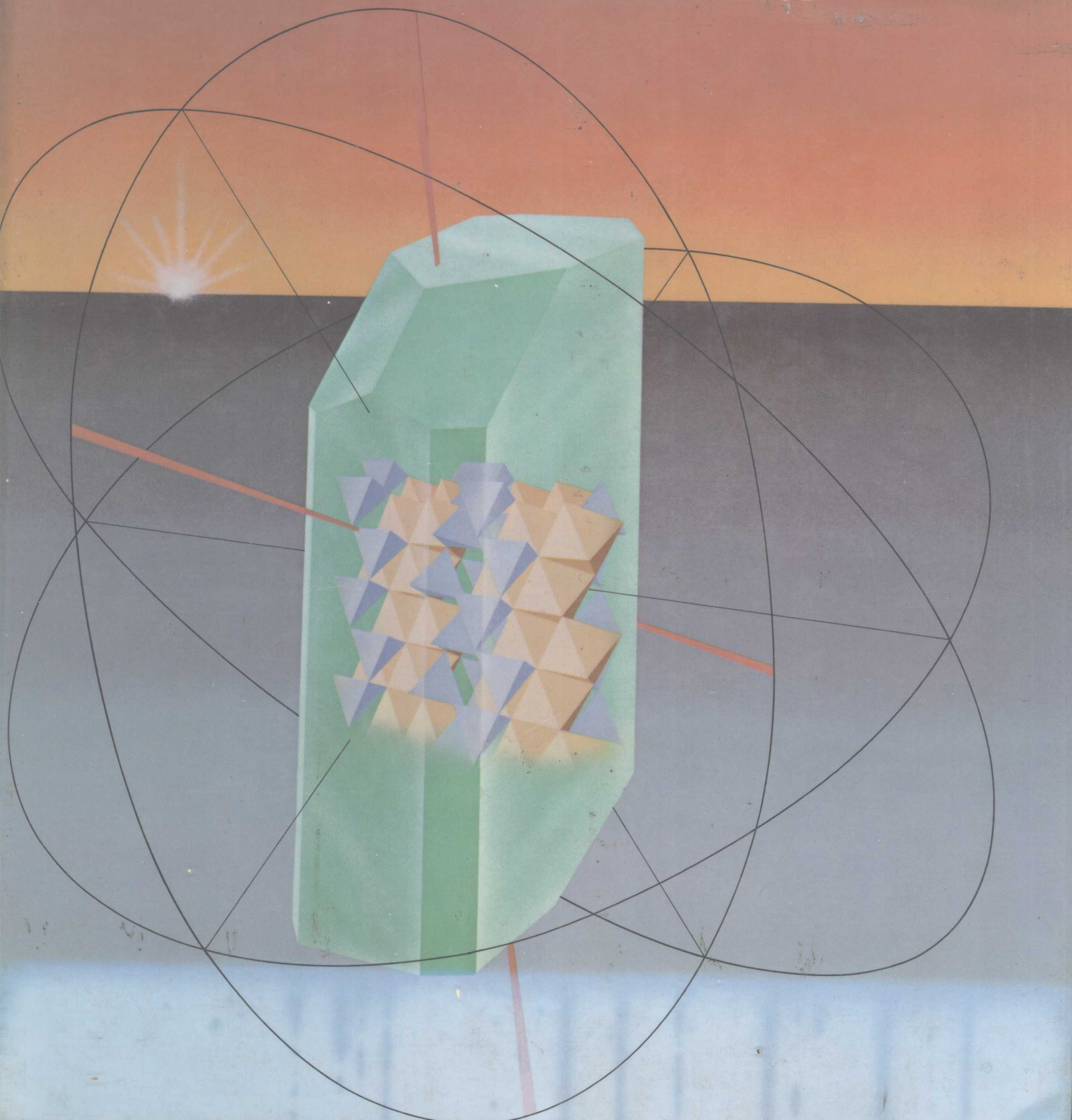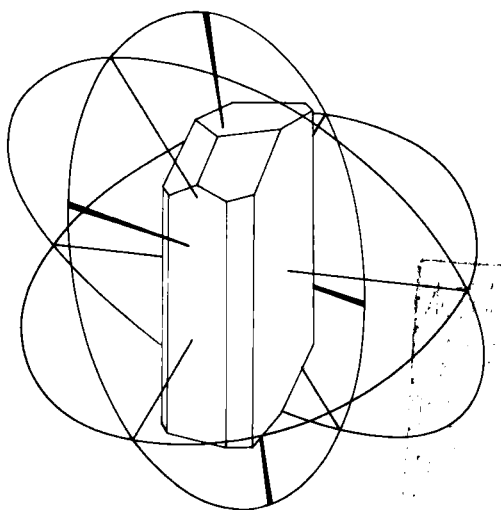# MINERALOGY
## CONCEPTS AND PRINCIPLES

