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Part I Minerals as chemical compounds

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Subject and history of mineralogy

Along with mathematics and astronomy, mineralogy is among the oldest branches of science. In this introductory chapter we explore the roots and evolution of mineralogy, with a first book written by Theophrastus in 300 BC to over 20 Nobel Prizes awarded for research involving crystals. We will discuss the different directions in mineralogy and provide a summary of the organization of the book.

I.I What is mineralogy?

The answer to the question posed above may seem obvious: mineralogy is the study of minerals. From introductory geology classes you may know that all rocks and ores consist of minerals. For instance, quartz, biotite, and feldspar are the main minerals of granites; and hematite and magnetite are the major minerals of iron ores. At one point mineralogy was well defined as dealing with those naturally occurring elementary building blocks of the Earth that are chemically and structurally homogeneous. This simple definition of a mineral has changed over time. As the definition of "mineral" has become more vague the boundaries of "mineralogy" have opened and increasingly overlap other sciences.

In this book we take a broad view of mineralogy. Minerals are naturally occurring, macroscopically homogeneous chemical compounds with regular crystal structures. Traditionally also included are homogeneous compounds that do not have a regular structure such as opal (a colloidal solid), natural liquid mercury, and amorphous mineral products formed by radioactive decay, known as *metamict* minerals. Rocks, ores, and mineral deposits, which are studied in petrology and geochemistry, will also be discussed in order to emphasize the geological processes that are of central interest to all who study Earth materials.

Other materials are more peripheral but nevertheless have similar properties and obey the same laws as the minerals mentioned above. For example, ice is mainly the object of glaciology, planetary and soils science. Apatite (a major constituent of bones and teeth), carbonates (which form the skeletons of mollusks), and oxalates and urates (of which human kidney stones are composed) are studied in medicine and in a specific branch of mineralogy called "biomineralogy". Crystals growing in concrete, known as *cement minerals*, are not natural products but they are of enormous economic importance. Other artificial compounds with a crystal structure occur as a result of industrial transformations in natural conditions. They may form because of chemical alteration of buried waste products or by means of interaction between the soils and contaminated groundwater. Modern environmental geology, hydrology, and soils science are concerned with these mineral-like materials and study them with methods similar to those employed in mineralogy.

Mineralogy is broadening its scope and now overlaps other disciplines in a way that was not envisioned a few years ago. For example, newly discovered hightemperature superconductors have a structure related to the mineral perovskite and often possess a morphology resembling clays. We will include a discussion of some of the new subjects of mineralogy in this text, but our focus is on those natural, chemically and structurally homogeneous substances that form due to geological and biogeological processes in the Earth. In particular, we concentrate on rock- and ore-forming minerals, which are a small subset of the almost 5000 mineral species that are currently known.

1.2 History

Mineralogy and crystallography are old branches of science. For example, crystals, with their regular

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morphology, are known to have fascinated Ancient Greek philosophers. Indeed, the name crystal derives from the Greek *krystallos* (meaning "ice") and was applied to quartz, since the Ancient Greeks thought that this mineral was water that had crystallized at high pressure deep inside the Earth. Accordingly, the German term *Bergkristall* (meaning "mountain crystal"), a synonym for quartz, has survived to this day. Note that the term crystal is also used for glass with a brilliant reflection. Such glass is not related to minerals and, in fact, is not even crystalline. In this section we will discuss a few highlights in the early history of mineralogy. Those interested in more details will find a great deal of information in Burke (1966) and Groth (1926).

The Greek philosopher Theophrastus (300 BC), a pupil of Aristotle, wrote the first known book on minerals, entitled On Stones (see Caley and Richards, 1956). Similar to the focus of this text, Theophrastus' book was greatly concerned with the origin of minerals. It begins: "Of those substances formed in the ground, some are made of water and some of earth. Metals obtained by mining come from water; stones, including the precious kinds, come from earth." As we will see later, this statement, although highly simplified, does contain some truth. Some minerals precipitate from solutions, others crystallize from a melt. The name mineral originates from Latin and relates to materials that are excavated in mines (mina is the Latin word for "mine", and minare is Latin for "to mine"). Pliny the Elder, who was killed in the eruption of Vesuvius in August AD 79, summarized the knowledge on minerals at his time, describing over 30 minerals in his Historia Naturalis (see Lenz, 1861), among them galena, molybdenite, chalcopyrite, beryl, and augite. The mineralogy of Pliny emphasized minerals that were of economic interest, giving descriptions and discussing their occurrence and usage. For example, he writes about diamond: "More expensive than all other gems and any other human possessions are diamonds (adamas). They are only known to kings, and even among them only to a few. Indian diamonds resemble quartz (krystallos). They are transparent, have a regular form with smooth surfaces and are the size of a hazelnut."

