# The changing science of
# mineralogy

Hurlbut and Wenden

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THE CHANGING SCIENCE OF

# MINERALOGY

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# PREFACE

Throughout most of its history, the science of mineralogy has been largely descriptive. The properties of minerals were measured and catalogued. Minerals were classified and reclassified in the light of refined measurements. Their occurrence and associations were noted and theories of their origin—unproven and untested—were advanced. Early in the 20th century, with the advent of X-ray crystal analysis, the purely descriptive era of mineralogy came to an end. With it came an understanding of the internal structure of minerals. With this new information, many of the problems that had baffled and perplexed the earlier mineralogists were solved. In spite of this revolution in mineralogical thought, most present-day books for the beginner in mineralogy are not greatly different from those of the 19th century and are completely descriptive.

*The Changing Science of Mineralogy* is written to give the reader an understanding of the impact 20th century advances have had on mineralogical thought and method. In Chapter 1 a high school senior visits a mineralogical laboratory and learns not only what a mineralogist does but also what training is necessary for a professional career. Chapters 2, 3, and 4 deal with the chemical elements, the regular arrangements of the atoms in crystals, and the forces which hold the atoms together. In Chapters 5 and 6 are discussed the physical properties of minerals and the outward shapes of crystals, resulting from internal structure. The final chapter illustrates how the knowledge gained from the study of natural minerals can be applied in laboratory and industry to the manufacture of like substances. Approximately eighty of the commonest minerals are mentioned in the book. These minerals and their physical properties that serve in identification are listed in the Appendix.

This book does not pretend in any sense to be a textbook of mineralogy. It is written in the hope that the brief glimpses it affords of the mineralogist's view of the basic concepts of mineral composition and structure will prompt the reader to pursue the subject further.

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# INTRODUCTION

There was not always a science of mineralogy. Indeed not long ago there was no science in the sense in which we use the word today. If we think of science as a purposeful enquiry into the nature of the universe by controlled experiments and quantitative observations, then science is a relatively new kind of human activity. The so-called science of the civilizations of the ancient world was very different from modern science. The priests, philosophers, and engineers of Egypt and Babylonia did not try to find out anything about the earth or the stars. They worked to disclose the wishes of inscrutable deities and to predict the fate of men and kings. The ancient philosophers rarely asked of the natural world "Why?" or "How?" but rather "Who?" This attitude, which peopled the world with invisible beings and unpredictable forces, persisted for a long time.

Further, manual labor, even to the extent necessary to perform a physical experiment, was regarded as demeaning by many. This prejudice against personal experimentation endured into medieval times. Its effect was to keep thought about the natural universe at the level of speculation unsupported by observation and untested by experiment. This was the age of fabulous stones with magical properties and minerals that conferred invisibility or invulnerability.

The great cultural and intellectual revolution in the 16th and 17th centuries, called the Renaissance, came to the rescue of natural science. Thus in this age of Galileo, Kepler, and Newton mineralogy as a science was born.

A 16th-century German physician Georgius Agricola deserves credit for some of the earliest factual accounts of minerals and mining. His writings are like a breath of fresh air, blowing away the cobwebs of superstition and prejudice. His best known work *De Re Metallica* (1546), translated into English by former president Herbert Hoover and Mrs. Hoover, may be seen in most public libraries.

In 1669, a thoughtful Dane, Nicolaus Steno, examined quartz crystals from many localities. He noted that despite their differences in size and overall form, they displayed constant angles between corresponding faces. This observation set the stage for investigation of crystals by establishing that the external form is not haphazard but a regular characteristic of the substance.

In 1784, René Just Hauy (how'y), a professor at the University of Paris, published a textbook containing a revolutionary view of crystals. Crystals, Hauy stated, were built up by the stacking together of minute, identical building blocks. Although too small to see, the shape and size of these units determine the external form of the crystal. Further, he showed how the relations between the smooth bounding faces on a crystal could be described by simple geometrical methods.

Hauy died in 1822, honored as the Father of Geometrical Crystallography. The ninety years after his death were filled with extensions of the ideas already laid down. Chemical analysis of minerals was developed into a fine art between 1810 and 1850 by the Swede Berzelius and his students. Optical mineralogy and the polarizing microscope, made possible by the invention in 1828 by Nicol of a device for producing polarized light, became a mainstay of mineralogists. Wollaston, an English chemist, invented in 1809 an optical goniometer for measuring angles between crystal faces. The theory of arrangement of points, and hence of atoms, in space was worked out in complete detail between 1850 and 1900. But this theory of space groups remained for many years without experimental verification.

Then in 1912, with a single experiment made under the direction of von Laue (rhymes with Hauy) in Munich, Germany, the old era ended and a new era began. X rays were found to be "reflected" by the atomic planes within crystals yielding data on the arrangement of atoms. In 1913, the first crystal structure was worked out by W. H. and W. L. Bragg in England. Of the several thousand papers published every year giving X-ray data on crystals, many are about minerals and are written by mineralogists.

With the knowledge of mineral structures, the mineralogist took a broader view of minerals, seeing them as crystalline solids, identical in many cases with the products of the laboratory. In the 1920's crystallography and chemistry met on common ground to create a new science, crystal chemistry, which has proved to be the most fruitful and illuminating approach to minerals.

Mineralogy today, although it can boast as long a history and as honorable a parentage as chemistry or physics, is not as large a field and is yet relatively uncrowded. Because of the comparatively small number of mineralogists, there are more opportunities for mineralogists in industry and teaching than there are qualified men and women to fill them. Women, incidentally, have in many cases, made distinguished careers in mineralogy, especially in its crystallographic aspects.

Mineralogists, because of their unique training, which generally includes much chemistry, physics, and mathematics, yet is grounded in earth science, bring to problems of the solid state a fresh point of view. They are employed in the steel, glass, ceramic, and chemical industries. Many mineralogists are also employed by the U. S. Geological Survey, the Atomic Energy Commission, the National Bureau of Standards, the U. S. Bureau of Mines, state geological surveys, and various military research establishments. It is somewhat surprising to find mineralogists working for the National Institute of Health and the Ohio State University College of Dentistry. However, their services in the study of the materials of teeth and bone are indispensable.

Of all the services mineralogists perform, none is more stimulating and rewarding than university teaching. Here the mineralogist of today teaches (and learns from!) students from all scientific disciplines. His classes often include metallurgists, chemists, ceramic engineers, geologists, physicists, mining engineers, agronomists, and even aspiring doctors, dentists, and lawyers! All the larger universities and many of the smaller colleges in the United States offer courses in mineralogy, that are usually taught in the departments of geology. In some

American universities, such as Ohio State University and Pennsylvania State University, and in most universities on other continents, mineralogy is a separate department of instruction.

A scientific revolution began in the 1890's with the discovery of radioactivity, X rays, radio waves, electrons, and the atomic nucleus. Today it continues and includes nuclear energy, space travel, and the greatest challenges and threats that have ever confronted man. Mineralogy has been borne along with it to a position of power and flexibility undreamed of a century ago.

These are stirring times in which to embark on the study of mineralogy. Let us join George Miller, a high-school senior who is considering such an undertaking, and who has come to his state university for advice.

CHAPTER 1

# A VISIT WITH A MINERALOGIST

GEORGE MILLER had stood for a full minute outside the open door of an office on which was printed J. F. WEEKS, PROFESSOR OF MINERALOGY. He had hoped that the gray head bent over the microscope in the far corner of the room would detach itself from the microscope and look in his direction, but finally he summoned enough courage to knock. "Excuse me, sir, are you Professor Weeks?"

With these words the head turned in his direction. "Yes, I am. Come in. What can I do for you?"

"My name is George Miller. I am interested in mineralogy, and my science teacher suggested that if I came to the city I should come in and talk with you. In a few weeks I have to make application to college if I am to enter next fall and I would like your advice as to which would be the best one in the state . . . that is, if you have the time now."

Professor Weeks rose, rubbing his eyes, and moved across the room to his desk. "Sit down and let's talk about it. I have been looking through that microscope for an hour and a half and my eyes deserve a rest. How did you become interested in mineralogy? Did you study it in your science course?"

"Yes, sir. Mr. Stevenson, our science teacher at Grandville High told us a little about minerals in our earth science course. I found it very interesting, but what really got me started was an old quarry behind our house that I have played in ever since I can remember. My father says that they used to mine mica and feldspar there. There are also a lot of other minerals there and I have collected seventeen different kinds from the quarry. I guess I really got interested in minerals when I took a trip out West with my family last summer. We visited lots of different places where minerals are found and I was able to collect quite a few. We even bought some from mineral dealers. I would like sometime to go on a real mineralogical collecting trip."

As though he were considering very carefully the reasons for George's interest in mineralogy, the professor leaned back in his chair and slowly lighted his pipe. Finally he said, "I guess you have become interested in minerals in the usual way. But tell me, George, have you ever collected butterflies?"

"Yes, I have," was the surprised reply, "and I must have at least forty different kinds of butterflies in my room at home."

"Perhaps you're just a collector. Some people collect old bottles, buttons, or matchboxes, as well as butterflies and minerals. Because you have made a large collection of butterflies, you are not necessarily an entomologist, any more than a large collection of minerals makes one a mineralogist. There are many different facets to the science of mineralogy, and collecting of minerals is perhaps the least important of any of them. But tell me, how can I help you with the choice of a college?"

George was pleased that the conversation had shifted to where he felt on firmer ground. "My father went to Blake and would like me to go there too, if I can get in."

"Blake is a very good college," said Professor Weeks. "I have a son who graduated from there two years ago."

"Yes, I know it's a good college, but I can't find any courses in mineralogy listed. I have the catalog here."

"I became very familiar with the Blake catalog when my son was in college, but that was several years ago. Let me see it. There have probably been some changes in the courses." Professor Weeks slowly turned the pages of the catalog. "Ah, here it is. I see my old friend Professor Newcomb is still teaching chemistry. He is an excellent teacher and his beginning course is an outstanding one. He apparently has given up his physical chemistry course and that is being given by

Assistant Professor Holmquist. He must be that young man who came to Blake from Chicago two years ago.

"They have added a new course, I see. Holmquist is teaching advanced inorganic. . . ."

"But, sir" put in a bewildered George, "I thought mineralogy was a kind of geology. What does chemistry have to do with mineralogy?"

"Let me answer that by asking you a question, George," replied Professor Weeks. "What do you consider a mineral to be?"

Although George had been keenly interested in minerals for several years and had thought he knew quite a lot about them, he now found himself at a loss for a ready answer. After a lengthy pause, George finally said "A mineral is . . . , that is, the rocks are made up of minerals, uh, what I mean is . . . the minerals make up rocks and the rocks make up the hard crust of the earth."

"Yes, that is quite right. Minerals do make up the rocks of the earth's crust. Furthermore it is assumed that the rocks are formed by nature and it is a necessary part of the definition that a mineral is a natural, not a man-made, substance. But that is not really enough. You still have not said what minerals are, only where they are found. This is where chemistry comes in. It is only through a knowledge of chemistry that we can understand what minerals are. Minerals are chemical elements or compounds, and it won't be until after you have had a good course in chemistry that you will understand the full meaning of this statement."

"Gosh," interjected George, "when I had my choice between physics and chemistry last year in high school, I took physics. I hope I wasn't wasting my time. Maybe I should have taken chemistry."

"It doesn't matter which you took," the professor hastened to reassure George. "If you want to be a mineralogist, you must have a good knowledge of both subjects. In order to understand the apparatus and instruments used in measuring the physical properties of minerals, one must have a good background in physics. Much of the research being done in mineralogy has to do with the physical properties of minerals and similar manufactured materials. For example, one of the men who received his Ph.D. in mineralogy from this university last year is now working for a company growing crystals that are used in lasers and masers."

The revelation that mineralogy involved so much more than collecting and field trips apparently showed on George's face. This caused the professor to remark, "I hope I am not discouraging you from your ambition to study mineralogy. However, it would be unfair not to point out that in order to handle well the necessary chemistry and physics you should probably plan on taking mathematics for two years in college. . . ."

George brightened visibly. "Math is one of my best subjects in high school, and I was planning to take it in college anyway. I was also planning to take biology, but with all this physics and chemistry I guess I better forget about that."

"I am glad to hear you are good at math," the professor replied. "It was quite a struggle for me. About the biology—although many definitions of a mineral say that a mineral is the 'product of inorganic processes,' some mineralogists work with biologists and doctors on such matters as the structure of teeth and bone. This could be a very rewarding field of study.

"Some time ago," Professor Weeks continued, "you remarked that you thought that mineralogy had something to do with geology. You were quite right, George; it does. A hundred and fifty years ago a geologist and a mineralogist were the same person. But today, even though mineralogy has split off from geology, it is still very important that the mineralogist go into the field. He should observe first-hand the places where his minerals occur and the other minerals with which they are associated. I didn't mean to imply a while ago that a mineralogist doesn't collect minerals, for he most certainly does. I did want to get across the idea that mineralogy is more than collecting, labeling, and cataloging minerals. And if you want to become a first-rate mineralogist, you must lay a firm foundation for it in the other sciences. Blake is only one of a hundred good colleges that can do this for you. In the geology course at Blake you can get a lot of mineralogy. If, when you graduate, you still feel you want to be a mineralogist, you should go to graduate school. That is the time you should pick carefully the university that can give you the best training in that particular branch of mineralogy in which you are most interested. Perhaps you might even want to come here."

The professor rose, signaling to George that the interview was at an end. "Thank you very much, Professor Weeks," said George as he gathered up his coat. "I appreciate your giving me so much of your time."

"Before you go, George," said Professor Weeks, moving back toward his microscope table, "take a look through this microscope. This is one of the instruments a mineralogist uses a good bit of the time."

George, delighted with this prospect, crossed the room where he could for the first time obtain a close-up view of the microscope. It reminded him of the microscope he once used in his science course to view a sample of his own blood, but it was larger and more elaborate. This caused him to remark, "This seems bigger than the microscope our science teacher has."

"It undoubtedly is," said Professor Weeks. "He probably has a biological microscope. This is a special kind called a polarizing microscope; with it we can tell a great deal about minerals using only tiny particles. This," he continued as he removed the glass slide from the microscope stage and held it so George could see it, "is the mount. In the liquid under the cover glass are some gray specks. They are bits of the mineral I've been working on. Let's put it back on the stage so you can see them magnified." Professor Weeks adjusted the glass slide and said, "There, that's a good grain for you to see."

George sat before the microscope and placed one eye above the ocular, but it took several seconds before he could find the correct position to bring the grain into focus. "Can you see anything?" asked the professor.

"Yes," George replied, "I see a big colorless grain with several little ones around it."

"Good. Now keep looking and tell me what you see." With that, Professor Weeks pushed a small accessory slide into the microscope tube.

"That's beautiful," exclaimed George. "The big grain is red on the outside and blue in the middle! What did you do?"

"I pushed in a polarizing filter, and the colors are due to interference of light as it passed through the mineral and then through the filter. The explanation of 'Why' is a long story. The mineral grains in this mount were broken from a specimen which an amateur mineralogist couldn't identify and sent to me. I've been having a hard time with it myself. I'm using the microscope to get its optical properties. I've just about worked them out, and I think they fit the mineral hopeite. Hopeite is a rather rare zinc phosphate. I'm taking an X-ray picture of it right now which should give me a definite answer. By the way, this picture should be ready to come off. Do you want to come along with me while I develop it?"