### TIBOR ZOLTAI and JAMES H. STOUT

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## CONCEPTS AND PRINCIPLES

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*To Olga and Ann*

# PREFACE

Education in mineralogy has undergone rapid change in the last few years with the development of new instrumentation and the input of current research. For an undergraduate student, the demands are great. Since the turn of the century, mineralogy as a science has developed more along the lines of classical chemistry and physics. Today's student of mineralogy must be well versed in a scientific community in which *crystal chemistry* and *crystal physics* are common terms. At the same time, every mineralogist should be exposed to and aware of the large body of observational data on which the explanations of physics and chemistry are based. Going to the extreme in either direction has disadvantages. Too much emphasis on the descriptive aspects of mineralogy leaves the student with an unmanageable body of observational data, with few underpinnings as a basis for understanding. At the other extreme, a crystal chemist who cannot distinguish quartz from feldspar cannot be considered a mineralogist. Students are somehow expected to learn all of descriptive mineralogy that has gone before, and then to learn much of what modern research considers important today.

For the instructor, the demands are also great. Decisions must be made as to what of the old can be sacrificed for the new. This seems unavoidable in light of current research and the realization that the needs of the modern student of mineralogy are changing. The contents of this book have evolved from more than 20 years of collective teaching in response to those needs. It is designed for an introductory course at the university level, and is prerequisite to a first course in petrology or geochemistry. We emphasize the importance of fundamental principles in the belief that students who are well grounded in basic concepts can better assimilate and systematize in their own mind the vast body of descriptive mineralogy. Much of the conventional descriptive mineral data has been excluded. In its place in Part II of this text are nearly 100 stereographic representations of mineral structures. These, we believe, are essential to the understanding of how mineral chemistry and physical properties are related to mineral structure. Students are expected to refer continually to these representations where appropriate to the content of Part I. Throughout the text, the mineral names are followed by a representative mineral formula designed to convey information about both structure and chemistry. We hope that by repeated exposure, students will be better able to relate a mineral name to the crystalline substance it represents.

Through the years we have experimented with the organization of the subject matter of mineralogy. In Part I, the sequence of topics finally adopted begins with a review of descriptive mineralogy. The purpose of the review is in part historical, for this descriptive information led early mineralogists to formalize the concepts of symmetry that are so important to all that follows in the text. The purpose of our review is also practical, for it starts students off with a three-dimensional conception of real minerals that is an immense aid when crystal structures and their relation to physical properties are introduced. In Chapters 2 and 3 we explain the language of symmetry and crystallography. That language combined with concepts of chemical bonding in Chapter 4 prepares the student for a discussion of crystal structures in Chapter 5. Chapters 6 and 7 focus on crystal physics and crystal growth, and Chapters 8 and 9 explore the relationships between mineral chemistry, mineral structure, the stability of minerals, and mineral associations. Chapters 10 and 11 describe the diagnostic techniques of x-ray mineral-

ogy and optical mineralogy. We introduce the methods of x-ray diffraction (Chapter 10) and optical mineralogy (Chapter 11) in our mineralogy laboratories as routine tools to be used and refined in later courses. The bulk of descriptive mineralogy is included in Part II of the text. Part II is intended as a supplement to Part I and for laboratory use.

Some chapters may have more depth of coverage than necessary for the average student. In our experience, most students gain from knowing that mineralogy involves more than just mineral identification, and the more conscientious students are provided the stimulation and challenge they want and need.

This is an exciting time to be in the field of mineralogy. We are now learning for the first time by direct experiment how single crystals behave at high temperature and pressure—the very conditions under which most minerals form. We are also on the verge of being able to predict the structure and properties of minerals that lie deep in the earth's crust and mantle where no human will probably ever tread. With modern microscopy, we are also beginning to see actual atoms in minerals—a goal mineralogists have long dreamed of but have not realized until now.

