavage—and used them as the basis for classification of minerals.

In 1611 Johannes Kepler gave the first description of the hexagonal symmetry of snowflakes; in 1669 Nicolaus Steno showed that the interfacial angles of quartz crystals are constant, disregarding their crystal habit. Thus, *crystallography* was established as a science distinct from mineralogy. W.H. Wollaston (who invented the reflecting goniometer), Romé de l'Isle, and René-Just Haüy made subsequent developments in crystallography. Ch. Weiss developed the idea of crystallographic axes and their relationship to symmetry axes. F. Mohs invented the Mohs' hardness scale, J. Hessel derived the 32 crystal classes, and A. Bravais derived 14 space groups. The classical age of crystallography came to a close with the derivation of the 230 space groups by E.S. Fedorov, A. Schoenflies, and W. Barlow. During the first half of the nineteenth century, P.L.A. Cordier, F. Becke, and W. Nicol significantly improved methods of optical microscopy. They permitted systematic study of minerals in the transmitted light and enabled microscopic study of rocks, their mineral composition, and textures, including relations among minerals in thin sections. Thus, it enabled establishment of *petrography* as another science derived from mineralogy (see *Early Earth* and *Time in the Geological Past of Earth*).

The classification of minerals based on physical properties and crystallography was significantly improved by systematic studies of chemistry of minerals, particularly by T. Bergman and J.J. Berzelius in the eighteenth and nineteenth centuries. New discoveries—such as the laws of stoichiometry of J. Dalton, the concept of solid solutions in minerals (isomorphism) by F. Beudant and W.H. Wollaston, and the idea of polymorphism by E. Mitscherlich—established the chemical basis of mineralogy. The "system of mineralogy" based on chemical classification scheme of J.J. Berzelius and published by J.D. Dana in 1837 was a real landmark of the history of mineralogy in the nineteenth century.

2.3. Twentieth Century

Revolution in mineralogy and crystallography began with the discovery of diffraction of X-rays by crystals in 1912 by Max von Laue. W.L. Bragg and W.H. Bragg gave a simple interpretation of this experiment and derived the crystal structure of halite NaCl. By the year 1935, crystal structures of most rock-forming minerals were known.

The enormous number of chemically analyzed minerals, which had been published by the 1920s, were not sufficiently understood, particularly due to complexity of many rock-forming minerals. V.M. Goldschmidt recognized relationships between the chemical composition of coexisting minerals in rocks and in 1937 demonstrated general laws governing the distribution of elements in minerals. This latter discovery explained the behavior of mineral in terms of their crystal structure and the crystal/chemical behavior of their constituent elements. Thus, *geochemistry* was established as additional science derived from mineralogy.

Development of mineral chemistry initiated works on the synthesis and stability of minerals and mineral assemblages. The magmatic theories of the famous petrographer H. Rosenbush, stemming from the second half of the nineteenth century, were a background for experimental phase petrology in the beginning of the twentieth century, and several works published by N.L. Bowen in 1915 and 1928 gave ideas of fractional crystallization in magmatic systems. *Experimental petrology* was established as a science, which allowed real temperature and pressure to be assigned to crystallization, breakdown, and melting minerals and rocks.

3. Current Instrumental Methods

The development of the electron microprobe and the introduction of various new instrumental techniques into mineralogy at the beginning of the 1960s represented a real revolution in geology. Many new instrumental methods are currently used in laboratories, and many new methods are developed; the most important of these are listed below.