It was nearly 1500 years later, with the publication of *De Re Metallica* in 1556 by the German mining engineer and physician Georg Bauer (known as

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Agricola) from Freiberg, Saxony (Figure 1.1a), that mineralogy emerged as a science. Succeeding centuries brought important advances, one of which was the discovery by Niels Stensen (Nicolas Steno) in 1669 (Figure 1.1b) that angles between the regular faces of crystals are always the same, in spite of differences in shape or size. Probably inspired by the observation of a regular cleavage in calcite by the Swedish mineralogist Torbern Bergmann (1773), in 1784 the French scientist René J. Haüy (Figure 1.1c) interpreted this law of constancy of interfacial angles. He suggested that all crystals are composed of elementary building blocks, which he called "integral molecules". The building blocks later became known as "unit cells". A macroscopic crystal can be thought of as a threedimensional periodic array of such unit cells. The regularity of faces and interfacial angles is obvious, for example in a cubic crystal of halite or in an octahedron of magnetite.

During the eighteenth and nineteenth centuries, most of the important minerals were described. A. G. Werner (Figure 1.1d), a mining geologist in Freiberg, proposed a chemical classification of minerals (e.g. Hoffmann, 1789). This classification was later refined by Swedish chemist J. J. Berzelius and is still in use today. It became the basis for the first comprehensive textbooks in mineralogy, such as those by Haüy (1801), Dana (1837), Breithaupt (1849), and Groth (1904). Mathematicians, among them J. F. C. Hessell (1830), A. Bravais (1850), E. S. Fedorow (1885, 1892), and A. Schoenflies (1891), investigated the possible symmetries of a material with a regular morphology and periodic internal structure, as suggested by Haüy, and developed a system to classify minerals according to symmetry. At that time there was considerable debate among chemists and mineralogists about whether the concept of internal structure (or "lattice") really applied or whether, instead, crystals were continuous. Johann Joseph Prechtl (1810) advanced the concept of stacking of spherical particles and hypothesized that "atoms" had no form in the liquid state but took spherical form during solidification. The sketches of William Hyde Wollaston (1813; Figure 1.2a) illustrate different arrangements of spheres that are the basis of simple metal structures, as we will see in Chapter 2. While Wollaston thought that all atoms were of the same size, William Barlow (1897) suggested that the size may be characteristic of elements and that

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Fig. 1.1 Four pioneers of modern mineralogy. (a) Georg Bauer (Agricola), (b) Niels Stensen (Nicolas Steno), (c) René J. Haüy, and (d) Abraham Gottlob Werner.

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Fig. 1.2 Early models of crystal structures. (a) Wollaston (1813) assumed that crystals consisted of close-packed spheres (different gray shades indicate different elements). (b) Barlow (1897) refined the model by assuming different sizes of atoms and correctly predicting the structure of halite.

a crystal structure of binary compounds could be obtained as close-packing of such spheres. He correctly predicted the structure of halite (Figure 1.2b).

Before 1800 most research on minerals and crystals was based on visual observations and measurements of angles between crystal faces with mechanical goniometers. This changed in 1809 when Wollaston developed a reflecting goniometer that allowed much more accurate measurements. It was perfected in 1893 with a two-circle goniometer (Figure 1.3a), independently by E. S. Fedorow in St. Petersburg, S. Czapski in Jena, and V. Goldschmidt in Heidelberg who published the fundamental "Kristallographische Winkeltabellen" (Goldschmidt, 1897) based on goniometer measurements (see, e.g., Burchard, 1998).