As they walked down the long corridor towards the X-ray laboratory, George felt a little more at home. Along one side were glass cases filled with minerals, a few of which he could recognize. There was a group of quartz crystals, a large sheet of muscovite mica, and a group of "sand crystals," very similar to the ones he had collected the summer before in South Dakota. On the other side of the corridor were similar glass cases containing models made of small colored spheres grouped together, each group having the name of a mineral beside it. "These," Professor Weeks explained, "are structure models and show the manner in which atoms are packed together in various minerals. The different colors represent different kinds of atoms."

As they approached the end of the corridor and a door labeled X-RAY LABORATORY, Professor Weeks stopped and called

**Figure 1a.** Quartz Crystals, Hot Springs, Arkansas. **b.** Sand Crystals, Rattlesnake Butte, South Dakota. The crystal shapes are those of calcite. Calcite has grown inclosing sand grains which make up over 50% of the material.

through the door of the adjacent room, "How's it going this time, Ray?"

The young man sitting at a table in front of a rack filled with dials and electronic gear stopped his slide-rule calculations and turned with a grin. "I won't say now," he said, "but I can in twenty minutes."

"Good luck," said the professor as he and George turned and proceeded to the X-ray laboratory. "Poor Ray has had hard luck," he explained to George. "He is working an hydrothermal mineral synthesis, and the last five runs, for one reason or another, have turned out to be duds. He'll know in a little while what's happened to number six. Well, here is the X-ray lab, and over there is the camera I've been using to take the picture of my unknown mineral. First I'll shut off the X rays," continued Professor Weeks, "and then we'll go into the darkroom and see what luck I've had with this picture."

Although George had an interest in photography and had seen many cameras, he had never seen one that looked like this before. It was made of brass and resembled a small biscuit tin, about seven inches in diameter and an inch and a half thick.

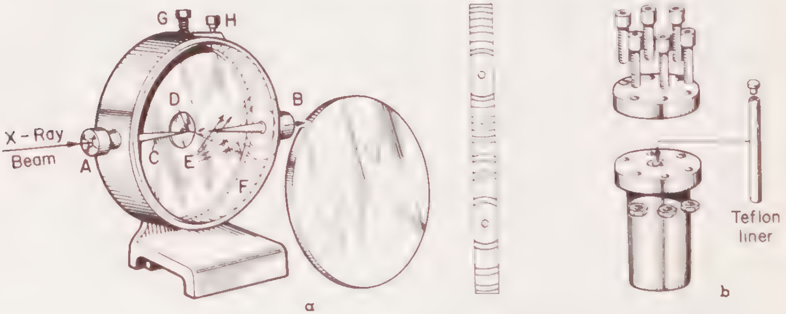

**Figure 2a.** X-ray powder camera and film. A. Opening through which X rays enter the camera. B. Opening through which X rays leave the camera. C. Collimator that permits only a very narrow X-ray beam to strike the sample. D. Sample. The sample is composed of a finely powdered mineral held together by flexible collodion and rolled into a thin spindle. E. Diffracted X rays. On striking the sample, some of the X rays are diffracted by the atomic planes of the crystalline particles. F. Photographic film exposed along curved lines by the diffracted X-ray beams. G. Screw for adjusting sample. H. Screw for locking film in place. b. Hydrothermal pot bomb for mineral synthesis at pressures up to 15,000 pounds per square inch and 900°F.

As Professor Weeks removed it from the X-ray unit, George couldn't restrain himself and asked, "Is that the camera? Where is the mineral that you're photographing?"

"The mineral is right in the middle of the camera, George. But let's get into the darkroom where I can open it and you can see for yourself." When they entered the darkroom, George couldn't see a thing, for the only illumination was a very dim, red safelight in the ceiling. Professor Weeks, however, knew his way around in the dark and proceeded to the bench where he took one of the sides off the camera. He then removed a strip of photographic film fourteen inches long and an inch wide, which had been held snugly against the inner circular portion of the camera. He clipped the film to a hanger and placed it in a tank labeled *developer*. "We'll stay in here while this is developing," said Professor Weeks. "It takes only a minute and a half; then while it is being fixed, we will go back into the laboratory where I can explain to you the workings of this camera."

When the film was placed in the fixing tank, they returned to the light of the laboratory. "This is our mineral specimen here," explained Professor Weeks, pointing to a slender rod in the center of the camera. "I know it doesn't look much like the specimen I showed you in my office, but it is a tiny bit broken from the same mineral, that has been ground very very fine in an agate mortar. The powder was then mixed with flexible collodion to hold the tiny particles together and rolled out into this little spindle that you see here. Because we work with powdered material, this method of taking an X-ray picture of a mineral is known as the *powder method*. The reason for grinding the mineral so fine is to make sure that the tiny particles are randomly oriented in the spindle.

"When the X ray comes through this hole," he continued, indicating a tiny opening on the curved surface of the camera, "it strikes the specimen and some of the X-ray beam is reflected from the many atomic planes of the tiny crystalline particles. These reflections strike the film and expose it as light does.

Just as the police use fingerprints to track down a criminal, so the mineralogist uses the position of the lines on the film to track down or identify his mineral. He can do so because the positions of the lines coming from a given mineral are always the same, but different from the position of the lines given by any other mineral. In fact, this method is sometimes called the method of fingerprinting minerals. Now let's go back into the darkroom and take a look at our photograph."

This time Professor Weeks turned on the white light, and George could see that the sink at one side of the darkroom contained three tanks labeled *developer*, *fixer*, *water*. On a bench on the opposite side were boxes containing photographic film, and close to the wall above the sink was a stretched wire from which was suspended a strip of film. Professor Weeks removed the film from the fixing tank, dipped it into the water tank to remove the excess hypo, and held it up to the light. The long strip of film was crossed by many dark curved lines of varying intensity.

"That is an excellent photograph. Let's see how it compares with this one," said Professor Weeks as he took down the strip of film hanging above the sink. "I took this photograph yesterday of a specimen I know is hopeite." He held the two films beside each other so the light would shine through both. "How do you think they compare; are they the same?" he asked.

"They look pretty much the same to me," said George.

"They do to me, too," said the professor. "At least the four darkest lines on both films are in the same place, as near as I can tell. After this film is washed and dried," he said, indicating the one he had just removed from the fixer, "I can compare them more carefully. If all the lines compare exactly, then I will be sure my unknown mineral is hopeite."

George had done his best to follow the professor in the explanation of the taking of a powder photograph. However, it seemed far from clear and somewhat mysterious but at the same time very exciting. He felt that he should ask the professor a question, but he couldn't think of one that seemed intelligent, so he finally remarked, "I'm afraid, sir, I don't understand the method completely."

Professor Weeks laughed. "I don't expect you to, George, after a ten-minute explanation. In fact, a course is given here at the university that takes a whole semester to bring out all the answers. Let's go into the next room and see whether Ray had a successful experiment."

When they re-entered the room they found Ray bending over a bench examining a tiny crystal in the center of a glass slide.

"Any luck this time, Ray?" asked Professor Weeks.

"So far, so good" was his reply. "The temperature control worked beautifully and there was no leak in the bomb. Here's the result," he said, holding up for inspection with obvious pride a test-tube-shaped bomb liner of white Teflon to which were adhering glittering, brown, pinhead-sized crystals. "When you're through with the powder camera, Professor Weeks, I'd like to take a picture of this material. Some of the crystals look big enough to measure on the goniometer too."

"I'm through with the camera now, Ray" said the Professor. "Let me know what the results are." As they walked down the corridor Professor Weeks remarked, "I can't blame Ray for feeling pretty excited about his experiment. He's been struggling a long time in an effort to make cerium phosphate, the substance which in nature is the mineral monazite. If he can measure the interfacial angles of his homemade crystals for comparison with those of natural monazite, this will be a definite achievement."

George didn't know what cerium was and until the moment before had never heard of monazite. Nevertheless, he felt that he knew much more about minerals than he did when he walked that same corridor a short while ago in the opposite direction. They stopped when they reached Professor Weeks' office. "We haven't talked much about minerals themselves," said the professor, "but you did come at a very fortunate time to see a little of what mineralogists do in the laboratory. By the way, on Saturday I am taking the students in the elementary course on a field trip to Pleasantville. We pass right through Grandville on the way. Ever since you mentioned that you lived near the old pegmatite quarry, I've been thinking about the possibility of visiting it and seeing what minerals can be found there. Would you like to meet us there on Saturday morning and show us around? We should get there by about ten o'clock."

"That would be great," said George. "I'll be there at ten o'clock. And thank you again, Professor Weeks, for spending so much time with me."

As George went down the steps two at a time he somehow felt he had a friend in Professor Weeks. He also felt that although his ideas about what mineralogy is and what mineralogists do had been drastically changed in the past hour, he had not lost his enthusiasm for the subject.

## CHAPTER 2

# ATOMS, MINERALS, AND THE PERIODIC LAW

IN THE LESS SCIENTIFIC BRANDS of science fiction we find reference to strange substances "hitherto unknown to science," having weird and unpredictable properties. These most certainly cannot be minerals. Undoubtedly many minerals are not known to science, inasmuch as new minerals are constantly being reported. During 1962 seven new mineral species were announced and described in the *American Mineralogist.* All were found by chemical analysis to be compounds of well-known chemical elements in fairly simple proportions, and none had any weird or unpredictable properties. Indeed, the authors of their descriptions were able to draw fairly close analogies between their new-found species and well-known minerals. In one case, the compound had already been made in the laboratory before it was found in nature.

But what, you may say, if we go to Mars or Venus or to remote, icy Pluto where conditions are so different from Earth? This question assumes a rather immediate urgency in view of the fact that human beings will doubtless soon be on the moon, and even on the nearer planets of our solar system. Fortunately, we have the comforting assurance that however far afield we go, we will find, if conditions of temperature and pressure permit, solids made from the same chemical elements we know on earth. Moreover, they will be, in their composition and properties, either identical to or very similar to the minerals we already know.

We can make so bold an assertion only because we feel quite sure that we know how many chemical elements are available from which to build minerals. Also we know roughly how much of each element nature has to work with and how each will combine with the others, if it combines at all. Why we are so sure is a fascinating story.

## ATOMIC THEORY

The story begins more than 150 years ago, with the statement of the atomic theory in its modern form. This theory upon which our present view of matter is based was first put forth by an English schoolmaster, John Dalton, in 1802. He published a more complete statement in 1808. The idea of atoms was not original with Dalton. Earlier, Isaac Newton argued eloquently that both matter and energy were particulate, and spoke of "solid, massy, hard, impenetrable and movable . . . primitive particles . . . so very hard as never to wear or break in pieces." For that matter, as long ago as the 6th century B.C. the Greeks conceived of all matter as being made up of atoms and void. The significance of Dalton's atomic theory was that it stressed and rested on the concept of chemical elements and called particular attention to the weights of atoms, thus making the atomic theory a working tool for chemists. A summary in modern language of the main points of Dalton's theory can be given as follows:

First, all matter is composed of atoms, which are indivisible.

Second, all the atoms of a given element have the same weight and are alike in all other ways.

Third, the atoms of different elements are of different weights, and differ in other ways.

Fourth, atoms are indestructible and are neither created, destroyed or changed in chemical reactions.

Dalton's first four proposals have stood up fairly well over the years. We no longer can say atoms are indivisible, and indeed we have a long list of particles that make up their structure. However, for mineralogical purposes atoms may well be considered indivisible, since none of the processes by which minerals are formed or the reactions that minerals undergo involve the splitting of atoms.

The second and third postulate gives a clear statement of a chemical element. However, today we now know that a typical sample of a pure chemical element as found in nature may contain several different kinds of atoms. All have the same properties and reactions but differ slightly in weight. These are the *isotopes.* Some elements such as aluminum are made up wholly of one isotope, that is, all aluminum atoms have the same weight. On the other hand, there are ten different kinds of tin atoms. All of these are present in ordinary tin in widely different amounts, but in proportions which remain nearly the same from one sample of tin to another. With this exception, Dalton's rules are still acceptable. A relatively new study has to do with the slight differences in proportion of the isotopes of a given element coming from different geologic environments. This is called *isotope geology.*

The fourth condition is still true, if the words *in chemical reactions* are noted. Today atoms can be destroyed, made, and altered in great particle accelerators like cyclotrons, or atomic piles. However, in reactions that take place in natural environments to form the minerals of rocks, veins, and volcanoes the atoms remain unchanged.

## PERIODIC LAW

It had often been noted that some chemical elements closely resembled others in physical properties, chemical behavior, compounds formed, etc. If certain elements were placed in a definite arrangement, their properties showed a regular progression, or systematic change. These ideas were not fully developed until 1869. At that time the idea of a systematic arrangement of the chemical elements was put forward by the Russian chemist, Dmitri Ivanovitch Mendeleeff, in his book, *Principles of Chemistry* (published in Russian). To quote from an address delivered by Mendeleeff twenty years later:

"Without entering into details, I will give the conclusions I then arrived at in the very words I used:

"1. The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties.

"2. Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (e.g. platinum, iridium, osmium) or which increase regularly (e.g. potassium, rubidium, cesium).

"3. The arrangement of the elements or of groups of elements in the order of their atomic weights, corresponds to their so-called *valences* (that is, power of combining with other elements, hydrogen taken as having a *valence* of one). . . .

"4. The elements which are most widely diffused have small atomic weights.

"5. The *magnitude* of the atomic weight determines the character of the element. . . .

"6. We must expect the discovery of many yet unknown elements—for example, elements analogous to aluminum and silicon, whose atomic weights would be between 65 and 75." (These two elements, gallium and germanium, had in fact been discovered as predicted by the time Mendeleeff gave this address.)

"7. The atomic weight of an element may sometimes be amended by a knowledge of those of contiguous elements.

"8. Certain characteristic properties of the elements can be foretold from their atomic weights." (Mendeleeff himself had accurately predicted the properties of the unknown elements whose existence he had also predicted, and the accuracy of his predictions was fully confirmed.)

These conclusions are still essentially valid today, and represent the essence of the *periodic law.* Mendeleeff further developed his ideas by arranging the 63 elements then known into a table. In this table similar elements were placed one above the other in vertical columns, while preserving the order of their atomic weights. This arrangement is called the *periodic table* and is one of the most useful tools of chemistry and mineralogy.