3.1. Chemical Analytical Methods

Classical wet methods typically used in the nineteenth century and the first half of the twentieth century were greatly improved by the microbeam techniques, particularly by the electron microprobe (EMP). This method enables rapid and fairly straightforward analyses of minerals and also noncrystalline (amorphous) materials (e.g., glasses). Our knowledge of mineral chemistry has significantly improved, because the analysis of minerals is not affected by exsolutions and inclusions, and, moreover, we can study zoning in crystals. The limit of the electron microprobe is the determination of light elements with atomic number less than nine (currently in new instruments, less than five); however, EMP definitely represents a basic method for the majority of mineralogical and petrological studies. Secondary-ion mass spectrometry (SIMS)—a so-called ion microprobe developed in the 1980s, is another microbeam method sensitive also to light elements (e.g., H, Li, Be, and B). In addition to being a chemical analysis tool for almost all known elements, SIMS is also powerful for microprobe dating of geological processes using radiogenic isotopes (e.g., $^{235}U/^{204}Pb$, $^{206}Pb/^{207}Pb$, and $^{147}Sm/^{142}Nd$), but due to economic reasons this method is still not widespread in geological laboratories. Atomic absorption spectroscopy (AAS), X-ray fluorescence Analysis (XRF), and ion coupled plasma mass spectrometry (ICP-MS) represent other rapid and accurate methods, commonly used for analyzing major to trace elements, they are particularly used for whole-rock samples. Synchrotron X-ray fluorescence (SXRF), a new method using in microbeam techniques, is under development in the early years of the twenty-first century. Several other methods dealing with the chemical composition of minerals are also described in the next chapters.

3.2. Crystal Structure Methods

X-ray techniques, both powder and single crystal, are widely used to determine minerals and to characterize their crystal structures. Due to the relative rarity of well-formed crystals in nature, powder methods are more widespread and are used especially for the determination of minerals. Use of the Rietveld refinement method allows the extraction of structural information also from powdered specimens, which is especially important for the determination of crystal structures of finely crystalline minerals, (e.g., clay minerals, Fe and Mn oxides and hydroxides, and some zeolites). An X-ray single crystal study using automated four-circle diffractometers enables expansion of the determination of crystal structures and the order/disorder state, including structure refinements at high temperature and high pressure. The introduction of the charge-coupled device (CCD) detectors of X-rays to structure research promises a revolution in crystal structure study of minerals. Single-crystal study is focused particularly on rock-forming minerals (olivine, pyroxenes, amphiboles, micas, and feldspars) to better understand the crystal chemistry of these minerals and apply these data in thermodynamic models. The combination of large-scale structure refinement and microprobe work (EMP, SIMS) that is widely used is a powerful tool for a more complete characterization of geological processes.

X-ray absorption spectroscopy (XAS), and its methods X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine-structure (EXAFS), represent other powerful methods for the study of coordination number, bond lengths, and complexing of elements in glasses, particularly if a synchrotron is used as X-ray source (Figure 2).