Throughout the text, we have adopted the international units of measurement (SI). Putting to rest the revered calorie and Ångström units may seem an unnecessarily harsh step for U.S. readers, but to resist is to postpone the inevitable. Our experience has been that resistance to change is more from educators than from students to whom the units of Ångström and nanometer (nm) are equally unfamiliar. A list of conversion factors is included in Appendix 1.

# CONTENTS

# PART I

# PRINCIPLES AND CONCEPTS

The first part of this text is devoted to the basic principles and concepts on which the science of mineralogy is based. The subject matter is organized in 11 chapters, each of which relies to some extent on material presented earlier. We begin in Chapter 1 with some historical background followed by an overview of the common physical properties of minerals. Chapters 2 and 3 introduce the language of symmetry and crystallography. In Chapter 4 these important relationships are combined with the concepts of chemical bonding to set the stage for crystal structures, the subject of Chapter 5. The following chapters, 6 and 7, on crystal physics and crystal growth, rely heavily on symmetry and structure. Chapters 8 and 9 deal with the important relationships between mineral chemistry and crystal structure, and the stability of minerals and their associations. The final two chapters deal with the theory and techniques of x-ray mineralogy and optical mineralogy.

1

# CHAPTER ONE

# MINERALS AND THEIR PROPERTIES

Mineralogy as a science dates back to the time when humans first wondered at the beauty and order of natural crystals. The use of minerals is as old as civilization itself. The first civilized humans survived because they recognized that certain minerals would provide sustenance and protection when fashioned as tools or weapons. As people came to depend on minerals, they became more selective of their various properties. Minerals for adornment and even for presumed magical powers became an important part of their life. Human intelligence to seek out certain minerals for their desirable properties was the basis for an early form of descriptive mineralogy.

Since then, nearly 3000 distinct minerals have been systematically studied and described in the mineralogical literature. This great accumulation of printed information has made impractical, if not impossible, the task of reading, analyzing, and digesting all of the information on one's own. Data collection is a necessary function of every science, and when gathered and assimilated, new concepts always emerge that guide further studies. In view of this, the approach employed in the following chapters is based on the belief that once students are armed with a relatively small number of fundamental concepts, they are able to discover and understand additional examples and applications far too numerous to be covered in a college course in mineralogy.

Before embarking on the subject, let us consider a few of the reasons why scientists study minerals. An important reason is that minerals occur in one form or another in nearly all inorganic materials of everyday life. Most familiar are the natural metals, which are derived from the earth and are used in everything from space-age alloys to amalgam to fill cavities in our teeth. A glance around any classroom quickly reveals that nearly every item has a mineral basis. The window glass is made primarily from feldspar and quartz, the chairs are metal, and even the wood and synthetic plastic items can be traced back ultimately to minerals in the earth.

Much of our space-age technology stems directly or indirectly from mineralogical studies. The quest to find and synthesize exceedingly pure crystals made possible the development of lasers and of oscillators, semiconductors, and transistors that form the essence of modern electronics. The Space Program and the first Apollo 12 samples from the moon marked a new era for mineralogical research in which numerous important advances have been made. These studies indicate that exploration of our neighboring planets is likely to reveal mineralogical problems similar to those encountered on earth.

Another reason to study minerals is that they are the constituents of nearly all rocks in the earth's crust and mantle. Research in the last 50 years has shown that some minerals can exist in a stable form over only a narrow range of pressure and temperature. Experimental confirmation of this range enables the scientist to make a correla-

tion between the occurrence of a mineral in a rock and the conditions under which the rock was formed. This approach, perhaps more properly considered in the field of petrology, has helped scientists to unravel the earth's complicated history.

Finally, the study of minerals satisfies our natural curiosity about how things happen in nature. The most fundamental principles of science are reflected in one form or another in all natural phenomena. By understanding how and why minerals behave in their unique manner, we gain insight into other processes. Those insights can then be applied to predict the properties and behavior of different minerals or substances.

## SOME EARLY HISTORY

The emergence of mineralogy as a separate field of study was signaled in 1556 by the publication of *De re metallica libris XII* by the German physician Georgius Agricola, known also as Georg Bauer. Agricola summarized for the first time a collection of observations that had accumulated for centuries in the midst of folklore and legend. Aided by his own factual observations, he outlined several categories of mineral properties that included color, transparency, luster, hardness, flexibility, and cleavage.