# PERIODIC TABLE OF THE ELEMENTS

|  | METALS |  |  |  |  |  |  |  |  |  |  |  | NONMETALS |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PERIODS | I | II | TRANSITION ELEMENTS |  |  |  |  |  |  |  |  |  | III | IV | V | VI | VII | O |
| 1 | 1 H | 2 |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 1 H | 2 He |
| 2 | 3 Li | 4 Be |  |  |  |  |  |  |  |  |  |  | 5 B | 6 C | 7 N | 8 O | 9 F | 10 Ne |
| 3 | 11 Na | 12 Mg |  |  |  |  |  |  |  |  |  |  | 13 Al | 14 Si | 15 P | 16 S | 17 Cl | 18 Ar |
| 4 | 19 K | 20 Ca | 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn | 31 Ga | 32 Ge | 33 As | 34 Se | 35 Br | 36 Kr |
| 5 | 37 Rb | 38 Sr | 39 Y | 40 Zr | 41 Nb | 42 Mo | 43 Tc | 44 Ru | 45 Rh | 46 Pd | 47 Ag | 48 Cd | 49 In | 50 Sn | 51 Sb | 52 Te | 53 I | 54 Xe |
| 6 | 55 Cs | 56 Ba | 57 * | 72 Hf | 73 Ta | 74 W | 75 Re | 76 Os | 77 Ir | 78 Pt | 79 Au | 80 Hg | 81 Tl | 82 Pb | 83 Bi | 84 Po | 85 At | 86 Rn |
| 7 | 87 Fr | 88 Ra | 89 ** | 104 | 105 | 106 |  |  |  |  |  |  |  |  |  |  |  |  |

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *LANTHANIDE SERIES | 57 La | 58 Ce | 59 Pr | 60 Nd | 61 Pm | 62 Sm | 63 Eu | 64 Gd | 65 Tb | 66 Dy | 67 Ho | 68 Er | 69 Tm | 70 Yb | 71 Lu |
| **ACTINIDE SERIES | 89 Ac | 90 Th | 91 Pa | 92 U | 93 Np | 94 Pu | 95 Am | 96 Cm | 97 Bk | 98 Cf | 99 Es | 100 Fm | 101 Md | 102 No | 103 Lw |

Mendeleeff's first periodic table, published in 1872, contained many blank spaces, and it was these spaces that prompted his dramatic prediction of properties of then unknown elements. A modern version of the periodic table, showing the 103 elements now known, is given on page 17. It can be seen at once that there are no blank spaces in this table. There is no room for any more elements except at the high numbered end; so we may forget forever the possibility of elements "hitherto unknown to science."

## TABLE OF ATOMIC WEIGHTS

**(Based on Carbon–12)**

**Values in parentheses are mass numbers of isotopes of longest half-life.**

| | SYMBOL | ATOMIC NO. | ATOMIC WEIGHT | | SYMBOL | ATOMIC NO. | ATOMIC WEIGHT |
|---|---|---|---|---|---|---|---|
| **Actinium** | **Ac** | 89 | (227) | **Erbium** | **Er** | 68 | 167.26 |
| **Aluminum** | **Al** | 13 | 26.9815 | **Europium** | **Eu** | 63 | 151.96 |
| **Americium** | **Am** | 95 | (243) | **Fermium** | **Fm** | 100 | (254) |
| **Antimony** | **Sb** | 51 | 121.75 | **Fluorine** | **F** | 9 | 18.9984 |
| **Argon** | **Ar** | 18 | 39.948 | **Francium** | **Fr** | 87 | (223) |
| **Arsenic** | **As** | 33 | 74.9216 | **Gadolinium** | **Gd** | 64 | 157.25 |
| **Astatine** | **At** | 85 | (210) | **Gallium** | **Ga** | 31 | 69.72 |
| **Barium** | **Ba** | 56 | 137.34 | **Germanium** | **Ge** | 32 | 72.59 |
| **Berkelium** | **Bk** | 97 | (249) | **Gold** | **Au** | 79 | 196.967 |
| **Beryllium** | **Be** | 4 | 9.0122 | **Hafnium** | **Hf** | 72 | 178.49 |
| **Bismuth** | **Bi** | 83 | 208.980 | **Helium** | **He** | 2 | 4.0026 |
| **Boron** | **B** | 5 | 10.811[a] | **Holmium** | **Ho** | 67 | 164.930 |
| **Bromine** | **Br** | 35 | 79.909[b] | **Hydrogen** | **H** | 1 | 1.00797 |
| **Cadmium** | **Cd** | 48 | 112.40 | **Indium** | **In** | 49 | 114.82 |
| **Calcium** | **Ca** | 20 | 40.08 | **Iodine** | **I** | 53 | 126.9044 |
| **Californium** | **Cf** | 98 | (249) | **Iridium** | **Ir** | 77 | 192.2 |
| **Carbon** | **C** | 6 | 12.01115[a] | **Iron** | **Fe** | 26 | 55.847[b] |
| **Cerium** | **Ce** | 58 | 140.12 | **Krypton** | **Kr** | 36 | 83.80 |
| **Cesium** | **Cs** | 55 | 132.905 | **Lanthanum** | **La** | 57 | 138.91 |
| **Chlorine** | **Cl** | 17 | 35.453[b] | **Lawrencium** | **Lw** | 103 | (257) |
| **Chromium** | **Cr** | 24 | 51.996[b] | **Lead** | **Pb** | 82 | 207.19 |
| **Cobalt** | **Co** | 27 | 58.9332 | **Lithium** | **Li** | 3 | 6.939 |
| **Copper** | **Cu** | 29 | 63.54 | **Lutetium** | **Lu** | 71 | 174.97 |
| **Curium** | **Cm** | 96 | (245) | **Magnesium** | **Mg** | 12 | 24.312 |
| **Dysprosium** | **Dy** | 66 | 162.50 | **Manganese** | **Mn** | 25 | 54.9380 |
| **Einsteinium** | **Es** | 99 | (253) | **Mendelevium** | **Md** | 101 | (256) |

[a] The atomic weight varies because of natural variations in the isotopic composition of the element. The observed ranges are boron, ± 0.003; carbon, ± 0.00005; hydrogen, ± 0.00001; oxygen, ± 0.0001; silicon, ± 0.001; sulfur, ± 0.003.

Mendeleeff's point 4 is especially interesting, as it is an early intimation of a line of thought that has become very important in mineralogy; that is, the abundance of elements. Mendeleeff makes the point that the most abundant and widespread elements are the light ones. This is perfectly true.

Of the 103 elements known, numbers 43, 61, and all elements with numbers higher than 83 are radioactive and break down spontaneously into simpler elements. They are thus very rare, not only on earth, but in the entire universe. We can be sure, therefore, that the minerals of the planets of our own and other stellar systems as well will be made predominantly of the 81

## TABLE OF ATOMIC WEIGHTS *(continued)*

| | SYMBOL | ATOMIC NO. | ATOMIC WEIGHT | | SYMBOL | ATOMIC NO. | ATOMIC WEIGHT |
|---|---|---|---|---|---|---|---|
| **Mercury** | **Hg** | 80 | 200.59 | **Samarium** | **Sm** | 62 | 150.35 |
| **Molybdenum** | **Mo** | 42 | 95.94 | **Scandium** | **Sc** | 21 | 44.956 |
| **Neodymium** | **Nd** | 60 | 144.24 | **Selenium** | **Se** | 34 | 78.96 |
| **Neon** | **Ne** | 10 | 20.183 | **Silicon** | **Si** | 14 | 28.086[a] |
| **Neptunium** | **Np** | 93 | (237) | **Silver** | **Ag** | 47 | 107.870[b] |
| **Nickel** | **Ni** | 28 | 58.71 | **Sodium** | **Na** | 11 | 22.9898 |
| **Niobium** | **Nb** | 41 | 92.906 | **Strontium** | **Sr** | 38 | 87.62 |
| **Nitrogen** | **N** | 7 | 14.0067 | **Sulfur** | **S** | 16 | 32.064[a] |
| **Nobelium** | **No** | 102 | (254) | **Tantalum** | **Ta** | 73 | 180.948 |
| **Osmium** | **Os** | 76 | 190.2 | **Technetium** | **Tc** | 43 | (99) |
| **Oxygen** | **O** | 8 | 15.9994[a] | **Tellurium** | **Te** | 52 | 127.60 |
| **Palladium** | **Pd** | 46 | 106.4 | **Terbium** | **Tb** | 65 | 158.924 |
| **Phosphorus** | **P** | 15 | 30.9738 | **Thallium** | **Tl** | 81 | 204.37 |
| **Platinum** | **Pt** | 78 | 195.09 | **Thorium** | **Th** | 90 | 232.038 |
| **Plutonium** | **Pu** | 94 | (242) | **Thulium** | **Tm** | 69 | 168.934 |
| **Polonium** | **Po** | 84 | (210) | **Tin** | **Sn** | 50 | 118.69 |
| **Potassium** | **K** | 19 | 39.102 | **Titanium** | **Ti** | 22 | 47.90 |
| **Praseodymium** | **Pr** | 59 | 140.907 | **Tungsten** | **W** | 74 | 183.85 |
| **Promethium** | **Pm** | 61 | (145) | **Uranium** | **U** | 92 | 238.03 |
| **Protactinium** | **Pa** | 91 | (231) | **Vanadium** | **V** | 23 | 50.942 |
| **Radium** | **Ra** | 88 | 226.05 | **Xenon** | **Xe** | 54 | 131.30 |
| **Radon** | **Rn** | 86 | (222) | **Ytterbium** | **Yb** | 70 | 173.04 |
| **Rhenium** | **Re** | 75 | 186.2 | **Yttrium** | **Y** | 39 | 88.905 |
| **Rhodium** | **Rh** | 45 | 102.905 | **Zinc** | **Zn** | 30 | 65.37 |
| **Rubidium** | **Rb** | 37 | 85.47 | **Zirconium** | **Zr** | 40 | 91.22 |
| **Ruthenium** | **Ru** | 44 | 101.07 | | | | |

[b] The atomic weight is believed to have an experimental uncertainty of the following magnitude: bromine, ± 0.002; chlorine, ± 0.001; chromium, ± 0.001; iron, ± 0.003; silver, ± 0.003. For other elements the last digit given is believed to be reliable to ± 0.5.

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stable elements, especially the lighter ones. In this we can count ourselves very fortunate. In a less orderly and more whimsical universe we might have had to grapple with thousands of chemical elements. The periodic table is such a fundamental guide to the universe that every one should have some familiarity with it.

Not only does the periodic table tell us how many elements are available to build the minerals of the universe, it also tells us much about them and their relations to each other. In the modern version of the periodic table on page 17, the elements are arranged according to their *atomic numbers* rather than their atomic weights. The order is just about the same except for a few minor reversals, as at potassium-argon. The atomic number is equal to the number of positive charges on the atomic nucleus. It also equals the number of electrons in the superstructure of the neutral atom. Nuclei, electrons, and atomic number may mean little to you at this point, but a course in chemistry will quickly set matters right.

On the extreme left of the table we see a vertical column containing the elements lithium, sodium, potassium, rubidium, and cesium. These elements are all very similar in physical properties, being light, silvery metals that react vigorously with water to form strong bases like household lye, called alkalis. Hence, these metals are often called "the alkali metals." These elements all have similar reactions and form similar compounds; thus, all react with chlorine to form compounds somewhat like sodium chloride, common salt.

Next to the alkali metals is a column containing beryllium, magnesium, calcium, strontium, and barium. These elements are likewise similar to each other in properties and reactions, and are often called "the alkali earth metals." If these elements combine with chlorine, they take into combination *two* atoms of chlorine, hence their valence is two, to use the language of Mendeleeff's point 3.

Skipping to the extreme right end of the table, we see a column containing the noble, or inert, gases: helium, neon, argon, krypton, and xenon. These gases are present in small amounts in the earth's atmosphere; we breathe them continually. Yet, because they are almost wholly inactive chemically they do not readily form compounds, do not support life, and if they were removed from the air we would not miss them. In the adjacent seventh column we find fluorine, chlorine, bromine, and iodine. These elements are nonmetals, and since they react with metals to form salt, they are known as *halogens* (Greek: salt-former). Column six contains a series of related nonmetals: oxygen, sulfur, selenium, and tellurium. These react in one-to-one proportions with the members of the alkali earth group to form such compounds as calcium oxide, magnesium sulfide, barium telluride, and strontium selenide. Hence, these nonmetals are considered to have a valence of two, but with the opposite sign, or polarity, from the alkali earth metals.

Columns three, four, and five contain elements which can act at times like metals, at times like nonmetals. Between column two and column three we find a large group of elements. Most of them are like metals in their properties, characterized by showing a wide variety of combining ratios in their compounds. These are known as the *transition elements* and include elements 21–30, 39–48 and 57–80 in three groups of ten each. Two other groups of elements do not fit as well into the pattern of the periodic table. There is a good reason why they do not, and their existence in no way invalidates the periodic law. The first of these groups is the rare earth, or *lanthanides*, elements 58–71, fourteen in number. All have very similar chemical behavior and are hard to separate from each other analytically. The second group consists of radioactive elements, the *actinides*, and includes elements 89–103, a group total of fifteen. When element 104 is manufactured in one of the great particle accelerators, it will be a transition element analogous to number 71, lutetium.

There are several features of the periodic table to keep in mind. First, the arrangement of the elements into vertical columns within which the member elements of the chart show uniform gradation of properties from top to bottom. There is also a strong similarity of properties within the group, including similar valence. Second, the arrangement of the elements into horizontal periods or rows in which the character of the elements changes progressively from metallic to nonmetallic from left to right. Third, positive valence increases to the right, and negative valence decreases.

## ABUNDANCE OF ELEMENTS

In attempting to relate the chemical elements to the world of minerals, we must keep in mind that the elements are not equally abundant. In order to make an intelligent guess as to the composition of the minerals on other planets, or in the deeper parts of the earth, we must know something about the relative abundance of the elements in the universe as a whole. But how can we do this when we cannot leave the surface of our little space cinder by more than a few hundred miles? Even journeying to the moon would gain us very little in this respect, so far as direct observation is concerned. Yet a fairly good estimate of cosmic abundances can be made. The information comes from three sources. The most important is stellar spectrography.

The light coming from distant stars is made up of a mixture of many colors, or wavelengths. Each of these wavelengths is produced by a given element. A spectrograph can sort out these wavelengths by spreading the light out into a rainbowlike spectrum. For instance, the strongest color in light produced by glowing neon gas is, as anyone knows who has seen a neon sign, red. Sodium vapor lights on our highways show us the characteristic yellow light produced by glowing sodium vapor. If sodium and neon are present in the atmosphere of a hot star, then the characteristic red light of neon and yellow light of sodium can be seen by spreading the light from the star out into a spectrum. The relative intensity of the various wavelengths indicates the relative amounts of each of the elements contributing to the light of the star. In this way, by spectrographic analysis of the light of distant stars, astronomers have learned more about the atmosphere of stars than geologists have of the composition of deeper parts of the earth.

Another source of information is the chemical analysis of meteorites. These little visitors from space give us some idea of the composition of solid bodies other than our own earth. Many or most of the meteorites recovered by collision with the earth are thought to be fragments of a small disrupted planet of our own solar system. If this is so, these fragments may tell us something of the composition of the unknown depths of our own earth.

The last source of information, most detailed, yet contributing least to our knowledge of cosmic abundances, is the analyses of rocks, surface waters, and atmosphere of our own planet. Averages from these three sources of information, duly weighted, afford the best estimate we can make of cosmic abundances of the elements. In the universe as a whole we find the very light elements hydrogen and helium are more abundant than all the rest put together. In decreasing order oxygen, neon, nitrogen, carbon, silicon, magnesium, and iron are also very abundant. The table, page 24, gives the relative cosmic abundance for the 13 most abundant elements. For all the remaining elements there is less than one atom for every 10,000 silicon atoms.