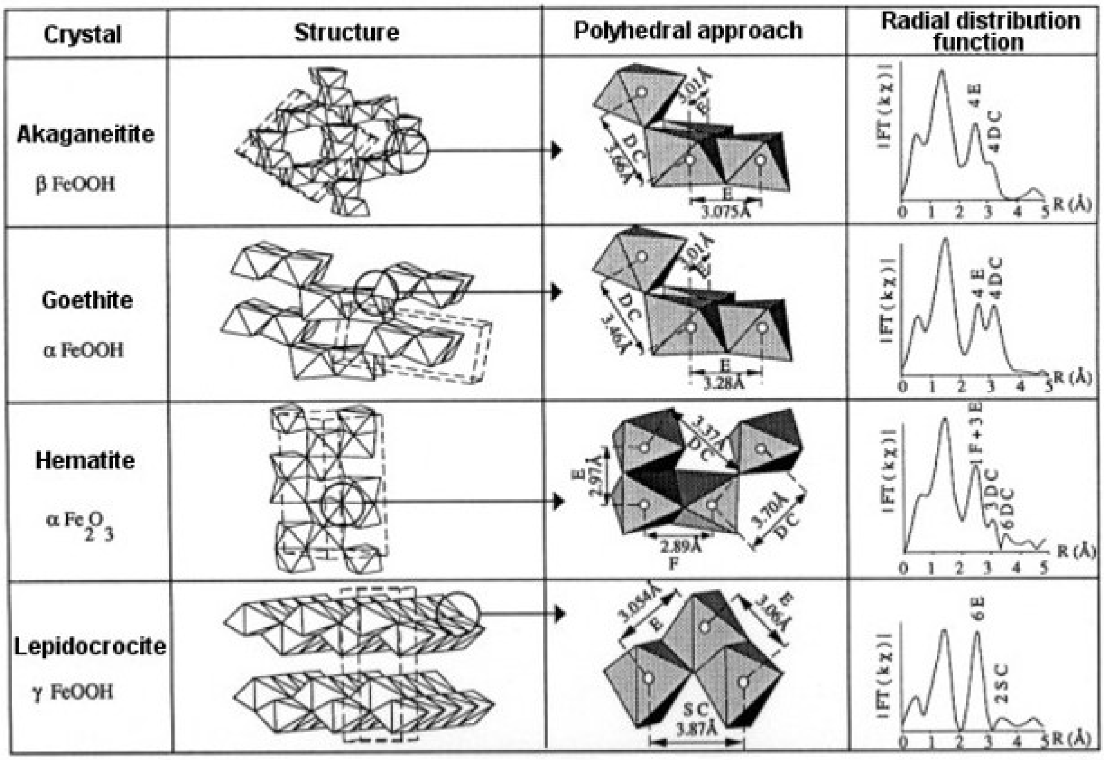

Figure 2. Polyhedral approach of the structure of Fe oxides differentiated on the local scale by EXAFS (from Marfunin A.S., ed. (1995). *Methods and Instrumentations, Results and Recent Developments*. Springer Verlag.).

The electron microscope is used in mineralogical research from the early 1970s to study various microstructures and to extend our power of observation below the resolution of the optical microscope. Scanning electron microscopy (SEM) has been widely used for several decades. Transmission electron microscopy (TEM) is used for the study of fine exsolutions-induced textures and is capable of revealing the presence of low-temperature solvi in many rock-forming minerals. The development of the technique of analytical electron microscopy (AEM) enables the quantification of chemical characteristics of such structures. High-resolution transmission electron microscopy (HRTEM) is used in the early years of the twenty-first century for such studies as radiation damage in crystal structures of minerals, which is quite important for the problem of nuclear-waste disposal.

3.3. Spectroscopic Methods

Spectroscopic methods may provide information concerning both chemical composition and crystal structure arrangements. Mössbauer spectroscopy (MS) enables reliable determination of the Fe^{2+}/Fe^{3+} ratio and different site populations to be derived in rock-forming minerals. The species ^{119}Sn, ^{121}Sb, ^{151}Eu, and ^{197}Au represent other suitable elements to be studied by this method. Vibrational spectroscopy includes two basic methods, infrared (IR) absorption spectroscopy and Raman spectroscopy (Figure 3). The IR spectroscopy is used to characterize the role of hydrogen (OH, H_2O, or both) in hydrous and also nominally anhydrous minerals, as well as in noncrystalline materials. It provides information about structure and complexity present in glasses and melts.