Based on observations of this kind, attempts were made as early as the 17th century to relate the physical appearance and properties of minerals to their internal structure. The internal structure of exactly *what* was still a fundamental question that would not be answered for another three centuries. Nonetheless, early scientists and philosophers conceived of tiny building blocks arranged in an internally periodic array long before the existence of atoms was demonstrated. The physicist and astronomer Johannes Kepler speculated in 1611 on the planar arrangement of spheres as a possible explanation of the symmetry of snowflakes. He recognized the two unique geometrical arrangements that today form the basis for the study of closest-packed structures (Chapter 5). Other 17th century scholars, such as René Descartes, Robert Hooke, and Christian Huygens, subsequently made contributions to the concept that mineral properties were more fundamentally related to internal structure.

Niels Stensen, whose name was latinized to Nicolaus Steno, studied further the external forms of crystals. Stensen was a physician known in his time for his contributions to anatomy. Drawing on his knowledge of how plants and animals grow and are nourished by internal fluids, he asserted

that crystals grow by the addition of particles from an external fluid. He concluded, correctly, that the process of crystal growth is directional in nature, and that the eventual shape of a crystal depends on growth rates in different directions. Based on his study of the morphology of natural crystals, in 1669 he formulated the general relationship that the angles between the same two faces of a crystal are always constant, regardless of the size or shape of the crystal faces. This relationship later became known as Steno's law.

An important stage in the development of mineralogy came with the rising industrialism of the 18th century. There was a growing need to develop methods for identifying minerals and for systematizing mineral properties. In 1768, Carolus Linnaeus put forth one of the first systems of mineral classification. He was convinced that he had discovered in the mineral kingdom the same principles that had played such an important role in his botanical work. Based on common external properties, his system was divided into orders, classes, and species. The external form of the crystal was central to his classification, and his descriptions of crystals were so carefully done that later researchers referred to him as the founder of the science of crystallography.

In 1774, Abraham Werner, a professor of mineralogy at Freiburg, Germany, proposed the first comprehensive and consistent system of mineralogy. In his system of about 300 species, external form was only one of several properties that required evaluation before identification could be made. Werner's students spread his teachings over most of the civilized world, but his work was later attacked as being unscientific because it was not based on any single established theory of that day.