The abundance of elements in the accessible rocks of the earth's crust is easier to estimate, and is done by averaging many thousands of chemical analyses of rocks from all over the earth. These analyses show that in the rocks of the earth's crust, and hence in the minerals that form these rocks, eight elements make up nearly 99% of the total by weight. Of these oxygen is vastly more abundant than the others, forming nearly half of the total weight. The predominance of oxygen is even more impressive if the percentage by volume is taken. Oxygen is a light element, taking up more space than the heavier metallic elements. In fact, oxygen makes up nearly 94% by volume of the solid crust! The crust can, therefore, be thought of simply as a boxwork of oxygen atoms held together by the common metal atoms. In a sense you are walking on air, because more than 90% of the rocks under your feet is made up of the same element that you are breathing in the atmosphere!

### ABUNDANCE OF THE CHEMICAL ELEMENTS[*]
*In Weight Percent*

IN THE COSMOS

| | | | | | |
|---|---|---|---|---|---|
| Hydrogen | 63.7 | Carbon | 0.084 | Phosphorus | 0.040 |
| Helium | 34.9 | Iron | 0.064 | Sodium | 0.037 |
| Oxygen | 0.41 | Sulfur | 0.054 | Magnesium | 0.036 |
| Nitrogen | 0.213 | Silicon | 0.048 | Argon | 0.017 |
| Neon | 0.213 | | | | |

IN THE EARTH'S CRUST

| | | | | | |
|---|---|---|---|---|---|
| Oxygen | 46.6 | Hydrogen | 0.14 | Chromium | 0.020 |
| Silicon | 27.72 | Phosphorus | 0.12 | Zirconium | 0.016 |
| Aluminum | 8.13 | Manganese | 0.10 | Rubidium | 0.012 |
| Iron | 5.00 | Fluorine | 0.07 | Vanadium | 0.011 |
| Calcium | 3.63 | Sulfur | 0.052 | Copper | 0.0045 |
| Sodium | 2.83 | Strontium | 0.045 | Lead | 0.0015 |
| Potassium | 2.59 | Barium | 0.040 | Silver | 0.00001 |
| Magnesium | 2.09 | Carbon | 0.032 | Gold | 0.0000005 |
| Titanium | 0.44 | Chlorine | 0.020 | | |

[*] Adapted from Jack Green, "Geochemical Table of the Elements for 1953," *Bull. Geol. Soc. Amer. 64* (1953). Tables are incomplete. Elements of abundance less than 0.01 percent are omitted, except for copper, lead, silver, and gold.

Of course, the oxygen in the crust is not present as a molecular gas, as the oxygen of the atmosphere. It is present as charged atoms bound to the metal atoms by powerful electrical forces. Of these metal atoms, silicon is the most important for most of the rock-making minerals are silicates. That is, they are compounds containing silicon and oxygen groups. Next in importance is aluminum. It plays an essential part in the composition of many important minerals. Feldspar, the most abundant mineral, and mica, one of the most interesting, contain aluminum. Quartz, a compound composed of only silicon and oxygen, is also an important mineral. Following aluminum in decreasing abundance are iron, magnesium, calcium, sodium, and potassium; iron is in somewhat greater amount than the rest which are about equal. These values apply only to the surface crust, that part of the earth we can sample with drill and hammer. If we knew the composition of the deeper levels of the crust, we can be sure they would contain quite different proportions of some of the elements.

Since the eight most abundant elements make up 99% of the rocks of the crust, this leaves only about 1% of the total for the rest. This small percentage includes most of the familiar metals of commerce such as lead, zinc, copper, silver, and gold. A table of abundances of elements in the crust contains many surprises. Titanium, a metal as yet little used in technology, is ninth in abundance, just under the top eight listed above. Rubidium, an element that is little known and little used, is 10 times more common than lead. Gadolinium is 60 times as abundant as silver. Zirconium is far more abundant than copper, and neodymium and niobium are more abundant than lead!

Why is it then that the ancient Babylonians used lead freely, whereas they never suspected the existence of neodymium and niobium? Why was copper a common object of trade and symbol of prestige among American Indians who could not have suspected the presence of the more abundant zirconium? The Aztecs, Incas, and Mayas had gold in vast store, yet could not have known of cerium, which is 10,000 times more abundant. The answer to these paradoxes lies in the mineralogy of these elements. Gold, silver, and copper occur as uncombined native elements at the surface of the earth. They were early found as nuggets in stream gravels, requiring only a little hammering to produce a tool or an ornament. Lead, copper, tin, zinc, silver, and mercury all occur as sulfides or oxygen salts at or near the surface of the earth. They were easily recognized and mined, and readily smelted to yield their contained metal. On the other hand, rubidium forms no minerals in which it is the chief or only metallic ingredient, but lies hidden in minor amount in the common potassium minerals. Zirconium occurs chiefly in zircon. This mineral, rich in zirconium, is found in almost all rocks in small amounts. However, it is usually present as minute, widely disseminated crystals not even visible to the naked eye. Further, even when the zircon is secured, producing zirconium metal is still a major technological feat.

So it may be seen that the usefulness of an element to man depends not only on its abundance, but also on its accessibility and ease of separation from the minerals that contain it. The study of the problems connected with the abundance and distribution of the chemical elements among minerals and rocks is called *geochemistry*, and is closely allied to mineralogy. Many mineralogists study the factors that lead to concentrations of useful minerals and ores in mineable amounts. A knowledge of mineralogy is indispensable to the intelligent locating, mining, and processing of such ores and materials. This sort of work is called *economic geology* or *economic mineralogy*.

In summation, we can say that minerals are made of the commoner and more stable elements, alone or in combination with each other. Hence chemical composition is a most fundamental characteristic of minerals, and the most useful and widely accepted basis of their classification. Since minerals are either elements or compounds, they can all be fitted somewhere into such a scheme. There are, however, a number of ways in which a system of chemical classification could be designed. For instance, minerals could be arranged in a list alphabetically by the initial letter of the chief chemical element present. Such a scheme would be suitable for the index to a book, but would be quite unsuitable for general use. It rests on an accidental factor that is unrelated to any of the properties of the mineral. A better arrangement might be to group together all the minerals of a given metal. Thus all copper minerals would be in one division, all lead minerals in another, etc. Such a classification might appeal to an economic or mining geologist, but is not of the most general applicability. This would be classification by the metal, or *cation* (see Chapter 4, page 43). On the other hand, we might group together all sulfates, all oxides, all silicates, and so on. This would be classification by the nonmetallic ion or group, or *anion* (see Chapter 4, page 43). If we do this, we find minerals with similar properties, occurrence, and structure grouped together. Thus all silicates are more like each other in important structural characteristics than are all minerals of, let us say, lead. For this and other reasons, the system of classifying by anions or anionic groups is followed by all mineralogists. One reason why this classification works so well is that the nonmetallic elements or groups, the anions, are in general larger than the metallic atoms or cations, and hence dominate the pattern of structural arrangement.

CHAPTER 3

# THE ARCHITECTURE OF CRYSTALS

IF YOU LOOK AT A MAP of the Great Lakes, you will see that there are several islands near the southern shore of Lake Erie not far from Sandusky, Ohio. Grapes have been raised here for over a century and the islands are covered with vineyards. There are no streams and to obtain water both for irrigation and domestic purposes wells must be drilled or dug. In 1897 a farmer on the largest island, Put-in-Bay, started to drill a well. Everything was proceeding in a normal fashion until a depth of 17 feet was reached. At this point the drilling bit suddenly dropped and was lost in an underground cavity.

Partly from curiosity and partly to recover his drilling equipment, the driller decided to dig a hole to enable him to explore beneath the surface. When the hole was dug, it was found that the bottom of the cavity was 30 feet below the surface. Descending into the cavity by a ladder, the driller beheld a most spectacular sight. In the light of his torch he saw a cavity about 25 feet long, 15 feet wide, and 12 feet high. There were flashes of light reflected from the walls, floor, and ceiling. Giant pale blue crystals up to 18 inches in length completely lined the cavern. It was from the smooth plane surfaces that covered each crystal that the light was reflected.

Although numerous small caverns with stalactites and stalagmites were known in the region, no one had seen any resembling the "Crystal Cave"; it was unique.

At the time of the discovery the owners of the cave made a very wise decision. Instead of stripping the cave and selling the crystals to museums and private collectors, they decided to preserve it as intact as possible. Thus for a small fee one can today visit "Crystal Cave" and see the same flashing crystals that the surprised driller saw many decades ago. If you go there, the guide will tell you that the crystals are celestite (strontium sulfate) and the largest of their kind in the world. He will also demonstrate to you one of the fundamental concepts of crystallography, that is, the *constancy of interfacial angles.* He has a small board with a V-shaped notch at one end. The V is cut at the angle at which two faces intersect on the large crystal at the foot of the stairway. He shows by placing the notch on corresponding pairs of faces on other crystals, that the angles on all of them are identical. This is true whether the crystal is large or small, flat and tabular, or nearly equidimensional.

Moreover, if one were to examine celestite crystals from nearby Clay Center, Ohio, or from the famous sulfur mines 5000 miles away at Girgenti, Sicily, he would find this corresponding angle to be the same. This observation of the constancy of interfacial angles was made long ago (1669) by Nicolaus Steno on another mineral, quartz. Today his name is given to a generalization known as Steno's law which states that *the angles between equivalent faces of crystals of the same substance are constant.*

But why this constancy of interfacial angles on crystals of a given mineral? To answer this question we must look deeper than the surface faces and consider the ultimate structure of crystalline materials and the units which make them up.

## States of Matter

With the most powerful telescope we can penetrate far into the outer universe, and with the most powerful microscope probe deep into the world of the very small. But all things we see—stars, planets, people, crystals, viruses—are made of atoms of a relatively small number of elements (Chapter 2). These atoms can exist in various degrees of orderliness of arrangement, called the *states of matter.* In the air you breathe, in the atmosphere of the stars, in the hydrogen that fills a balloon at a State Fair, the atoms exist in a state of chaotic disorder. They bump, jostle, and collide with each other and with the walls of their container. Rebounding, they mix and mingle; never are they still, and never twice in the same array. This condition of complete lack of order, violent movement, and inconstant arrangement is called the *gaseous state*.

Gases are made either of single atoms or of small groups of atoms called *molecules*. Some gases which are made of single atoms are neon, familiar in advertising signs, and helium, used in nonexplosive lighter-than-air balloons. Two example of molecular gases are water vapor and carbon dioxide. Water is made of molecules having two hydrogen atoms very tightly bound to an oxygen atom, and carbon dioxide is made of one carbon atom and two oxygen atoms. The most abundant gases of the atmosphere, oxygen and nitrogen, are molecular, with the molecules made of two atoms of the same kind linked together by sharing of electrons. Most small, simple molecules like water, carbon dioxide, and diatomic oxygen and nitrogen are very strongly joined together by powerful electrical forces. These result from the sharing of electrons between atoms and hence do not easily break down into their component atoms. The atoms and molecules in a gas are electrically neutral particles, but have a slight electrical attraction for each other that makes them act as though they were a bit "sticky."

If gases are cooled down to a certain temperature, different for each gas, this slight electrical attraction between atoms and molecules becomes stronger than the tendency to fly apart. As a result, atoms and molecules come into "contact"; that is, they approach each other as closely as they can. They are then said to be *close-packed*, but there is still no regular, orderly internal arrangement among the atoms or molecules. They are free to slide over one another, jostling, tumbling, and constantly changing their relationship to each other, filling and taking the shape of their container. This condition is called the *liquid state*. You have seen the transition from a gas to a liquid taking place on the sides of a cold pitcher of iced tea or lemonade on a sultry summer day. Mysteriously, liquid droplets appear on the cold glass, apparently from nowhere, frosting it with liquid. As larger droplets form they run down the sides of the pitcher and collect around its base, where the liquid is identifiable as ordinary water. This water was, a short time before, present in the humid atmosphere as a true gas, water vapor, whose molecules were inextricably mingled with those of oxygen and nitrogen and other gases of the air. Cooling by contact with the chilled pitcher took heat energy away from all the molecules in the air. In the case of water vapor, sufficient energy was removed so that the molecules clung together by virtue of their electrical "stickiness" to form liquid water. Although heat was also taken away from the oxygen and nitrogen molecules, they are less "sticky" than water vapor and cooling to a much lower temperature is necessary before these gases liquefy. If sufficiently low temperatures are provided, however, all gases can be liquefied.

If now, this process of taking away heat is continued, liquids may be cooled down to a definite temperature, called the *freezing point*, different for all liquids. At the freezing point a marvelous change takes place, much more dramatic than forming a liquid from a gas. The mobile, inconstant liquid suddenly changes to a rigid solid, and if conditions permit, develops the regular geometric form and smooth, shining faces of a crystal. Heat is given off during this change, and the liquid is said to have passed into the *solid state*. The solid state is the condition of lowest energy in which matter can exist. No matter how much energy we take away by cooling crystals, they do not change into any other state of matter.

Anyone can watch this wonderful transformation by looking out through a window on a cold day, when freezing rain or snow is falling. Very cold rain droplets or melted snowflakes are warmed slightly by the windowpane and trickle down until the liquid reaches a place where its temperature falls below the freezing point. There, in an instant, the liquid water, free a moment before to pursue a winding course down the windowpane, is locked into the rigid immobility of the crystalline state. The resulting crystals, as is usually the case in natural environments, are very imperfect. Adjacent crystals interfere with each other's growth, and few if any crystal faces may be visible. However, if the ice so formed is subjected to X-ray examination or studied with the mineralogist's polarizing microscope, it is found to be truly crystalline.

How does this crystalline state differ from any other? It is different in that every atom, molecule, or other building particle in a crystal has a definite environment, the same as every other like particle throughout the crystal. Thus, the crystal is built of regular, orderly rows of particles like soldiers on parade. Each particle has definite neighbors at definite distances from it that do not change as long as the crystal continues to exist. As in a company of soldiers drawn up for review, the rows of atomic particles or other building units are arranged into layers or planes. Here the analogy with a company of soldiers ends, because the order of crystals extends into three dimensions. To form a mental picture of the arrangement of atoms in a crystal, let us visualize airplanes flying in regular formation above, below, and beside each other. It is this regularity of arrangement in three dimensions extending throughout the entire crystal that characterizes the solid state. Thus, the term *crystalline* means essentially the same thing as *solid*. It is with the solid state that the mineralogist is chiefly concerned, because most minerals are true solids, have crystalline structure, and will form crystals of regular geometric shape when conditions permit. The study of *crystal structure* (the way in which the constituent particles are arranged) and relating it to the properties of minerals, is a very important part of mineralogy.