Another essential instrument is the petrographic microscope, which is still the most important tool used to identify minerals in rocks (Chapters 13 and 14). Its development started in 1828 with a microscope designed by W. Nicol that could analyze mineral fragments with polarized light and was advanced over many years. The instrument proposed by Rosenbusch (1876) and built with R. Fuess is basically the foundation of modern petrographic microscopes (Figure 1.3b), without which mineralogic–petrologic research would be unthinkable (e.g., Medenbach, 2014).

The theories about the atomic structure of crystals based on crystal morphology and symmetry were highly speculative and the issue was only resolved in 1912, when Max von Laue and his coworkers in

Munich irradiated crystals with X-rays and observed diffraction, proving that crystals have indeed a lattice structure and that X-rays are waves (Chapter 11). At this point mineralogy became an experimental science and expanded considerably, as will be detailed in Part III. In 1914 William Lawrence Bragg published the first crystal structure determination, which described the detailed atomic arrangements in halite. A modern textbook of mineralogy incorporating the new advances in structural investigations was written by Paul Niggli (1920). If you look through it, you will discover many figures that are still reproduced in textbooks today. X-ray diffraction was the favored analytical technique at that time. Much later, electron microscopes and spectrometers became important tools. Hightemperature and high-pressure techniques eventually became available to produce minerals in the laboratory under any conditions found in the Earth and beyond. A significant part of this research on minerals was carried out by physicists and chemists, and the boundaries of mineralogy became more and more blurred.

Mineralogy is established both as an independent science and as a support discipline for many other branches of science (Figure 1.4). Table 1.1 lists some famous mineralogists who have made outstanding contributions to science. The relevance of mineralogy– crystallography, in the context of scientific endeavor, is also highlighted by the unusual number of Nobel Prizes in Physics, Chemistry, and even Medicine that have been awarded for achievements related to Cambridge University Press & Assessment 978-1-107-51404-1 — Minerals 2nd Edition Hans-Rudolf Wenk , Andrey Bulakh Excerpt <u>More Information</u>



Fig. 1.3 (a) Two-circle Stoe goniometer developed by Goldschmidt to measure angular relationships between crystal faces (courtesy O. Medenbach). (b) The first "modern" petrographic microscope built by Fuess and Rosenbusch in 1876 (courtesy O. Medenbach and T. Mappes).



Fig. 1.4 Minerals are the core of mineralogy. But mineralogy is of interest to many different disciplines.

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Table 1.1 Some famous mineralogists (not including living mineralogists)

Name, date	Country	Contribution
Georg Bauer (Agricola) 1494–1555	Germany	Detailed description of minerals
Niels Stensen (Nicolas Steno) 1638-1686	Denmark	Law of interfacial angles
Torbern O. Bergman 1735–1784	Sweden	Cleavage of calcite
René Just Haüy 1743–1822	France	Concept of unit-parallelepipeds
Abraham G. Werner 1750–1817	Germany	Origin and properties of minerals
Lorentz Pansner 1777–1851	Germany/Russia	Hardness and density of minerals
Johan J. Berzelius 1779–1848	Sweden	Chemical mineralogy
Johann A. Breithaupt 1791–1873	Germany	Density of minerals, parageneses
Eilhard Mitscherlich 1794–1863	Germany	Isomorphism and polymorphism
Johann F.C. Hessel 1796–1872	Germany	Point-group symmetry
Auguste Bravais 1811–1863	France	Lattice types
James Dwight Dana 1813–1895	USA	Systematic mineralogy
Nicolai Koksharoff 1818–1892	Russia	Goniometry of crystals
Harry Rosenbusch 1836–1914	Germany	Optical mineralogy
Gustav Tschermak 1836–1927	Austria	Silicate structures
Paul von Groth 1843-1927	Germany	Chemical crystallography
Ephgraph S. Fedorow 1853–1919	Russia	Space-group symmetry
Artur Schoenflies 1853–1928	Germany	Space-group symmetry
Viktor Goldschmidt 1853–1933	Germany	Geometry of crystals
Penti Eskola 1883–1964	Finland	Igneous minerals
Alexander Fersman 1883–1945	Russia	Mineral-forming processes
Norman L. Bowen 1887–1956	USA	Experimental petrology
Paul Niggli 1888–1953	Switzerland	Mineral-forming geological processes
Viktor M. Goldschmidt 1888–1947	Norway/Germany	Crystal chemistry, geochemistry
William L. Bragg 1890–1971	Great Britain	Crystal structure of minerals
Nicolai Belov 1891–1982	Russia	Mineral structures
Paul Ramdohr 1890–1985	Germany	Ore minerals
Cecil E. Tilley 1894–1973	Great Britain	Igneous and metamorphic minerals
Tom F. W. Barth 1899–1971	Norway	Petrology
Francis J. Turner 1904–1985	New Zealand/USA	Metamorphic minerals and deformation
Dmitry P. Grigoriev 1909–2003	Russia	Crystal growth