A milestone came in 1784 when René Just Haüy, in his *Traité de cristallographie*, conceived of crystal structures made up of identical *molecules integrantes*, or integral molecules. Figure 1.1, from Haüy's treatise, illustrates how similar his thoughts were to the modern concept of the space lattice and how clearly he visualized the relationship of the lattice to external crystal form. Haüy's successful synthesis of the current ideas of his time was coupled with his own studies of calcite ($CaCO_3$) and its distinctive rhombohedral cleavage. Because the rhombohedral form could be observed down to the eye's limit of resolution, Haüy believed that form to be characteristic of one of several basic building blocks from which all minerals were derived. Implicit to Haüy's theory was that each integral molecule had a specified chemistry, although he relied much more on form than chemistry in his classification. In his
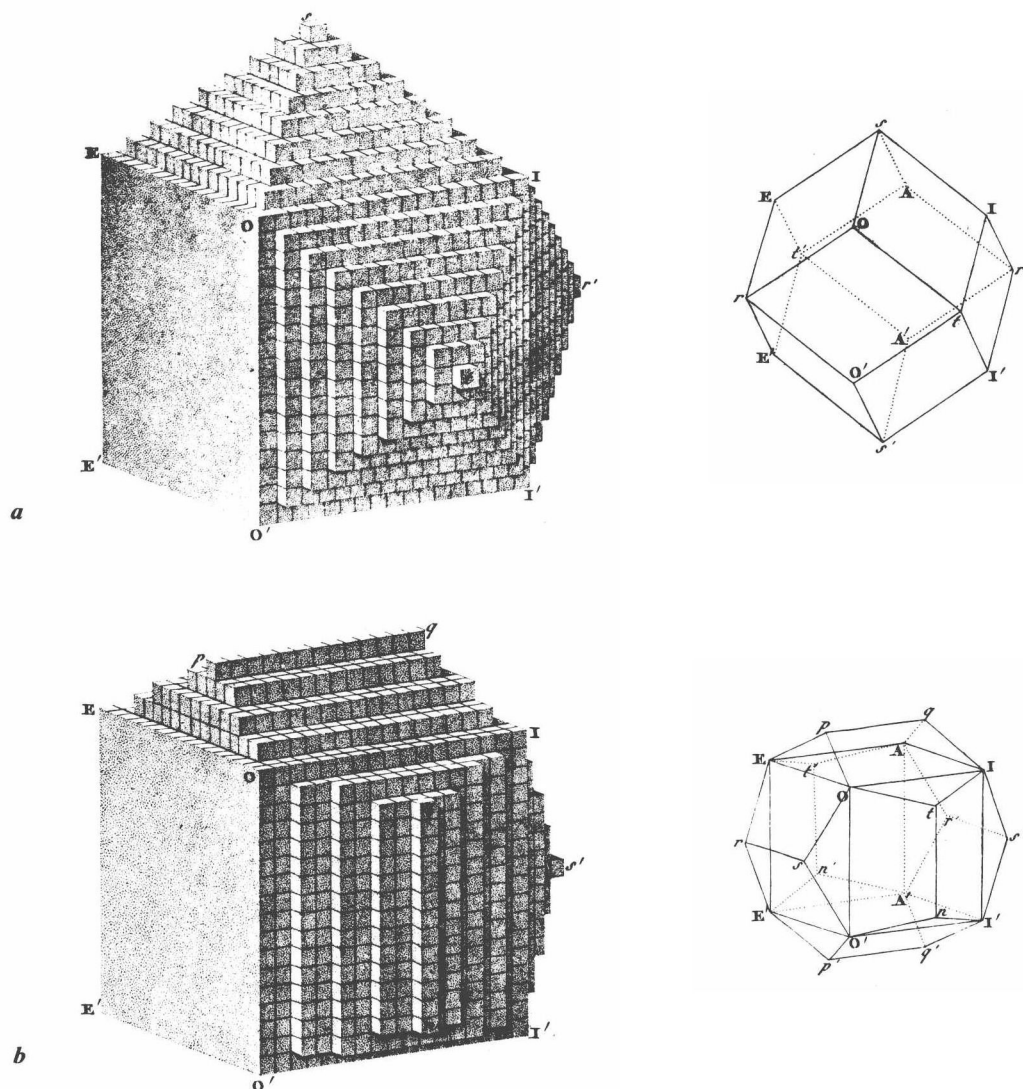
FIGURE 1.1 (a) René Haüy's illustration of how the dodecahedron (12 faces) crystal form with rhombic faces is derived from a cubic nucleus or integral molecule. (b) Haüy's derivation of the dodecahedron with pentagonal faces from the cubic nucleus. (From Haüy, R. J., 1801. *Traité de minéralogie*. vol. 5, plate II.)

view, the integral molecule was the basic substance itself, and any further division would destroy its identity as such.

The priority of Haüy's concept of the relationship between internal structure and external morphology is not entirely clear. Eight years earlier in 1773, the Swedish chemist and mineralogist Torbern O. Bergman demonstrated how the scalenohedron of calcite ($CaCO_3$) could be formed from the rhombohedral nucleus (Figure 1.2) with angles of 101.5 and 78.5 degrees. Haüy was apparently aware of Bergman's results, but he discusses them only in the context of Bergman's erroneous attempt to relate the dodecahedral form of garnet to the rhombohedral nucleus of calcite. Bergman's most significant contribution was in the chemical

analysis of minerals in the laboratory. In 1779, Bergman gave a full account of the use of the blowpipe for chemical tests on minerals. It was the chemical approach to mineralogy more than anything else that eventually led to the downfall of Haüy's theory.

As chemistry began to contribute more to the science of mineralogy, the role of crystal forms became less dominant. After the turn of the century, Francois Beudant, a former student of Haüy, discovered that aqueous solutions containing differing proportions of dissolved ferrous sulfate ($FeSO_4$) and zinc sulfate ($ZnSO_4$) always crystallized the same distinctive rhombohedral crystals on evaporation. Haüy's theory held that $FeSO_4$ and $ZnSO_4$ had different forms, and thus Beu-

dant's observation led to controversy. Beudant concluded that chemically composite compounds were not mechanical mixtures of two different, integral molecules as Haüy believed, but rather were chemical mixtures that exhibit a continuous range of physical properties. About the same time, William H. Wollaston completed a similar study



**FIGURE 1.2 Torbern Bergman's illustration of how the calcite prism (HURCIFP) and scalenohedron (HCIF) could be derived from a rhombic nucleus (COFD). (From Bergman, T. O., 1773. Variae crystallorium formae, e spatho ortae.** *Nova Acta Regiae Societatis Scientiarum Upsaliensis.* **vol. 2, plate II.)**

of calcite (CaCO$_3$), magnesite (MgCO$_3$), and siderite (FeCO$_3$), concluding like Beudant that those minerals should be regarded as homogeneous chemical mixtures having the same crystal form. With these results, the modern concept of *solid solution* or *isomorphism* was established.