## Crystal Structure

Airplanes in formation, in spite of all the skill and attention of their pilots, change their positions relative to each other slightly as a result of the "bumpiness" of the moving air in which they fly. Likewise, atoms in crystals are in constant movement relative to each other as a result of the heat energy they possess. They vibrate, however, around an average position and it is this average, or "ideal" position which we talk about when we discuss crystal structures. Also, just as in the best-disciplined classroom, there are usually some vacant seats because students are absent for one reason or another, there are always some vacant places in crystals where atoms should be, but are not. These are *vacancies*, and in real crystals, there are a surprisingly large number of such imperfections. So too, just as every classroom now and then has a visitor, so every crystal has some atoms that do not "belong" in the crystal and are not part of its ideal composition. This condition is so generally found, that it is the rule in real crystals, not the exception. So, although we must stress the orderliness of crystals as setting them apart from liquids and gases, we must also keep in mind that crystals are not perfect. In all crystals some places where atoms should be are vacant and some places are occupied by atoms normally not found in such a place in the structure. All atoms are in constant movement about their average positions. These and various other types of imperfections are often very important to an understanding of the properties of the crystal. Thus, transistors, those tiny wonders that are revolutionizing electronics, are little pieces of crystals of the elements germanium and silicon. If the germanium or silicon crystals were completely pure and free from imperfections, the transistor would not work. It is only because of the presence of vacancies and impurities, deliberately introduced by the manufacturer, that transistors work at all.

Let us for the moment overlook the many imperfections of real crystals, and consider only ideal crystals. One of the first questions that we should settle is the number of possible geometric plans on which crystals can be built. As we drive past a cornfield, it is a familiar experience to note how the plants seem to line up first in one direction, then as we move a little farther, another direction, then another. It is obvious that in a regular array of essentially identical objects like corn plants, there are rows in many directions made up of regularly spaced objects. When a plan of the situation is made, these rows can be drawn on the plan (Figure 3a). Now suppose we pass another cornfield in which the farmer has chosen a slightly different arrangement of his corn plants. Once again, there are many directions which can be made to "line up" corn plants in a regular spacing. Now, the fundamental question is: Is the arrangement in Figure 3a really different from the arrangement in Figure 3b or is the difference merely one of degree rather than of kind?

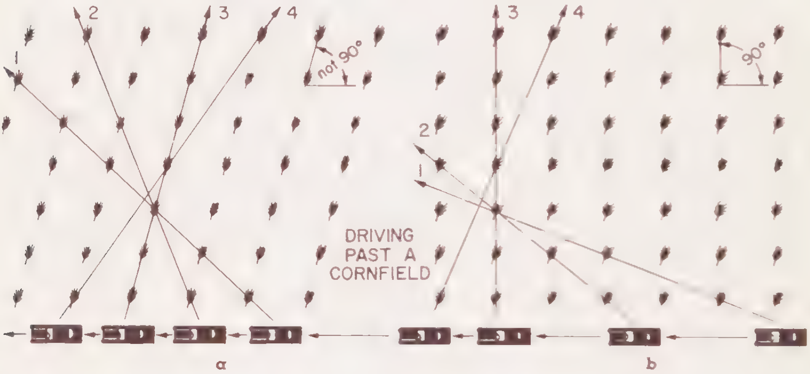


**Figure 3a, b. Driving past a cornfield.**

When we go from two to three dimensions, as is necessary in crystals, the problem is more complicated. Here the question is: How many ways can identical points be arranged in space so that every one has the same environment? By environment is meant the same number of neighbors at the same distances and directions. This tantalizing question bothered students of crystals early in the 19th century. In 1842 a German mathematician, Moritz L. Frankenheim, answered the question. He claimed that there were fifteen such ways. A few years later, in 1849, a French naval officer, physicist and astronomer, Auguste Bravais, showed that two of Frankenheim's arrangements were the same. Thus there are really fourteen ways identical points can be arranged in space. Rather unfairly to Frankenheim, these fourteen arrangements are generally called the fourteen *Bravais lattices.* These lattices are not crystal structures, but merely frameworks to be thought of as blueprints for the regular arrangement of any pattern units that are repeated in space.

Let us see how Frankenheim and Bravais approached this problem by considering pattern units arranged on a surface, such as a necktie fabric or wallpaper (Figure 4a). In a row there is only one way that points can be arranged so that each one has the same number of neighbors at the same directions and distances; that is, spaced out at equal intervals along the row. If we arrange points on a plane, they fall as we have seen in the case of the cornfield into such rows. In order to describe the whole pattern we must find *two* rows that intersect at some angle we will call *a.* Now the *pattern unit* is a little parallelogram from which an infinitely extended pattern can be made simply by repeating the parallelogram. As we can see in Figure 4, there are many possible parallelograms that can be chosen. Any one of these permits an infinite repetition, and could be made up as a printing block by a manufacturer interested in making the pattern, as for wallpaper.

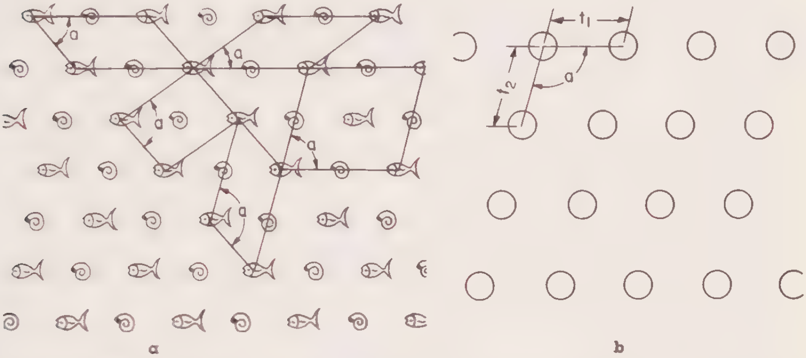


**Figure 4a.** Wallpaper pattern showing a few possible choices of pattern unit. The same pattern units could be shown with their corners at the snail motif instead of at the fish motif. **b.** Clinonet showing unequal identity periods $t_1$ and $t_2$, and angle $a$ not equal to 90°.

Which unit shall we choose? It is not really important since all have in common the essential properties of the pattern. These are that the angle *a* is neither 90° nor 120°, and the spacing between points in the row making one side of the parallelogram is *not* the same as the spacing between the points in the row making the other side. Such a pattern with *a* not 90° or 120° and the two spacings unequal can be called a *clinonet*, because it is a network made up of rows that are in*clin*ed to each other. We will call it network number 1. Now, in a similar way we can find several other networks: 2. where *a* is equal to 90° and the spacings are different; 3. where *a* equals 90° and the spacings are the same; 4. where *a* is not equal to 90° and the spacings are the same, and 5. a case where *a* equals 120° and the spacings are the same. These five ways are the only ways in which identical points can be arranged in a regular pattern in a plane. Try drawing each type. The next time you see a necktie pattern or a wallpaper pattern, a figured dress material or a tile floor, see if you can figure out which kind of two-dimensional network was used as a basic pattern.

If you do this, you will soon find that the task is more difficult than you might suppose, because most patterns have more than one figure or motif. If, for instance, a wallpaper pattern has flowers and stars, then there must be two networks, one for the flowers and another for the stars interpenetrating each other. The pattern unit must contain one whole sample of each network in order to be infinitely reproducible. If a sports tie has tennis rackets, golf clubs, fishing rods, and water skis on it, there must be four interpenetrating networks, one for each of the pattern motifs.

These same considerations apply to crystals, but since crystals are three-dimensional objects, we have 14 different possibilities of arrangements. If there are four different kinds of atoms or atomic groupings in a crystal, then there must be four interpenetrating space lattices, one for each kind of atom or atomic group. These space lattices must, however, all have the same dimensions and the same symmetry. The unit repeated in three dimensions to build up the crystal must contain at least one of each of these subgroups, and the symmetry of the crystal depends on the symmetry of arrangement of the constituents. There is much more to say about the arrangement of atoms in crystals than we can say here. This discussion, however, will give you an idea of how mineralogists have come into the ways and means of understanding crystal structures.

When we imagine the bare bones of the space lattice, which is just a mathematical abstraction, clothed with the flesh and blood of real atoms, and molecules, we are visualizing the *crystal structure*. By crystal structure we mean the actual arrangement in space of the atoms of which the crystal is made. For this arrangement, the space lattice serves merely as an abstract plan. It is like the basic house plan of a housing development to which the prospective owner must adhere although he is free to select his own building materials.

In the real structure, we choose a pattern unit similar to the space lattice in general properties, but having absolute physical dimensions. These are determined by the size and number of the atoms that build the structure. Thus, referring to our earlier discussion, a layer in the structure of a real crystal might be a clinonet, but the row spacings would be determined by the size of the atoms at the points in the net, the spacing increasing as atomic size increases. The angle $a$ will be determined by the size and shape of building units at the points of the net. Another crystal might have an analogous layer also a clinonet, but with very different spacings and different angle $a$. These interatomic distances and angles can be measured by X-ray crystal analysis and are known for almost all minerals. The little box or parallelopipedon which by repetition builds the whole crystal is called the *unit cell*. We view it merely as a unit sample of an indefinitely extended and continuous structure which continues uninterrupted and undivided through the entire crystal. We can pick this sample anywhere in the crystal. The actual lengths of the edges of this little box are called the *unit cell dimensions*. Sometimes they are called *identity periods*, because they go from any point in the structure to the next point identical with it.

Unit cell dimensions in minerals are very small and are usually expressed in terms of a very small unit, called the Angstrom unit. There are 100,000,000 Angstrom units in one centimeter, which is about the width of your little fingernail. Most unit cell dimensions in minerals lie between two or three Angstrom units on the low side to about 100 Angstrom units on the high side. Some proteins and complex organic substances have cell dimensions of several hundred Angstroms. This means that, on the average, about 10 million unit cells of most minerals could be placed side by side across your little fingernail.

In the knowledge that a crystal is made up of identical building blocks, each with the size and shape of the unit cell, lies the understanding of the angular relations of the crystal faces.

The outward shapes of crystals result partly from the shape of the building units, and partly from the way new units are added to the growing crystal. Everyone who as a child has played with blocks having identical size and shape, knows that they can be stacked above and beside each other so that many different outward shapes result. A miniature flight of stairs is built by placing one block on the floor, beside it a stack of two, then three, then four, etc. Another flight going down the other side can be made by stacking in reverse order. A steeper flight of stairs is made if the first stack contains two blocks, the second four, the third six, etc. If straight edges are placed along the stairs indicating their general slope, they will meet at angles which depend on the dimensions of the blocks and the stacking arrangement. See Figure 5.

**Figure 5.** Stacking of identical blocks (or unit cells) showing different slopes and angles for different arrangements.

Using identical building blocks, the unit cells, nature in somewhat similar manner builds up crystals having different external shapes. The tremendous variety in shape and interfacial angles of crystals can all be explained by the stacking up or the leaving off of these tiny units. Sloping crystal faces can simply be thought of as flights of steps. They will have treads one, two, three, or some whole number of unit cells wide and risers one, two, three, or some whole number of unit cells high. Two faces on the same crystal will have different slopes if underlain by a different flight of steps. One flight may be one unit cell wide and one unit cell high, whereas the other may be two unit cells wide and one unit cell high. Two corresponding faces on crystals of different mineral species will have different slopes even with the same stacking. This is because the height and width of the unit cell of one species differs from the height and width of the unit cell of the other. The building units are so small that instead of seeing steplike surfaces, we see only smooth planes. These are the crystal faces, which like the slopes of the steps built of blocks have a constant angular relation to each other. The outward appearance and shapes of crystals are discussed in Chapter 5.

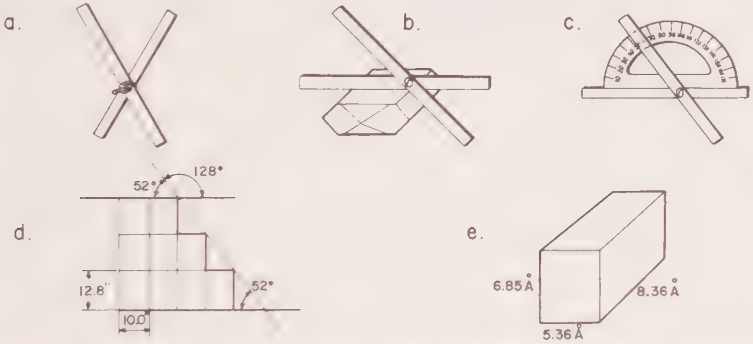


**Figure 6.** The contact goniometer. **a.** Making the goniometer. **b.** Measuring the interfacial angle. **c.** Reading the angle on a protractor. **d.** Diagram for determining an axial ratio of celestite. **e.** Unit cell of celestite.

In 1780 Carangeot invented the contact goniometer, a simple instrument for the measurement of interfacial angles. It is still in use today. For precise work, however, an optical goniometer, a much more refined and elaborate instrument, is used. A contact goniometer can be made easily, using a protractor and two straight strips of plastic or heavy cardboard joined together by a single bolt. See Figure 6a: The plastic arms are adjusted to fit the angle formed by the intersection of two crystal faces. Care must be used to insure that the strips are at right angles to the faces and the edge between them (Figure 6b). The arms are then placed against the protractor and the angle read directly (Figure 6c). Even without a protractor one can compare angles of two crystals by using the two arms of the goniometer as rulers and marking the angles on paper.

Since the interfacial angles on crystals of one mineral differ from the interfacial angles of crystals of another mineral, measurement of these angles is an important means of distinguishing between them. Although it is not possible to determine the absolute dimensions of the unit cell by these measurements, it is possible to find the ratio of the cell dimensions to each other in this way. The ratio is obtained by assuming the length of one cell edge to be equal to 1.0 and then expressing the lengths of the other two edges in terms of it. These ratios, called *axial ratios*, were all that mineralogists could determine about the unit cell until after 1912 when X-ray investigation of crystals became possible.

You can determine an axial ratio from interfacial angles as was done by the 19th-century crystallographers. For example, the interfacial angle between the face on celestite parallel to the top of the unit cell and an intersecting sloping face parallel to a cell edge is 52 03′. This particular face can be thought of as underlain by a flight of steps having treads one unit cell wide and one unit cell high. On a large piece of paper draw a horizontal line and at one end of it, using a protractor, draw an intersecting line at 52°03′. Now draw the flight of steps with the horizontal treads (all the same length) and the vertical risers making right triangles, with the sloping line the hypotenuse. Make the triangles as large as possible, for example, 10 inches for the width of treads. Using a ruler, measure the length of the "tread"; this length is proportional to the smaller of the two cell dimensions. Now measure the height of the "riser." This is proportional to the larger of the two cell dimensions. To obtain the ratio divide the smaller dimension into the larger. Your answer should be 1.28, one of the axial ratios of celestite. Had you taken 10 inches for the width of the "tread" the height of the "riser" should be 12.8 inches. This means that one of these two dimensions of the unit cell of celestite is a little more than one and one quarter times the length of the other that we see in this view of the crystal. You have calculated an axial ratio using the same data available to the 19th-century mineralogist.

The unit cell dimensions of celestite have been found by X-ray analysis to be 5.37Å in the direction of the "treads" in your drawing, 6.85Å in the direction of the risers. Divide these dimensions through by 5.37 in order to obtain a ratio in which the horizontal dimension has the value of 1.

$$\frac{5.37}{5.37} : \frac{6.85}{5.37} = 1 : 1.276$$

This ratio is a *structural axial ratio*, obtained from X-ray determined unit cell dimensions. It agrees closely with your graphical determination of the axial ratio from interfacial angles, as it should.