crystallography and research methods used in mineralogy, beginning with Röntgen (1901), von Laue (1914), and the Braggs (1915) for X-rays and more recently to Brockhouse and Shull for neutron diffraction (1994), to Curt, Kroto, and Smalley for the structure of fullerenes (1996), and to Geim and Novoselov for the structure of graphene (2010).

1.3 Major directions of investigation

Mineralogy is concerned with the characterization of properties and chemical composition of minerals and the study of the conditions of their formation. Since minerals are substances that concentrate certain chemical elements (such as metals), they are economically important and are studied to define mineral resources and exploration techniques. Any mineralogist must be able to identify minerals in order to search for them in the field and to investigate mineral samples with the most important laboratory techniques. Mineralogy is also the science that relates naturally occurring substances of crystalline structure to the more basic sciences of crystallography, chemistry, materials science, and solid-state physics. Mineralogy borrows from these disciplines information about the atomic structure, bonding characteristics, chemical stability, and growth processes of various compounds, and adopts various analytical

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1.4 Some preliminary advice

methods. In return, mineralogy often provides answers to puzzling features in complex human-made products.

We can distinguish several major directions in mineralogical studies. Sometimes they are independent, but often they overlap and cannot be separated. Some investigations may be classified as "basic mineralogy", whereas others can be considered as "applied mineralogy"; both types of investigation include experimentation and theory. It is in part this diversity that makes mineralogy such a fascinating topic.

There are several major branches of basic mineralogy:

- Crystal chemistry of minerals (composition, structure, and bonding)
- Physical properties of minerals (e.g., density, optical properties, color)
- Studies of mineral formation including:
 - General principles of crystal growth
 - Geological processes on the surface and in the interior of the Earth
 - Chemical reactions, and the influence of temperature and pressure
- Relationships between mineral structure, chemical composition, properties, crystal habit, and the conditions under which minerals form

The most important directions of *applied mineralogy* are:

- Mineral identification, determination of morphology, composition, and properties
- · Exploration mineralogy and ore deposits
- Industrial mineralogy (cement minerals and zeolites are examples)
- Gemology
- Mineralogical aspects of material science and solidstate physics (many ceramic products have mineral equivalents)
- Biomineralogy
- Minerals as health hazards (e.g., asbestos)

This book is organized into six parts that cover these various fields. Part I deals with the chemistry and elementary structure of crystals. The chemical composition of minerals has become the basis for classification. In order to connect readers early with macroscopic properties, we will also have a section on basic mineral identification of hand specimens. An intrinsic feature of crystals is symmetry, and it will be discussed in some detail in Part II. Symmetry is expressed in the external morphology of crystals as well as in the arrangement of atoms in the crystal structure. Part III introduces methods used for the physical investigation of minerals, ranging from X-ray diffraction to optical microscopy and advanced techniques such as spectroscopy and electron microscopy. Of the physical properties, the optical properties are most important for petrologists, who study minerals in rocks by means of thin sections with the petrographic microscope. Part IV deals with the diversity of minerals and explores the general conditions and processes of mineral formation, with a discussion of thermodynamic principles that govern the chemical reactions. Part V contains a systematic survey of the most important minerals, including their structure, diagnostic properties, geological occurrence, and industrial use. We also highlight in this part some of the major geological processes of mineral formation in sedimentary, igneous, and metamorphic environments. Part VI introduces applied mineralogy outlining the major branches, from mineral resources to cement minerals - and the major methods of investigation. Included in this part are chapters on gemology and the health aspects of minerals. The concluding two chapters provide an overview and review of the distribution of minerals in the universe, the solar system, and the Earth. Four appendices follow the main part of the book: the first two may be used for mineral identification from hand specimens, the third and fourth for identification with the petrographic microscope.