Similar problems with Haüy's theories arose with the recognition that even though calcite (CaCO$_3$) and aragonite (CaCO$_3$) have entirely different physical properties, they have identical chemistries. In 1821, Eilhard Mitscherlich, a student of the Swedish chemist and mineralogist Jons J. Berzelius, proposed the modern concept of *polymorphism* by demonstrating that an identical number of the same elements can arrange themselves in such different ways that resulting external forms and physical properties are different.

With evidence mounting that the internal arrangement of chemical elements in minerals is highly symmetric, Christian Samuel Weiss set the science of crystallography on a new course. A brilliant scholar who received his doctorate at the age of 20, Weiss was a proponent of the polar theory of matter, which held that elementary particles were drawn together by attractive forces and held apart by repulsive forces. His formulation of the concept of crystallographic axes and their relationship to symmetry axes in a three-dimensional space was published in 1815. By considering mutually perpendicular axes, he identified the isometric, tetragonal, and orthorhombic crystal systems. He also recognized the natural divisions of minerals into those with sixfold rotational symmetry and those with threefold rotational symmetry. Hence hexagonal and trigonal crystal systems came into being. Then in 1825, Friedrich Mohs, the successor to Werner at Freiburg and inventor of the hardness scale that bears his name, demonstrated that both monoclinic and triclinic systems exist by considering nonorthogonal crystallographic axes.

The science of crystallography now developed rapidly. Johann Hessel, the German physician and mineralogist, derived in 1830 the fact that there are exactly 32 crystal classes, and that only twofold, threefold, fourfold, and sixfold axes of rotational symmetry are compatible with translation. Hessel's findings were based on his exhaustive study of the possible types of symmetry any geometrical form might have. In 1840, Gabriel Delafosse wrote correctly that the integral molecule of Haüy was the outline of nodes in the crystal lattice—that is, a geometrical element distinct from the physical and chemical entity we now call the unit cell. This observation was a major turning point conceptually, for it stripped
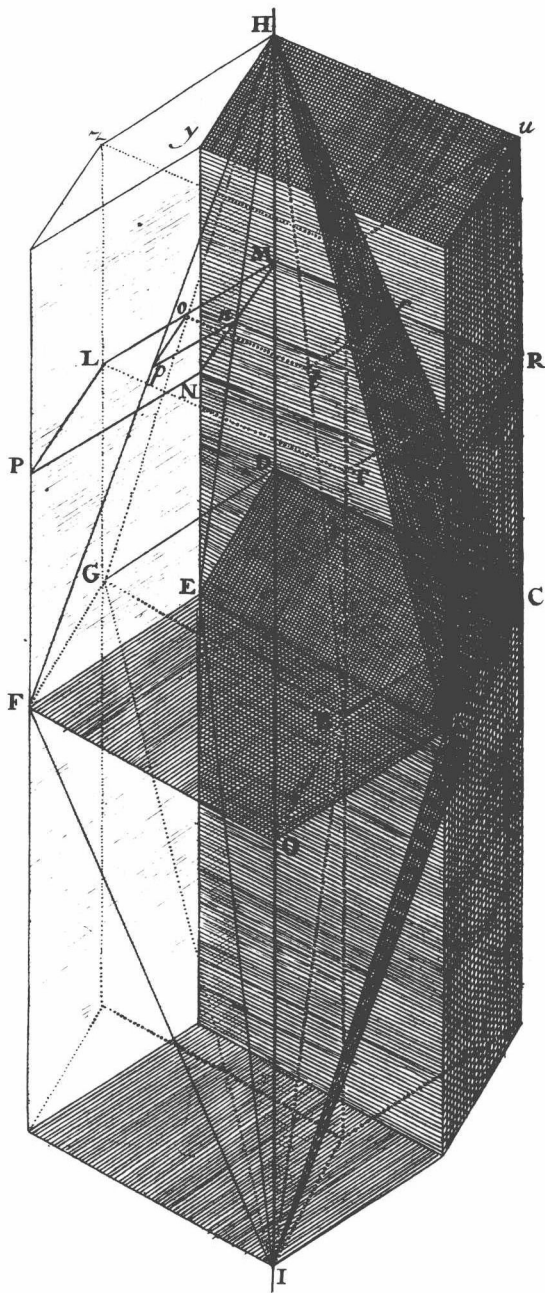
Haüy's form of any chemical significance. In 1848, Auguste Bravais proposed independently the 32 crystal classes that Hessel derived earlier. More importantly, Bravais proposed the 14 space lattices that were the forerunner of space group theory. Bravais perceived that the 14 lattices consisted of seven different lattice symmetries, which corresponded to the previously recognized seven crystal systems. His work established the fact that external symmetry is grounded on the concept of the space lattice.