CHAPTER 4

# INSIDE THE CRYSTAL

UNTIL EARLY IN THE 20TH CENTURY minerals were studied and described by their physical properties. Interfacial crystal angles were measured and axial ratios calculated. Chemical analyses were made and thus chemical formulas could be written indicating the elements present. But the arrangement of the atoms of the various elements within the minerals remained a mystery. In 1912 it was discovered that X rays could be used to probe deep within a crystal and on emerging bring with them some of the secrets hidden in the interior. This pointed the way to a new approach to mineralogy. In the succeeding years, X-ray study has yielded a large mass of quantitative data that has broadened our understanding of minerals.

We have learned that the atoms which make up crystals are arranged in an orderly manner on one of the fourteen three-dimensional lattices. The dimensions of the lattice vary with the different atoms and atomic groups. When an X-ray beam enters a crystal, part of it is diffracted by the atomic planes of the crystal lattice. These diffracted or reflected X rays, as they may be called, when allowed to fall on a photographic film darken the film as would a ray of light. From the positions of these dark spots and their intensities, the lattice dimensions can be calculated and the positions of the various atoms within the lattice determined. In such a way the unit cell dimensions of most minerals have been measured, and for many minerals the arrangement of the atoms has been worked out.

By the 1930's a great many mineral structures had been worked out by X-ray methods. It then became apparent that there were many *structure types*, some of which were common with hundreds of representatives; others were rare. Furthermore, it was found that some atoms could replace others in crystal structures to almost any extent, whereas other atoms could enter the structure only in minor amounts. Also some chemical compounds as iron sulfide and calcium carbonate existed as minerals in more than one stable crystal structure. Like all great advances in science, X-ray study of crystal structures created almost as many new problems as it solved old ones.

It was apparent that a new approach to crystals and the solid state was necessary to explain all these facts that were piling up so untidily. Chemists, crystallographers, and mineralogists all struggled to reconcile the apparent contradictions and anomalies. Gradually through this effort a new field of study came into being. It is called *crystal chemistry* because it attempts to make the chemical aspects of crystals understandable in the light of their structures and to predict the structures of crystals yet unstudied in the light of their chemistry. In modern mineralogy crystal chemistry has become the dominant theme, the thread on which the disconnected and apparently unrelated facts of mineralogy may be strung.

## Crystal Chemistry

The grand goal of crystal chemistry is nothing less than the bold vision of a future in which it will be possible to explain all the properties of any compound in terms of the crystal structure and the chemical composition. Conversely, the goal also includes the synthesis of compounds having any desired combination of properties by choosing the proper structure and composition. This goal may never be fully achieved, but present-day mineralogists and crystal chemists have progressed a surprisingly long way toward it. Many of the high-temperature refractory materials used in making spaceships are substances either wholly new or previously little known and poorly understood. They were selected for study and trial not by blind cut-and-try but by intelligent choice according to crystal chemical principles. The application of these principles has aided in the development of semiconductors, transistors, and materials for thermoelectric cooling and power generation. For the mineralogist crystal chemistry has made understandable the occurrence in nature and the structure of many complex mineral groups. Most complex of all are the silicate minerals which dominate the composition of the earth's crust. It is in the understanding of this group of minerals that crystal chemistry has made its most striking contribution. What does crystal chemistry tell us that makes it so valuable?

If we try to explain the assemblage of the world of inorganic compounds in terms of its parts, we first must know what the available materials are. This question has been discussed at some length in Chapter 2. There we learned that there are known at present 103 different kinds of atoms, of which only about half are at all common or abundant. These are the materials with which we have to start. The structural units that enter into minerals are not, however, neutral atoms except in a few cases of native or uncombined elements. Neither are the structural units molecules, except in few rather rare cases. In general, minerals are built from *ions* (eye′ons), or charged atoms. They are called ions from the Greek word for *going*, because when an atom possesses an electrical charge it "goes" to an object of opposite electrical charge. The charge on ions is a static electric charge much like that developed by rubbing a hard rubber comb with wool, or a glass rod with silk. The charge arises from a deficiency or excess of electrons. If there is an excess of electrons, the charge is *negative* and is like that developed on a hard rubber comb. An atom having a negative charge is called an *anion* (an′eye·on) because it goes to the *an*ode or positive electrode. If there is a deficiency of electrons, the charge is *positive*, and is like that developed on a glass rod. A positively charged atom is called a *cation* (kat′eye·on) because it goes to the cathode, or negatively charged electrode. Most crystals of minerals are made of cations and anions, and it is the attraction between these unlike charged units that, in general, holds crystals together and gives them their strength and coherence.

If you would like to demonstrate the action of the forces that hold crystals together, you can easily do so. Take two small corks and wrap them with very thin aluminum foil. Then thread a silk thread through each, using a needle, and hang each cork from a wooden or plastic support. Rub a comb or something made of hard rubber or bakelite with a piece of soft wool or fur. Touch the comb to one of the corks. Then touch the other cork with a glass rod rubbed with a piece of silk. Now move the supports so that the corks slowly approach each other. If you have used the proper materials throughout, the two corks should show strong attraction and swing toward each other. The reason for the attraction is that you have transferred a negative charge to the cork touched by the comb, and a positive charge to the cork touched by the glass rod. The unlike charges attract each other. If the corks touch, charge is transferred from the cork with the higher charge to that with the lesser until both have the same charge. Thereafter they will repel each other.

If your experiment did not work, you may have corks that are too heavy or thread that is not silk and permits the charge to leak off. Your "hard rubber" may be something else that does not develop a charge when rubbed with wool, or your "silk" may not be silk. Try different materials until the experiment works. It works better on a dry, cool day than on a hot, humid one because moisture in the air permits static charges to leak off quickly.

Now that the experiment is working, discharge the corks by touching them, then move the supports apart and charge them up again as fully as possible. Slowly move the stands together. When the supports are far apart, there is little or no sign of attractive force. As they come closer together, the corks show a very rapid increase in attractive force, straining toward each other on their supporting threads. Bring them close enough so the corks almost touch. They will remain like this for a long time, pulling their suspending threads out at a decided angle.

The force that pulls these corks together is the chief agency that holds the ions in crystals together; it is this invisible, intangible web of electrical force that holds the earth's crust together.

Such a force, existing between ions, is called an *ionic bond*, or an *electrostatic bond*. It is the chief type of chemical binding force in crystals of inorganic materials such as minerals.

We learned in Chapter 2 that every kind of atom has a characteristic number of electrons called its atomic number. When atoms join in crystals, there is a strong tendency for all of them to adjust the number of electrons in their electron superstructures. They strive to attain the number of electrons of one of the "noble" or inert gases—helium, neon, argon. krypton, and xenon. In crystals having ionic bonding, the atoms do this by losing or gaining electrons to form ions.

Another way atoms can achieve the noble gas configuration of electrons is by *sharing electrons*. They may interpenetrate so that some of the electrons in the outer part of the atoms do double duty in both or all of the joined atoms. When atoms are held together by sharing of part of their electron superstructure, like Siamese twins, they are very strongly joined. and like Siamese twins, cannot easily be separated. Most atoms in crystal structures are held together by chemical bonds that involve some electron sharing and also some electrostatic attraction. The relative amounts of the two kinds of binding force differ from crystal to crystal. In fact, in a complex crystal with several kinds of atoms some of the atoms may be linked by bonds that are more electron-shared while other pairs of atoms in the same crystal may be linked by bonds that are more purely electrostatic. The properties of the crystal are often very strongly influenced by the difference in strength between these different kinds of bonds. A property that shows the effect of the presence in the crystal of two kinds of bonding is *cleavage*. Cleavage is easy breaking of a crystal along a plane through the body of the crystal, and always takes place so as to break the weakest bonds. Hence, if there are two kinds of bond in a crystal having different strengths, the weaker tends to produce a cleavage across it.

The weakest kind of bonding in crystals, and one that almost always results in localizing a prominent cleavage, is called *stray-field* bonding. More often it is called, after the Dutch physicist who described it, *van der Waal's* bonding. This is a very weak kind of electrical binding force that exists between large, electrically neutral structure units such as extended sheets of atoms or molecules. It arises from the fact that although molecules or sheets of atoms may be electrically neutral as a whole, the electrical charges holding them together are not distributed evenly. There are places here and there that have some deficiency or excess of charge. Attractive forces linking places of opposite charge tend to hold the larger units together, but not very powerfully. The weakness of this kind of bond accounts for the usually low hardness and low melting point of molecular crystals. A mineral in which the van der Waal's bond occurs is graphite, the familiar material of "lead" pencils. Graphite consists of carbon atoms powerfully linked together in sheets by electron-sharing, the sheets being bonded to one another only by van der Waal's forces. As a result, the little sheets of carbon atoms can slip over each other very easily (cleave). Graphite is thus a good lubricant and so soft that it can rub off in little flakes on paper and make a mark.

To sum up: With the exception of some elements that occur pure in nature, most minerals are inorganic compounds. Most of them are held together by some combination of electron-sharing and electrostatic binding. Occasionally electrically neutral units are weakly bound together by stray-field, or van der Waal's, bonds. The weakest bonds in a crystal having more than one kind of bond generally localize a good cleavage.

Crystal chemistry not only gives an explanation of the forces which hold crystals together but also gives an understanding of the arrangement in space, the solid geometry, of the constituent atoms. This arrangement, the structure of minerals, depends on the *relative size* of the ions. It may be difficult at first to picture how an atom or ion that is mostly empty space can be said to have any size at all. However, under the influence of electrostatic attraction oppositely charged ions approach each other only up to a certain distance, different for each pair of ions. At this critical distance, the repelling force of the negatively charged electron clouds balances the attractive force caused by the difference in charge between the two atoms. Other even more powerful repulsive forces arise if the two ions come closer together than the equilibrium distance. This distance is the characteristic *interionic distance* for a given pair of ions, and is equal to the sum of the "radii" of the two ions. It is in this way that we can speak of "radius" in connection with an ion: it is the proportionate share of the interionic distance when the given ion is linked to another. Under these conditions the ions behave like elastic spheres in contact. Ions are not little hard balls, of course, but since they act as though they were, we can speak of them as having "radius," "diameter," and "surface." Models of mineral structures can thus be made using solid balls to represent the ions.

## Models of Crystal Structures

Models are very helpful in visualizing crystal structures and can be made from a wide variety of materials. Spheres of wood, plastic, rubber, or metal, hollow or solid, joined by brass rods, wooden pegs, glue, solder, or toothpicks can all be used. Successful, although short-lived, models have been made of gumdrops and toothpicks. One teacher, lacking other materials, showed his class crystal structure models made of dried peas! The least expensive, lightest and generally most satisfactory models are made of Styrofoam spheres such as those sold for "snowball" decorations at Christmas time. These spheres can be joined easily and securely by means of short lengths of pipe cleaner, and can be colored easily as desired with India ink or showcard colors. See Figure 7.

Assuming, as we may without serious error, that minerals are, mainly, ionic bonded and that their constituent ions can hence be represented correctly by spheres in contact, we may investigate the geometrical basis of crystal structures experimentally. Obtain about two dozen Styrofoam spheres of different sizes. One and a half dozen spheres 1½-inch in diameter, the same number of ¾-inch diameter, and a half dozen each of 1-inch, and 2-inch sizes will permit a number of experiments. If Styrofoam spheres are not easily obtainable, ping pong balls, tennis balls, croquet balls, golf balls, wooden balls from a child's bead-stringing set, or other substitutes can be pressed into service.

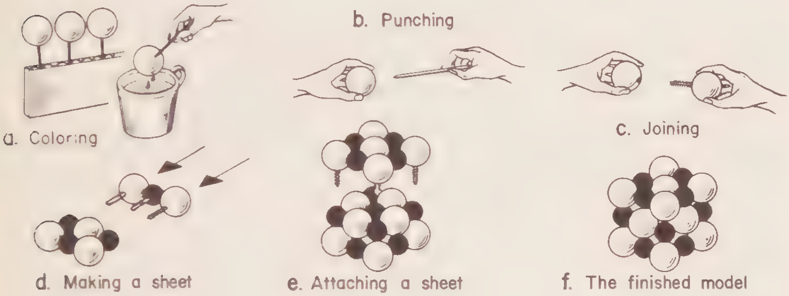


**Figure 7.** How to make a crystal packing model.

Take a sphere of your most abundant size and see how many spheres of the same size can be packed around it so that all touch the central sphere and also each other. You will find that an extra hand helps! Do you find that the number is 12, three below, six in a plane with the central sphere and three above? This is the most economical way in which spheres can be packed and is hence called *closest packing*. You have now made a model of a possible crystal structure, which in fact occurs in a number of minerals. Since there are 12 spheres surrounding the central sphere, which is thought of as holding them together, or *coordinating* them, this arrangement is also called *twelvefold coordination*. Coordination in crystals means much the same thing that it does in ordinary speech. Thus, a Coordinator of Labor Relations is a man who is supposed to *bring together* representatives from unions and management to discuss their problems.

Try arranging 1½-inch spheres around a ¾-inch sphere, or any size spheres around one about half the diameter. Can you now arrange 12 so that all touch the central sphere? You will find you cannot. If you arrange 12 spheres so that all touch each other, as in closest packing, the smaller sphere rattles around in the cage formed by the larger spheres. Such an arrangement is obviously not stable and cannot exist in crystals. Hence the smaller central ion must have fewer than 12 closest neighbors. Try six closest neighbors and you will find that you have a very solidly packed arrangement in which the larger spheres all touch the smaller central one. This arrangement, in which six closest neighbors surround a given ion, is called *six-fold coordination* because the center ion coordinates, or holds together, six neighboring ions. You have now made a model of the fundamental grouping, or coordination group, that characterizes the famous sodium chloride structure.

If you wish to make a model of the sodium chloride structure, you may easily do so. You will need 14 1½-inch and 13 ¾-inch Styrofoam balls. The model will go together more easily and be more nearly to true scale if you can get 1¾-inch balls and 1-inch balls. Skewer each ball with a toothpick. Color the larger balls green to represent chlorine by dipping them in a teacup partly filled with show-card color diluted with water, or India ink. Color the smaller balls yellow to represent sodium. After dipping each ball, spin it to remove excess color and set it aside on its toothpick to dry. The edge of a piece of corrugated cardboard makes a good rack. Join three balls in a row in the order chlorine-sodium-chlorine by punching each ball with a $\frac{1}{16}$-inch steel skewer and inserting the ends of a 1-inch piece of pipe cleaner into the holes. After inserting the pipe cleaner, push the balls gently together until they touch. The little hairs on the pipe cleaner will engage the many minute holes in the Styrofoam and make a surprisingly strong bond. Now join three more in the order sodium-chlorine-sodium, and attach this row to the first one you made, side by side. Now make a third row just like the first and attach it to the second row. You will now have a square in which sodium and chlorine alternate front to back and side to side. Make a second layer of nine balls like the first except that this one has sodium at the corners instead of chlorine. Then make a third layer of nine balls just like the first one. Now stack the layers one on top of the other so that you have a cube in which chlorine and sodium alternate vertically as well as side to side and back to front. This is the sodium chloride structure.

Imagine that the structure extends in all directions to infinity so that your model is just the smallest possible sample of the infinite array at whose heart you stand. This is what it feels like to be inside a crystal. Study your model carefully. Note that there are six chlorines around each sodium, just as there are six sodiums around each chlorine. The chlorines are bigger than the sodiums, however, so they seem to dominate the structure. It is generally true that anions, or negative ions, are larger than cations. This is because anions have more electrons than cations of similar atomic number, and are hence larger in effective size.