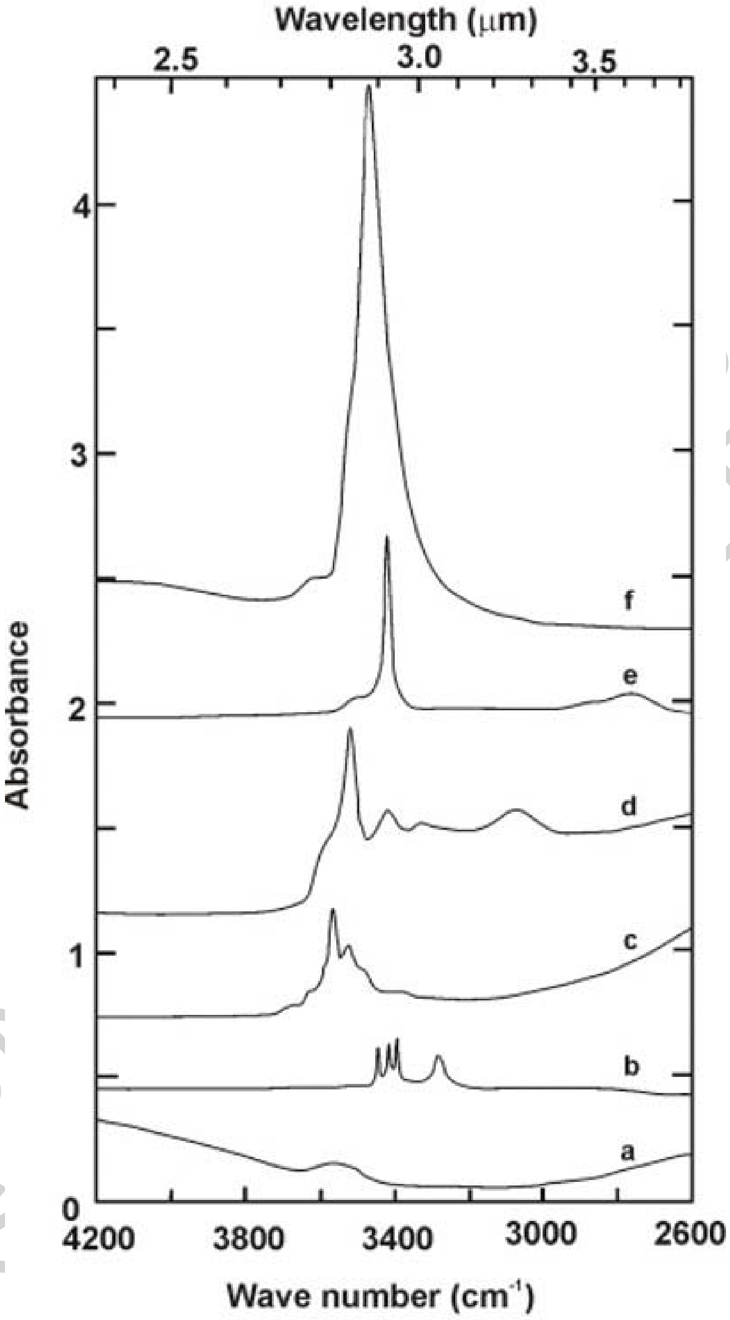

Figure 3. Polarized single-crystal IR spectra in the principal OH-stretching region of nominally anhydrous mantle minerals: (a) garnet, (b) kyanite, (c) olivine, (d) enstatite, (e) zircon, and (f) omphacite (after Bell D.R. and Rossman G.R. (1992). Water in the Earth’s mantel: the role of nominally anhydrous minerals. *Science* **255**, 1391–1397.).

Nuclear magnetic resonance (NMR) spectroscopy is used on diamagnetic minerals and noncrystalline materials (glasses and melts). The technique of magic-angle spinning

(MAS NMR) developed in 1980s is able to provide information about Si–Al distribution and local structure in silicate minerals (Figure 4). It is useful for local arrangement of other cations (e.g., B, Na, and Li). Electronic absorption spectroscopy (EAS) is used to specify valences of some cations (e.g., Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{3+}, V^{3+}, V^{4+}, etc.) in mineral crystals. This method is important to our understanding of coloration mechanisms in minerals.