The last major question that remained was exactly how atoms were arranged within unit cells. It became a geometrical problem for scientists to determine the number of symmetrical ways in which points could be arranged in space such that the environment around each point was identical. In 1879, Leonard Sohncke provided part of the answer by recognizing two new symmetry elements called a screw axis and a glide plane. Armed with these concepts, the Russian crystallographer E. S. Federov derived the 230 space groups and published his results in 1881. Artur Schoenflies, a German mathematician who was unaware of Federov's work, used mathematical group theory and published the same results in 1890. About the same time, William Barlow, a self-educated genius who had the unusual advantage of independent wealth, also concluded after studying the symmetrical arrangement of spheres that there must be 230 space groups.

With Röntgen's discovery of x-rays in 1895, the stage was set to test the earlier structural models. In 1911, Max von Laue, professor of physics at the University of Munich, and his two assistants Walter Friedrich and Paul Knipping, passed a narrow beam of x-rays through a crystal of copper sulfate, and history was made. Diffraction spots appeared on a photographic plate placed behind the crystal. The group concluded that such a response could only occur if (1) x-rays were electromagnetic in nature and had short wavelengths and (2) those wavelengths were diffracted by a regular arrangement of atoms with spacing comparable to those wavelengths.

This result launched the entire field of crystal structure analysis. Two years later in 1913, the first crystal structure was determined by the father-and-son team of William H. Bragg and William L. Bragg. For their discovery, the Braggs jointly received the Nobel Prize for physics in 1915. The fields of solid-state physics and crystal chemistry were born. The precise positions of atoms in structures and the distances between atoms were determined for the first time. Inferences on the actual sizes of atoms, and the types and strengths of chemical bonds between atoms followed.

In the 70 years since the first crystal structure was determined, mineralogy as a science has benefited from important technological advances. The advent of sophisticated x-ray precession cameras in the 1940s enabled crystallographers to collect better data for crystal structure refinements. Today, with the aid of automated diffractometers, the basic structures of all but a few minerals are known. With the development of the electron probe microanalyzer (microprobe) in the 1960s, determining the chemical composition of a single crystal over areas no greater than a few hundredths of a millimeter in diameter is now a routine procedure. The scanning electron microscope (SEM) is another instrument that has opened an entirely new world of observation, providing magnification and resolution far beyond that obtainable with the optical microscope. A related instrument, the transmission electron microscope (TEM), has signaled a new, exciting era of mineralogical research. With the TEM, atoms and their arrangements are directly imaged to yield a view of minerals never before possible.

## MINERAL CLASSIFICATION

Every beginning student of mineralogy soon discovers an incredible variety of minerals. They occur in all colors, shapes, and sizes, and in all rocks from the most beautiful museum specimens to common roadside gravel. All minerals have one common property—they are crystalline. That is, their internal structure is characterized by a periodic and predictable array of atoms, ions, or molecules. This property alone distinguishes minerals from chemically equivalent liquids and gases, and imparts to minerals their unique chemical and physical characteristics. We therefore define a *mineral* as *any naturally occurring crystalline substance*. The condition that a mineral must be naturally occurring is mostly for convenience. There is an entire field of study that involves the manufacture of exceedingly pure crystals for electronic and other industrial purposes. Some of these crystals are equivalent in every respect to naturally occurring minerals. The condition that all minerals be crystalline is generally valid, although in a few instances the degree of crystallinity might be questioned. The term *mineraloid* applies to naturally occurring substances such as obsidian and opal, the structures of which may be only partially crystalline or even noncrystalline.

An important consequence of the periodic arrangement of atoms in crystalline structures is

that certain groups of minerals have common properties that clearly set them apart from all other mineral groups. Crystalline structure imposes definite limits on the range of chemical composition in each group, and no intermediate states of symmetry, chemistry, or other physical properties will exist within certain limits.