Sodium chloride is representative of a structure type characteristic of many simple chemical compounds. It is common because any compound made up of equal numbers of two different ions, one of which is about twice as big as the other, will tend to have sixfold coordination and hence the sodium chloride structure. Actually the limits of size permissible for the ions is wide; one need not be just twice the diameter of the other.

When the central coordinating ion is so small that it cannot touch six nearest neighbors, what regular arrangement tends to form? Try putting four 2-inch balls around a ¾-inch ball, or four 1½-inch balls around a 5/16-inch ball. This is *fourfold* coordination. It is very important in nature because silicon, the world's second most abundant element, is a small cation and when it joins with oxygen, the world's most abundant element, it gathers about itself four oxygens in a very sturdy fourfold coordination grouping. These groups of one silicon and four oxygens are the main building blocks of the silicate minerals, and hence of the earth's crust.

If the central coordinating ion is just a little smaller than the coordinated ions, eight closest neighbors is the number that leads to a solid, stable grouping. Try it with 2-inch and $1\frac{1}{2}$-inch balls. This is called *eightfold coordination.*

On the other hand, when the coordinating ion is even smaller than silicon is with respect to oxygen, it will rattle around in the space formed by the four coordinated ions forming an unstable situation. In this case the stable group is a planar triangle of large ions with the very small coordinating ion occupying the little pocket in the center of the three larger ions. This is the way in which the very important element carbon combines with oxygen to form carbonates, such as calcite, the chief mineral of limestone and marble. This is called *threefold* coordination.

Suppose we tabulate the results of your experiments with spheres as in columns 1 and 2 of the table on the next page.

By making a cross-sectional drawing of each of the coordination groupings, 12-, 8-, 6-, and 4-fold, we can scale off exactly what the ratio of the radius of the smaller spheres is to the radius of the larger spheres. This ratio is called the *radius ratio.* If the sizes of the two coordinated ions are known, in order to obtain the radius ratio, simply divide the radius of the smaller ion by the radius of the larger. The radius ratio can never exceed 1, and is equal to 1 only when the coordinated ions are of the same size. Since anions are generally larger than cations, the radius ratio is usually the radius of the cation divided by the radius of the anion.

We can now go back and add a third column, RADIUS RATIO, to the table prepared from your experiments with spheres. This not only makes our table look more scientific but gives us numerical limits for the various kinds of coordination.

Let us see how to use these limits of radius ratio. Suppose we wish to know the probable coordination of oxygen ion (an anion of ionic radius 1.40Å) around silicon (a cation of ionic radius 0.42Å). The radius ratio is 0.42/1.40 which equals 0.30. This

| *1*<br>SIZE OF CENTRAL COORDINATING SPHERE | *2*<br>NUMBER OF NEAREST NEIGHBORS OR NUMBER OF COORDINATED SPHERES | *3*<br>RADIUS RATIO |
|---|---|---|
| Same as coordinated spheres | 12 closest packing (twelvefold coordination) | |
| Slightly smaller than coordinated spheres | 8 (eightfold) | 1–0.732 |
| About ¾ to less than ½ the diameter of the coordinated spheres | 6 (sixfold) | 0.732–0.414 |
| Less than ½ to about ¼ the diameter of the coordinated spheres | 4 (fourfold) | 0.414–0.225 |
| Less than about ¼ the diameter of the coordinated spheres | 3 (threefold) | 0.225–0.155 |
| | 2 (twofold) | less than 0.155 |

radius ratio lies between 0.414 and 0.225 indicating that fourfold coordination is the most probable. This is the stable arrangement of silicon and oxygen that makes up most of the earth's crust.

Of course, there are many factors other than radius ratio that slightly influence the coordination pattern in a crystal; so the radius ratio principle must be used with caution. Its predictions are generally accurate when dealing with large, weakly charged ions between which the binding forces are dominantly electrostatic. It falls down badly when the units of the structure are small, very highly charged, of unsymmetrical shape, or joined by dominantly electron-shared bonds. For most minerals, the radius ratio principle works well.

If we know that there are equal numbers of cations and anions in a crystal, the number of possible ways of arrangement is limited. If there are six anions grouped about each cation, there must be six cations grouped around each anion to make the cation-anion ratio one to one. Only one structure type is possible, the sodium chloride type which we have already considered. Similarly, if the relative sizes of the cations and anions lead to fourfold coordination, then the coordination is fourfold for both cations and anions. Under these conditions only a few structure types are possible, the commonest of which is the *sphalerite* structure. Sphalerite is zinc sulphide, the chief ore of zinc, and is a very common mineral. The rather surprising conclusion has now become inevitable, that if we know the sizes of the cations and anions and how many of each there is in the crystal, we can predict the structure type! Since we can find out how many of each ion there must be by ordinary chemical analysis, all that remains is to find the sizes of the ions.

Unfortunately, the ionic size cannot be measured directly. The clue lies in a statement made earlier in this chapter, that the "radius" of an ion is simply the proportional share of the interionic distance. The interionic distances in a crystal can be found by X-ray studies. Look at your model of sodium chloride again. Suppose you are informed by an X-ray crystallographer that the unit cell dimension of sodium chloride is 5.58 Angstrom units, can you find the distance between the centers of the sodium ions and the chlorine ions? Of course you can! It is just half the unit cell dimension, since the edge of the unit cell is always made up of three ions, either ½-sodium—1-chlorine—½-sodium or ½-chlorine—1-sodium—½-chlorine. Hence the distance sodium-chlorine is 2.79 Angstrom units. But how shall we divide this distance between sodium and chlorine? It is necessary to know one or the other to find its neighbor's radius. The way this problem was cracked was by estimation of the *volume* taken by an ion, oxygen as it happened, from the behavior of light in substances containing that ion. From the volume the radius of the oxygen was calculated, then the radius of any ion associated with oxygen could be found by substration. In this way, a table of ionic radii including sodium and chlorine was built up, an ion at a time. We now know that the proper division of the 2.79 Angstroms is about 1.81 Angstroms for the radius of chlorine and 0.98 Angstrom for the radius of sodium.

In the table on this page are given the ionic radii of some of the elements. Let us see how we can use them. Chemical analysis shows that there is one atom of magnesium to each atom of oxygen in magnesium oxide ($MgO$), the mineral periclase. Looking in the table, we find that the radius of magnesium ion is 0.66 Angstrom, whereas oxygen is 1.40 Angstroms. This means that the ratio of the radius of magnesium to that of oxygen is 0.66/1.40, which is 0.47. Consulting the table below, we find that when the radius ratio lies between 0.414 and 0.732, sixfold is the stable coordination. But there must be six magne-

IONIC RADII IN ANGSTROM UNITS (Å)

| ION | RADIUS | ION | RADIUS | ION | RADIUS |
|---|---|---|---|---|---|
| Aluminum$^{3+}$ | .51Å | Copper$^{1+}$ | .96Å | Oxygen$^{2-}$ | 1.40Å |
| Antimony$^{3+}$ | .76 | Copper$^{2+}$ | .72 | Phosphorus$^{5+}$ | .35 |
| Antimony$^{5+}$ | .62 | Fluorine$^{1-}$ | 1.36 | Potassium$^{1+}$ | 1.33 |
| Arsenic$^{3+}$ | .58 | Germanium$^{4+}$ | .53 | Rubidium$^{1+}$ | 1.47 |
| Arsenic$^{5+}$ | .46 | Gold$^{1+}$ | 1.37 | Selenium$^{2-}$ | 1.91 |
| Barium$^{2+}$ | 1.34 | Gold$^{3+}$ | .85 | Selenium$^{6+}$ | .42 |
| Beryllium$^{2+}$ | .35 | Hydrogen$^{1+}$ | 1.36 | Silicon$^{4+}$ | .42 |
| Bismuth$^{3+}$ | .96 | Iodine$^{1-}$ | 2.20 | Silver$^{1+}$ | 1.26 |
| Bismuth$^{5+}$ | .74 | Iron$^{2+}$ | .74 | Sodium$^{1+}$ | .97 |
| Boron$^{3+}$ | .23 | Iron$^{3+}$ | .64 | Strontium$^{2+}$ | 1.12 |
| Bromine$^{1-}$ | 1.96 | Lead$^{2+}$ | 1.20 | Sulfur$^{2-}$ | 1.85 |
| Cadmium$^{2+}$ | .97 | Lead$^{4+}$ | .84 | Sulfur$^{6+}$ | .30 |
| Calcium$^{2+}$ | .99 | Lithium$^{1+}$ | .68 | Tantalum$^{5+}$ | .68 |
| Carbon$^{4+}$ | .16 | Magnesium$^{2+}$ | .66 | Tellurium$^{2-}$ | 2.11 |
| Cerium$^{4+}$ | .94 | Manganese$^{2+}$ | .80 | Tellurium$^{6+}$ | .56 |
| Cesium$^{1+}$ | 1.67 | Manganese$^{3+}$ | .66 | Tin $^{4+}$ | .71 |
| Chlorine$^{1-}$ | 1.81 | Manganese$^{4+}$ | .60 | Titanium$^{4+}$ | .68 |
| Chromium$^{3+}$ | .63 | Mercury$^{2+}$ | 1.10 | Tungsten$^{6+}$ | .62 |
| Chromium$^{6+}$ | .52 | Molybdenum$^{6+}$ | .62 | Vanadium$^{5+}$ | .59 |
| Cobalt$^{2+}$ | .72 | Nickel$^{2+}$ | .69 | Zinc$^{2+}$ | .74 |
|  |  | Niobium$^{5+}$ | .69 | Zirconium$^{4+}$ | .79 |

siums around every oxygen as well as six oxygens around every magnesium, so the structure must be that of sodium chloride! Your model will serve fairly well as a model of periclase as well as of sodium chloride. You are now actually predicting structures from chemical data. The thrill of correctly predicting the structure of a compound from general crystal chemical principles never grows old. The professional mineralogist gets just as much of a glow of satisfaction from such a success as you may when first you try such a prediction. Of course, you do not have enough information here to predict very complicated structures. But you should be able to answer the following questions.

1. What will be the structure of the mineral bunsenite, NiO, nickel oxide, named for the inventor of the Bunsen burner? Answer: Sodium chloride structure.

2. What will be the coordination of oxygen around nitrogen ($Ni^{5+}$ ion) in the nitrates? Answer: Threefold.

3. What is the probable structure of beryllium oxide, BeO, in the mineral bromellite? Answer: Sphalerite structure.

4. What is the coordination of oxygen around ferric iron ($Fe^{3+}$) in hematite, an iron ore? Answer: Sixfold.

5. What is the structure of galena, lead sulfide, PbS, the most abundant ore of lead? Answer: Sodium chloride structure.

So far we have said nothing about the magnitude of the charge on an ion, merely whether the ion is negative or positive. The *amount* of charge, sometimes called the *valence*, is also very important. It not only determines the number of atoms of each ingredient in the compound, but also it determines the strength of the ionic bond. An ionic bond between two ions, one positive and one negative, each of which carries three charges, is vastly stronger than the bond between ions carrying just one charge. However, if both ions have the same charge the number of each in the compound remains unaltered. If, however, one ion has a charge of three and the other only one, then there must be three times as many of the one-charge ions as of the triply charged ions. The general rule is that the entire crystal must be electrically neutral. The number of positive charges must equal the number of negative charges in the whole crystal. If it did not, the crystal would give you a shock! Although each "charge" of which we speak is just one electron, there are so many atoms in any good-sized crystal that an unbalance of even one electron per atom would add up to a formidable charge.

It is the rule rather than the exception that minerals contain "impurities"; that is, there are present ions that are not called for by the simplest chemical formula. Thus, chemical analyses show that all sphalerite, naturally occurring zinc sulfide, contains some iron. The formula for sphalerite, ZnS, does not mention iron. The iron is not present as little pieces of metallic iron, for microscopic examination shows such sphalerite to be quite homogeneous. Furthermore, it is not present as iron sulfide, FeS, the mineral troilite, because X-ray study does not show the characteristic "fingerprint" lines of troilite (see Chapter 1, page 10). How, then, is this iron present? It is present as iron atoms occupying places in the lattice that would normally be filled by zinc ions. This is possible because the iron ion is very nearly the same size as the zinc ion and acts as though it had been dissolved in the sphalerite as solvent. Such substitution of one ion for another is called ionic or atomic substitution or *solid solution*. The iron has disappeared as a recognizable substance, just as sugar disappears as a recognizable solid when it is put into hot tea. Although the sugar disappears, you can tell it is there by tasting the tea. It has conferred a characteristic property on the tea; namely, sweetness. Likewise, the iron confers a characteristic property on the sphalerite, namely, dark color. Zinc sulfide which does not contain iron is pure white. Even a little iron makes it yellow to brown, and much iron makes it black. Just as we can tell how much sugar has been added to tea by tasting it, so we can tell how much iron has been naturally "dissolved" in sphalerite by noting how dark its color is. Of course, the iron does not really "dissolve" in solid sphalerite, it enters the sphalerite during its growth, substituting for zinc.

Iron is not a perfect "fit" for zinc and iron cannot substitute for all the zinc without a change of structure. The maximum amount of iron that can enter zinc sites depends on the temperature. Increasing the temperature loosens up the crystal and makes substitution of any sort easier. Hence, the higher the temperature, the greater the amount of iron that can enter a growing sphalerite crystal. If it can be shown that there was plenty of iron available while a sphalerite crystal was growing, then the amount of iron in the sphalerite is a measure of the temperature at which it formed! A mineral which gives a clue to the temperature of formation, as does iron-bearing sphalerite, is called a *geologic thermometer.* Any mineral in which solid solution takes place, but with some difficulty so that the process is not complete, and hence is affected by temperature, may be a geologic thermometer. In this way, a modern mineralogist may be able to say with considerable confidence that an ore deposit formed more than a billion years ago was deposited from solutions at a temperature of 700°C, rather than 600° or 800°C!

Practically all minerals display solid solution, and this explains the "impurities" noted in their chemical analyses. We see now that these impurities are not accidental or random inclusions as dirt or straw in milk. They are a real part of the crystal, as much so as the ions that are "supposed" to be there according to the ideal formula. Of course, mechanical inclusion of bits of other minerals also takes place, but this is not solid solution.

The silicates, which compose most of the earth's crust, practically all show extensive solid solution. For example, sodium and calcium can substitute for each other in all proportions in the world's most abundant mineral, feldspar, forming a *solid solution* series. This series varies in composition between pure sodium aluminum silicate (albite) and pure calcium aluminum silicate (anorthite). When we consider that 60% of the earth's crust is made up of feldspar, we might almost be tempted to call this series the World Series!