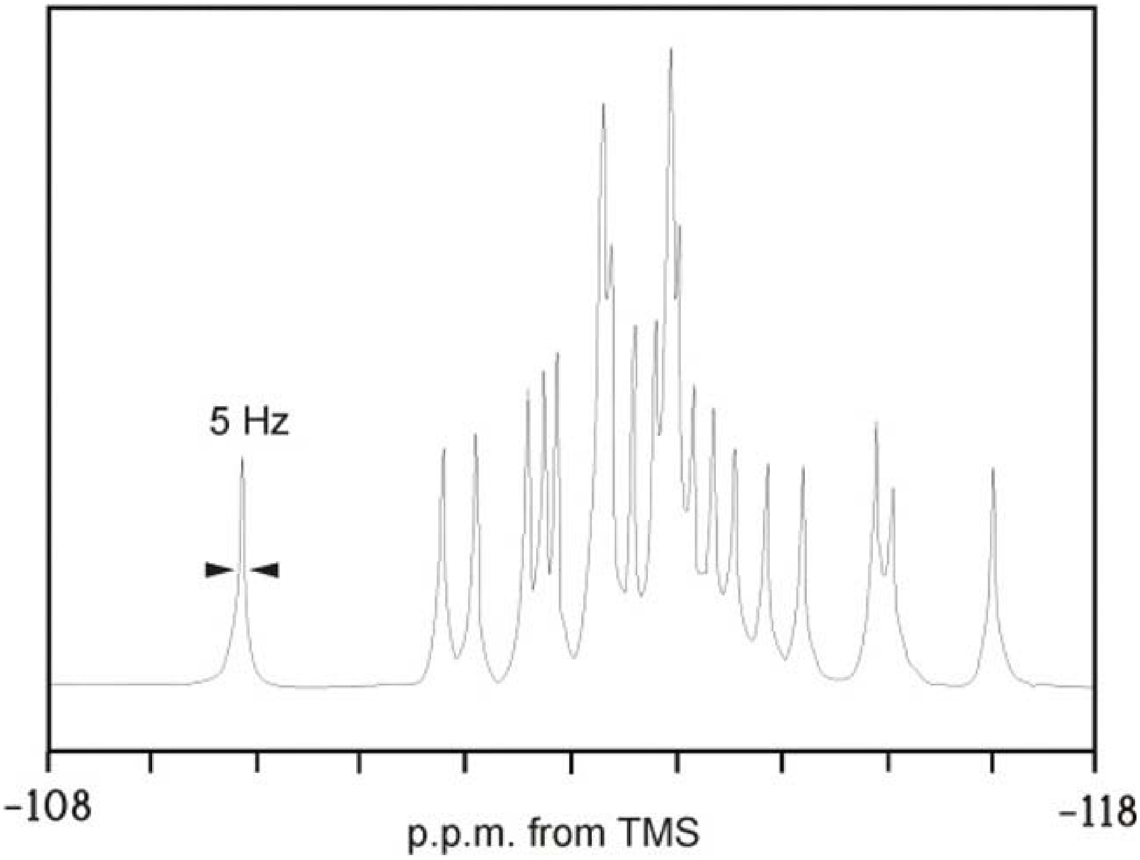

Figure 4. Ultrahigh-resolution MAS NMR spectrum of highly siliceous synthetic zeolite (ZSM-5), showing 21 of 24 crystallographically distinct Si sites resolved (from from Fyfe C.A., O'Brien J.H. and Strobl H. (1987). Ultra-high resolution 29SiMAS NMR spectra of highly siliceous zeolites. *Nature* **326**, 281-283.).

3.4. Mineral Surfaces Methods

The minerals participate during various geological processes in chemical reactions, which often occur at the mineral surface—that is, at the interface between solid mineral and the medium of interaction, which is commonly some sort of fluid. Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and several other techniques were used for characterization of surface processes at atomic level. Development of more recent methods, such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) (Figure 5), which are able to give images of the surface at atomic or near-atomic resolution, enable us to characterize such processes in much greater detail. This increase in knowledge of the atomic structure of surfaces has also led to extensive modeling of geochemical processes at or near mineral surfaces.