1.4 Some preliminary advice

Mineralogy is not an easy field for a novice to enter. Not only are you confronted with many new concepts, there are also new names to absorb and you need to develop your own judgment to distinguish the crucial from the optional. Memorizing mineral names is not the most inspiring aspect of mineralogy, but it is useful to learn the most important minerals and their general composition, just as it is useful in language studies to learn the important words. In addition to reading books on the subject, you have to become practically acquainted by working with actual mineral specimens. The lectures in a mineralogy course need to be complemented with a laboratory that uses hand specimens and introduces laboratory techniques such as the petrographic microscope and X-ray diffraction. A good start is to visit museum collections that display spectacular and aesthetically beautiful mineral

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Fig. 1.5 (a) Crystal of sucrose $(C_{12}H_{22}O_{11})$ with regular flat faces. Sugar is not a mineral because it is industrially manufactured (from Baikow, 1967). (b) Crystal of halite (NaCl) from Fulda, Germany (courtesy O. Medenbach). The morphology displays cubic building blocks that suggest an internal structure with cubic unit cells as suggested by Haüy.

samples. If you have the opportunity, begin collecting some of your own samples in the field, buy some at flea markets and bring them to class. For beginners, get some specimens first from pegmatites, skarns, and hydrothermal deposits because these predominantly coarse and well-developed crystals can be easily recognized.

In the process of these practical exercises begin to use a notebook in which you enter mineral descriptions. It is enough to allot just half a page to a mineral or a page to a deposit. Relate minerals to their geological occurrence and classify them into minerals observed in igneous rocks (ultrabasic, basic, acid, alkaline, and volcanic rocks), pegmatites (mica-bearing, quartz-bearing, etc.), skarns (developing at a contact of igneous rock with limestone or dolomite), deposits of the weathering crusts (laterites, bauxites, and oxidized ores), chemical (from real and colloidal solutions), biogenic, and diagenetic deposits (alteration of sediments during compaction and burial). Describe in detail which features of major minerals you have observed with your own eyes. Slowly integrate your knowledge so that each mineral becomes an entity with a name, a chemical fingerprint (for some remember the formula, for complex ones remember at least a list of major elements), distinguishing features, the geological system in which they occur, and, for many, an industrial application (ranging from metal ore to food additive). As you familiarize yourself with mineralogy, minerals will become much more than dry names. They will emerge as multifaceted building blocks that help us understand the processes that govern the Earth.

1.5 Definition of crystal and mineral

Before we enter the field let us try to define *crystal* and *mineral*. This is a first attempt which will become clearer as we gain more background:

- A *crystal* is a homogeneous chemical compound with a regular and periodic arrangement of atoms. Examples are halite, "salt" (NaCl), and quartz (SiO₂). But crystals are not restricted to minerals: they make up most solid matter such as sugar (Figure 1.5a), cellulose, metals, bones, and even DNA.
- A *mineral* is a chemical compound that forms by a geological process. Figure 1.5b shows a crystal of halite where the cubic morphology suggests an internal structure with cubic unit cells. Most minerals are crystalline.

1.6 Summary

Mineralogy dates back to antiquity but evolved as a main branch of modern science in the eighteenth century. Much of our present knowledge about minerals was attained by research done in the twentieth century with modern analytical techniques such as X-ray diffraction. Minerals are defined as homogeneous chemical compounds that form by a geological process. Most minerals are crystals with a periodic arrangement of atoms.

Test your knowledge

- 1. What is a mineral and what is a crystal?
- 2. Name some principal objects and applications of mineralogy?

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I.6 Summary

- 3. Which branches of science and engineering are most closely related to mineralogy?
- 4. What are the major directions of modern mineralogical research?
- 5. Find a mineral in your daily environment.

Further reading

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