One objective of mineralogical studies is to provide a meaningful scheme by which a large body of mineral properties can be organized. In creating such a scheme, the best place to begin is to recognize that all properties of minerals are fundamentally related to their *chemistry* and *structure*. Any attempt to classify minerals in terms of chemistry at the exclusion of structure, or vice versa, shows immediately how closely these two factors are related. An examination of the elemental composition of the earth's crust (all of the rocks on earth down to a depth of about 40 km beneath the continents and to a depth of about 10 km beneath the oceans) reveals that oxygen is unquestionably the most abundant element (Table 1.1). For every 100 atoms in the earth's crust, 63 are oxygen and 21 are silicon. By volume, oxygen constitutes well over 90% of most crustal rocks and over 90% of most minerals that occur within crustal rocks (Table 1.1).

Because of the abundance and relatively large size of the oxygen anion ($O^{2-}$), the possible geometric arrangements of $O^{2-}$ determine to a great extent the structural framework of most of the silicate and oxide minerals. As a first approximation, the structure of these minerals may be considered in terms of a symmetrical framework of oxygen anions, with the interstitial voids that remain being occupied by the smaller, less abundant cations. The other common anions are sulfur

($S^{2-}$), chlorine ($Cl^{1-}$), and fluorine ($F^{1-}$). Although much less abundant than $O^{2-}$, they behave in much the same way by dominating the structural framework of the sulfide and halide minerals. In addition, a number of cations combine with oxygen to form *anionic groups*, which, like oxygen or sulfur alone in other minerals, dominate the volume and structural framework of mineral groups such as the carbonates, sulfates, and nitrates.

The generally recognized chemical classification of minerals based on the predominant anion or anionic group is listed here in the same order as described in Part II. Of these categories, the silicate minerals are easily the most abundant in most crustal rocks.

1. Silicate minerals: Oxygen anions combined with silicon cations to form either $SiO_2$ or various $SiO_x$ anionic groups. The latter groups combine with various cations. Example: wollastonite ($CaSiO_3$).
2. Native elements: naturally occurring metallic and nonmetallic elements. Example: gold (Au).
3. Sulfide minerals: Sulfur anions combined with various cations. Example: pyrite ($FeS_2$). The anions As, Se, and Te are included in this category.
4. Halide minerals: F, Cl, and I anions combined with various cations. Example: halite (NaCl).
5. Oxide minerals: Oxygen anions combined with various cations other than Si. Example: periclase (MgO).
6. Hydroxide minerals: Hydroxyl (OH) groups combined with various cations. Example: brucite ($Mg(OH)_2$).

**TABLE 1.1.** *Atomic Abundances of the Common Elements in the Earth's Crust and in Some Common Silicate Minerals*

| Element | Ionic Radius* | Crustal Composition | | | Quartz ($SiO_2$) Vol.% | Albite ($NaSi_3AlO_8$) Vol.% | Anorthite ($CaSi_2Al_2O_8$) Vol.% | Diopside ($CaMgSi_2O_6$) Vol.% |
|---------|---------------|--------------|------------|-------------|---|---|---|---|
| | | Weight Percent | Atom Percent | Volume Percent | | | | |
| O | 0.134 | 46.6 | 62.6 | 93.8 | 98.7 | 93.3 | 91.6 | 88.6 |
| Si | 0.034 | 27.7 | 21.2 | 0.9 | 1.3 | 0.9 | 0.6 | 0.8 |
| Al | 0.047 | 8.1 | 6.5 | 0.5 | — | 1.0 | 1.9 | — |
| Fe | 0.069 | 5.0 | 1.9 | 0.4 | — | — | — | — |
| Mg | 0.080 | 2.1 | 1.8 | 0.3 | — | — | — | 3.0 |
| Ca | 0.108 | 3.6 | 1.9 | 1.0 | — | — | 5.9 | 7.6 |
| Na | 0.124 | 2.8 | 2.6 | 1.3 | — | 4.8 | — | — |
| K | 0.168 | 2.6 | 1.4 | 1.8 | — | — | — | — |

*Ionic radii from Appendix 5 are for the most common coordinations: $O^{2-}$ (8), $Si^{4+}$ (4), $Al^{3+}$ (4), $Fe^{2+}$ (6), $Mg^{2+}$ (6), $Ca^{2+}$ (6), $Na^{1+}$ (8), and $K^{1+}$ (12).