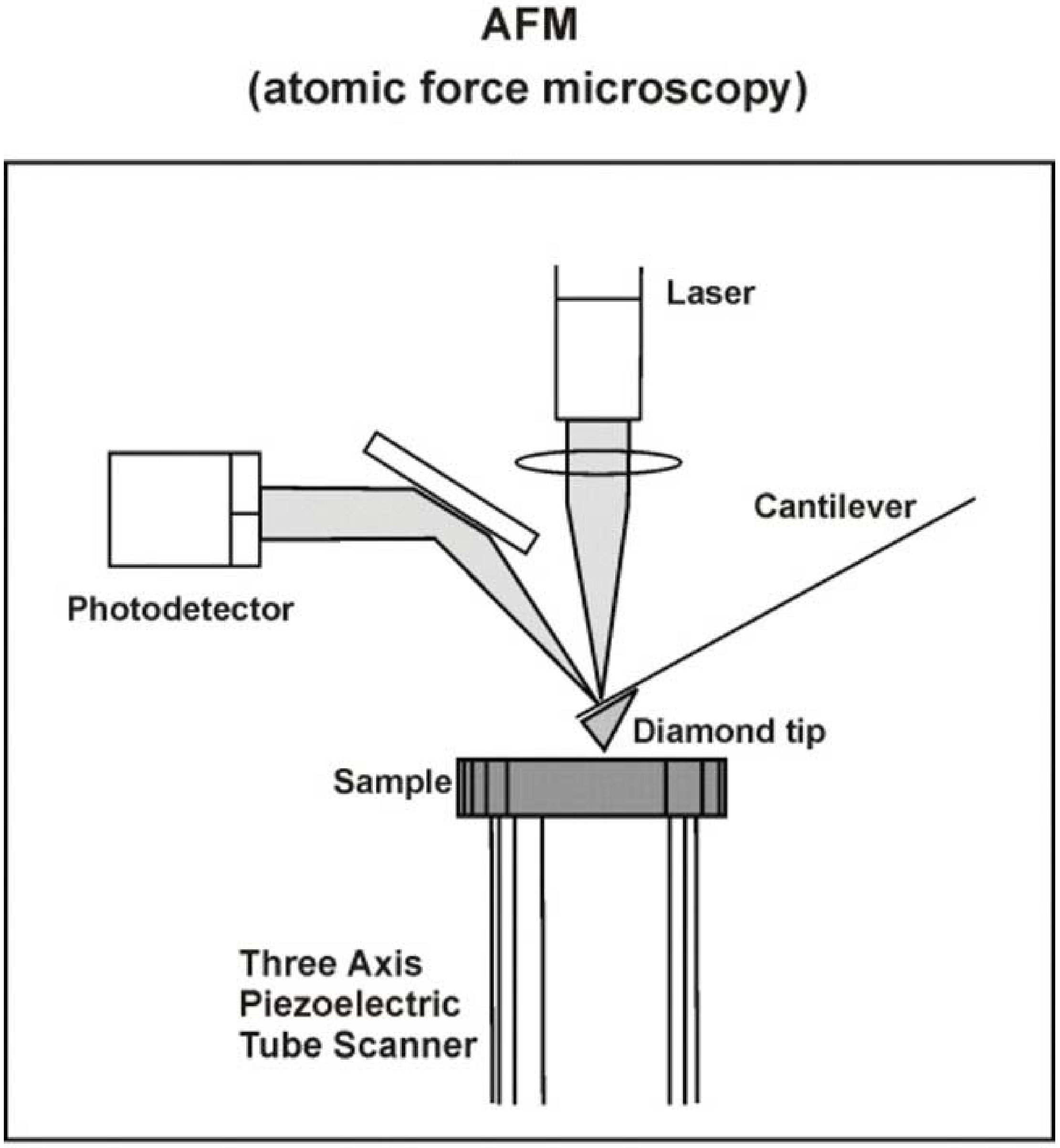

Figure 5. Atomic force microscopy (AFM)

Disregarding the fact that some of the above-mentioned methods require very expensive instruments and, therefore, they are currently utilized only at several laboratories worldwide, their significance in mineralogical research is on the upswing. Particularly valuable are those methods that may provide information about the behavior of minerals in variable environments, including biomineralization (see *Early Earth* and *Time in the Geological Past of Earth*).

4. Mineralogical System

4.1. Theoretical Basis

The systematic classification of the individual species, as in many other scientific disciplines, represents a basis for the study; simply said, we have to use the same terms for the same items—in our case, minerals. The current mineralogical system is based on chemical classification scheme published already by J.D. Dana in the middle of the nineteenth century. It currently includes ~3700 mineral species, but only small portion of them (several hundred) are abundant and have economic importance. Minerals are divided into classes depending on the dominant anion or anionic group (e.g., sulfides, oxides, carbonates, borates, and silicates). The reasons why this criterion is a valid basis for the mineral classification are as follows: (a) minerals having the same anion or anionic group in their composition have apparent family resemblances, (b) minerals with the same anion tend to occur in similar geological environments, and (c) such a scheme of mineral classification agrees very well with the current classification of inorganic chemical compounds. Chemistry alone does not adequately characterize a mineral. Internal structure was introduced to the mineral classifications, and crystal structures are the basis for the division into subclasses; within the silicate class, for example, chains, sheet, and framework silicate subclasses exist. Although it is not easy to provide a simple definition of *mineral*, the following is generally accepted: A mineral is a naturally occurring homogeneous solid with a definite (but generally not fixed) chemical composition and a highly ordered atomic arrangement. It usually formed by inorganic processes. This view, however, seems to be now too restrictive, and the role of minerals in inorganic and organic (biological) processes will be discussed in Section 5.

4.2. Elements

With the exception of the free gases of the atmosphere, only ~25 elements were found in the native state. This class can be divided into three subclasses: metals, semimetals, and nonmetals. Typical minerals include native copper, silver, gold, sulfur, platinum, graphite, and diamond, all of which have current and historical industrial significance as ore minerals (Au, Ag, Pt), gems, and/or raw materials in chemical industry.

4.3. Sulfides

This important class involves majority of ore minerals; ~550 mineral species are known. The general formula is given as X_mZ_n, where X represents the metallic element (Cu, Pb, Zn, Ag, Hg, Sb, Co, Ni, Mo, etc.) and Z represents the nonmetallic element (commonly sulfur, but also As, Te, or Se). Most of the sulfide minerals are opaque and metallic with distinctive colors. The sulfides are divided into small groups with similar structure and formulas. Typical and abundant sulfide minerals include pyrite, sphalerite, chalcopyrite, pyrrhotite, galenite, antimonite, bornite, cinnabarite, molybdenite, arsenopyrite, and tetrahedrite. Oxidation of some widespread sulfides (e.g., pyrite and pyrrhotite), known from variable rocks and ore deposits, plays a very important role in pollution of local supplies of water. The sulfide minerals from ore deposits are also the source of various heavy metals that pollute water and soils. Some sulfide minerals (e.g., pyrite and markazite) originated during biological processes.

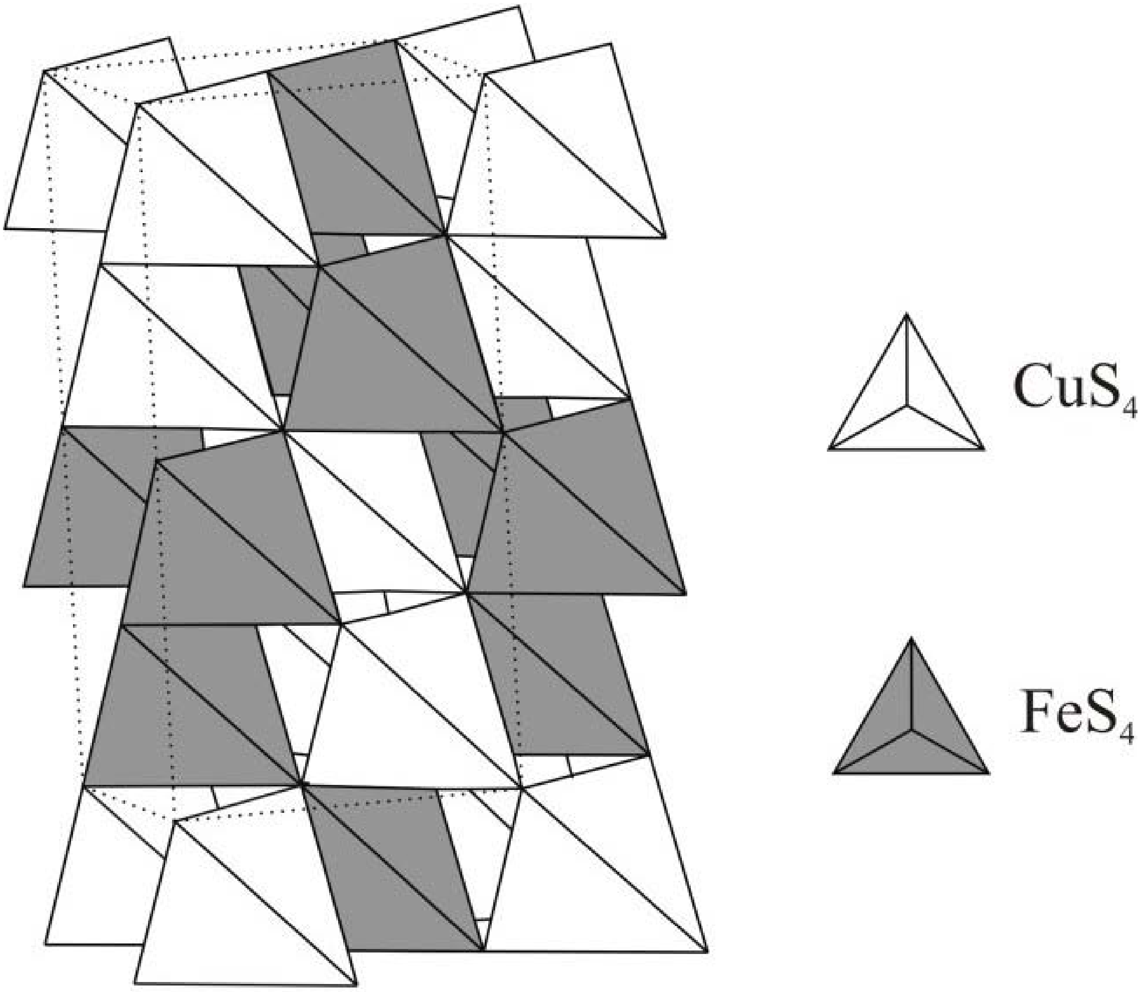

Figure 6. Crystal structure of chalcopyrite

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Biographical Sketch

M. Novák is employed in Masaryk University, Brno, Czech Republic, as head of the Department of Mineralogy, Petrology, and Geochemistry. However, he spent most of his career at the Moravian Museum, Brno, as a mineralogist and curator of the mineralogical collection, as well as director of the Section of Earth Sciences. In 1977, he graduated from Masaryk University and in 1988 completed his doctoral dissertation at the Department of Petrology, Charles University, Praha. Between 1991 and 1993 he was a postdoctoral fellow at the University of Manitoba, Winnipeg, Canada. His research interests include mineralogy, petrology, and geochemistry of leucocratic granitic rocks (pegmatites, granites), crystal chemistry, petrology, and physical properties of tourmaline, Nb,Ta-oxide minerals, borates, and other silicate minerals. He has published ~150 journal papers and abstracts, some of them issued in leading scientific journals. Since 1994, he has been a national representative of the Czech Republic to the International Mineralogical Association (IMA), member of the Commission for New Minerals and Mineral Names, and member of the Commission on Museums. In cooperation with the University of Manitoba, Winnipeg, he organized the scientific symposiums Lepidolite 200 in 1992 and Tourmaline in 1997.