CHAPTER 5

# SHAPES OF CRYSTALS

THE TIMELESS APPEAL of minerals to man's sense of beauty arises in large part from the symmetry and regularity of their external shape. Minerals are made of atoms of the elements held together by powerful electrical forces. With few exceptions these atoms are arranged in the orderly three-dimensional array characteristic of the crystalline state. The regularity of external shape, that is one of the most satisfying yet thought-provoking of the properties of a mineral, derives directly from that regularity of internal arrangement. The minerals that we can handle, collect, and on which we can make tests are crystalline, and under favorable conditions develop smooth, plane faces. These faced crystals, although they conform to rigorous physical laws, are not like mass-produced objects. The interfacial angles between corresponding faces on crystals of the same species are constant, yet the sizes and shapes of these faces vary from crystal to crystal so that no two are exactly alike. This combination of rigorous order, subtle symmetry, and complete individuality in crystals is doubtless the source of much of their ageless charm. Of course the colors of minerals, now bold and vivid as the scarlet of cinnabar or the green of malachite, now tender and delicate as the smoky blue-violet of cordierite or the sunny yellow of golden beryl, contribute much to their beauty.

In mineralogy museums one can see perfect, mirror-bright cubes of brassy pyrite and ice-blue topazes covered with flashing facets that suggest the art of a master gem cutter. Many visitors refuse to believe that these objects are the product of natural processes. Yet they are, and crystals can achieve a very high

**Figure 8a.** Perfect octahedral crystal of diamond weighing 84 carats. Kimberley, South Africa. **b.** Gypsum crystals, Naica, Mexico. This group is on exhibit in the Mineralogical Museum, Harvard University, Cambridge, Massachusetts. The largest crystals are about 5 feet long.

degree of perfection in their external form if conditions of growth are favorable. The great 84-carat diamond recently stolen from the Harvard Mineralogical Collection, Figure 8a, had the form of a perfect octahedron whose 12 edges differed less than a sixteenth of an inch in length. Some crystals show not only a great perfection of form but are also of exceptional size. Gypsum crystals (Figure 8b) found in Naica, Mexico, and exhibited at both the Smithsonian Museum and Harvard University, form groups like giant yucca plants with enormous leaflike bladed crystals seven to eight feet in length radiating from a center.

Unfortunately for lovers of beautiful things, minerals do not usually form such spectacular crystals as the celestite crystals of Crystal Cave and the gypsum blades from Naica, Mexico. Crystals, like organisms, come into being by a process of growth. But unlike organisms which are nourished from inside, crystals grow by having material added to the outside. For a crystal to grow it must be surrounded in whole or in part by a fluid medium. The process of crystallization requires that an atom go from an environment in which it is free to move in all directions into a fixed position in a rigid framework. The fluid medium may be a gas, a liquid solution, or a melt.

Usually when the melt or the solution cools sufficiently for crystallization to begin, many nuclei form simultaneously and all grow at the same rate. On continued growth the crystals interfere with one another, producing a polycrystalline aggregate having no crystal faces. Such is the appearance of most mineral specimens. Beautiful quartz crystals are frequently seen in mineral collections, but the collector does not usually exhibit the infinitely more common, but less interesting, milky quartz composed of many small interfering grains. The rock granite, which you may see in polished slabs in the trim of many public and business buildings, contains countless small grains of quartz, feldspar, and mica. Each of these minerals is crystalline with the regular internal structure of a crystal, but the interference of neighboring grains prevented the development of crystal faces.

Large crystals result only when the growth of the crystals is very slow. Under these conditions the atoms have time to migrate relatively long distances to a few centers of crystallization. Even here a polycrystalline aggregate would result unless crystallization stops before the crystals interfere with each other. It is thus only when crystals grow freely without interference from others, that they assume characteristic geometrical shapes. The shapes of the crystals of many minerals are so typical that alone they permit identification. For example, garnet and staurolite are both hard, reddish brown, and have no cleavage. Both occur in the same kinds of rocks. Yet the cross-shaped twinned crystals of staurolite and the almost spherical dodecahedrons and trapezohedrons of garnet instantly distinguish these otherwise very similar minerals.

Under ideal conditions the faces of a crystal are smooth and plane, resembling the facets of a cut gem stone. However, there is a major difference between a cut gem and a crystal. The facets of the gem, although arranged in a geometrical fashion, bear no regular relation to the underlying atomic structure. Crystal faces, on the other hand, are the outward expression of the internal order and reflect the symmetry of arrangement of the interior. The concept of *symmetry* is very important in crystallography, since it is by recognition of its inherent symmetry that the crystal is placed in the proper pigeonhole in the accepted scheme of classification. Symmetry figures largely in art and architecture, and almost everyone is responsive to at least some kinds of symmetry.

## Symmetry Plane

The kind of symmetry displayed by many public buildings, such as the national Capitol, in which a central mass is flanked by identical outthrust wings, is familiar to all. This sort of symmetry is perhaps easy for human beings to perceive because human beings have it! This is symmetry with respect to a plane, and the operation we perform is reflection. Imagine an object that can be cut in two in such a way that the reflection in a mirror placed against the cut surface will appear to restore the complete object. This book is an example. If a mirror is placed against the center page, the first 64 pages plus their reflection will appear to restore the total thickness. Although not as easy to demonstrate, a chair has a similar plane of symmetry. A matchbox has three symmetry planes, a rectangular table two, and a square table four. Can you locate these planes? Crystals can have 1, 2, 3, 4, 5, 6, 7, or 9 symmetry planes, but some have none at all.

There are two more kinds of symmetry less easy to see at first than the plane of symmetry. These are symmetry about a line, or *symmetry axis*, in which the operation we perform is rotation, and symmetry about a point, or *symmetry center*, in which the operation we perform is inversion, or turning upside down.

## Symmetry Axis

Imagine a line passed through a crystal (or any object) and the crystal rotated about it as an axis. A rotation of 360° about any line will bring the crystal back to its original position. However, if the line is passed in certain particular directions, rotation about it may cause the crystal to repeat itself in space before a complete revolution. If this is the case, the line is a symmetry axis. If, in a 360° rotation, the crystal repeats itself twice, the axis is twofold; three times, threefold; etc. The rectangular table thus has a twofold axis perpendicular to the top, the square table has a fourfold axis, but the chair only a onefold axis, equivalent to having none at all. On the other hand, the matchbox has three twofold axes at right angles to each other.

The two points of emergence of a symmetry axis on a crystal may be identical and thus interchangeable, and one would find the same arrangement of faces at both ends. This would be true in a crystal having a symmetry plane at right angles to the symmetry axis, as for example, in the matchbox. In crystals in which a symmetry plane is not at right angles to the symmetry axis, the arrangement of crystal faces may be quite different at opposite ends of the axis. Such an axis showing different properties at its two ends is called a *polar axis*. In a way it resembles a bar magnet or compass needle with the south pole at one end and the north pole at the other. Several minerals have interesting uses because their crystals have polar symmetry axes. Outstanding examples are quartz and tourmaline. The Washington Monument, a table, and a three-legged stool all have polar axes.

## SYMMETRY CENTER

*Symmetry center* is found in many crystals having planes and axes of symmetry, but they are not necessary for its presence. To determine it involves another imaginary operation. Consider the matchbox again. A line beginning at any point on its surface and passed through the exact center, will emerge at a simi-

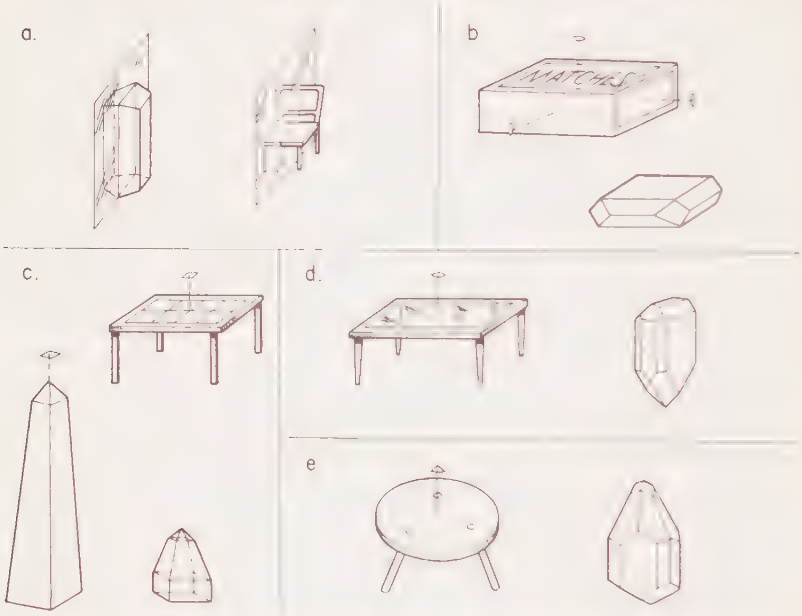


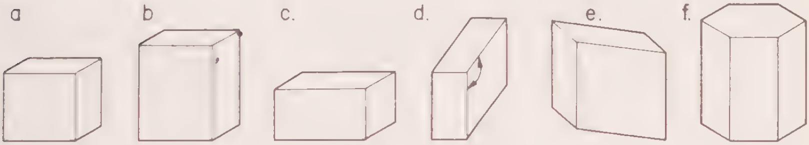
**Figure 9.** Symmetry. **a.** Symmetry plane dividing an object into two halves such that one is the mirror image of the other. **b.** Three 2-fold symmetry axes, three symmetry planes. **c.** One 4-fold symmetry axis, four symmetry planes. **d.** One 2-fold symmetry axis; two symmetry planes. **e.** One 3-fold symmetry axis, three symmetry planes. (Symbols: oval on table and matchbox—2-fold, triangle on monument—3-fold, square on table—4-fold.)

lar point on the opposite side. In general, crystals with parallel opposite faces have a center of symmetry.

## Crystal Classes and Systems

One might think there would be an almost limitless number of combinations of axes, planes, and center of symmetry. Actually there are only 31. These make up 31 of the 32 *crystal classes*. The 32nd class has no symmetry at all.

We have seen that crystals may be pictured as built up by stacking together identical unit cells. These building blocks have for each crystal a definite size and shape that can be determined by X-ray study. However, for a complete understanding of the crystal structure, the grouping of the atoms within the unit must be known. Two unit cells with the same size and shape may have not only different atoms but also a completely different atomic arrangement. The difference in arrangement may be reflected in the external geometry and symmetry of the crystal. We thus find that the same shaped unit of structure may give rise to several symmetry classes. On the basis of the



Isometric Tetragonal Orthorhombic Monoclinic Triclinic Hexagonal

**Figure 10.** The building units found in the six crystal systems. For the *isometric* or *cubic* system the unit is a cube with the edges in the three directions equal and at right angles to each other. In the *tetragonal* system the angles between the edges are at right angles but the vertical edge is of a different length (the illustration shows it longer but it could be shorter) than the horizontal edges. In the *orthorhombic* system the edges of the unit are all at right angles to each other but each edge has a length different from the other two. In the *monoclinic* system the vertical edge is at right angles to one of the other edges but inclined to the third, and the three edges are of different length. In the unit of the *triclinic* system the three edges are of different length and there are no right angles between them. The unit in the *hexagonal* system is a regular hexagonal prism with the vertical edges at right angles to the horizontal edges.

shapes of the fundamental building units the crystal classes are grouped into six larger divisions called the *crystal systems.*

These six basic shapes are illustrated in Figure 10. There is a conventional orientation for these units. One edge is always set vertical, another edge right to left, and the third set of edges front and back (or nearly so) as shown in the drawings. Lines representing the directions and relative lengths of these three sets of edges are used as lines of reference. They are different for each crystal system and are called the *crystallographic axes.*

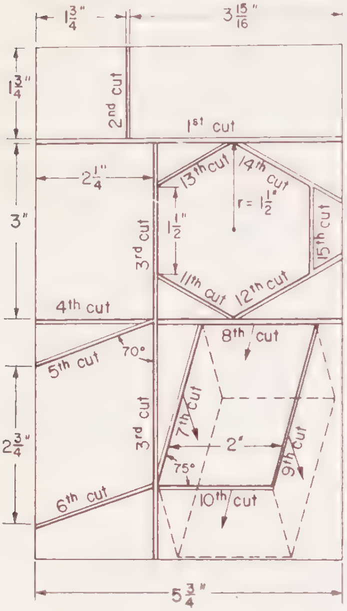


**Figure 11.** Plan for cutting board to make crystal models. Lay off on the board, with a try square and a triangle or straightedge, the lines shown on the cutting plan. All saw cuts should be made carefully so as to keep the cut parallel to the surface of the board with the exception of the triclinic model. In making this model the cuts should be deliberately inclined. The angle is not critical, but cuts 7 and 9 should be parallel, as should cuts 8 and 10. Smooth the cut surfaces by rubbing them down with sandpaper. Using chalk, you can now mark the elements of symmetry on the models, as described on page 68.

It is difficult to visualize the shapes of these units from drawings and word descriptions. To understand them and their symmetry better one should have models to turn and twist and on which symmetry planes and axes can be indicated. Models of the six basic units resembling those illustrated in Figure 10 can be made easily from a small board.

All six models can be made from a single piece of soft pine board one foot long of the size called "two by six." "Two by six" actually measures 1⅝ to 1¾ inches in thickness and 5½ inches in width. A cutting plan (Figure 11) will make the sawing simple. Square up the end of the board with a try square, making a saw cut if necessary to get the end exactly square with the long edges.

Now lay off, with a try square and a triangle or straightedge, the lines shown on the cutting plan. If the cuts are made in the order indicated, only 15 cuts are necessary to make all six models. All cuts should be made carefully so as to keep the cut perpendicular to the surface of the board with the exception of the triclinic model. In making this model, the cuts should be deliberately inclined.

Assuming that the board is 1¾ inches thick, it may be laid out just as shown in Figure 11. If the board is thicker or thinner, then the first cut should be made closer to or farther from the end of the board to make the distance from the end to the first cut equal to the thickness of the board. The second cut should be made a distance from the left end of the board equal to the thickness.

If the cuts are made in the order indicated in Figure 11, allowing $\frac{1}{16}$ inch for the width of the saw cut, the second cut will produce both the isometric and the tetragonal models. The isometric model should be a cube 1¾ inches on an edge, the tetragonal model a square prism 1¾ x 1¾ x $3\frac{15}{16}$ inches. The third and fourth cuts will yield four blocks. One of these is the orthorhombic model measuring 1¾ x 2¼ x 3 inches. Making cuts number five and six perpendicular to the top surface of the board will yield the monoclinic model. Cuts 7, 8, 9, and 10 should be made at an angle to the top surface of the board. The angle is not critical, but cuts 7 and 9 should be parallel, as should be cuts 8 and 10. The resulting model illustrates the triclinic. On the last block, draw, with a pair of compasses, a circle of radius 1½ inches. On the circumference of the circle, lay off six equal segments, using the 1½-inch setting of the compasses. Join the ends of the segments with straight lines to form a regular hexagon. Make cuts 11, 12, 13, 14, and 15 perpendicular to the board to form the hexagonal model.

Now smooth the cut surfaces and remove all splinters by rubbing all surfaces on a sheet of medium (1-0) sandpaper tacked down to a smooth surface. You may now study each model to determine its symmetry. You can mark the elements of symmetry on the models with chalk as you find them, using a solid line for a plane of symmetry, a hexagon for the emergence of a sixfold axis, a square for the emergence of a fourfold axis, a triangle for an axis of threefold, and an ellipse for an axis of twofold.

Isometric model: You should find nine planes of symmetry, three fourfold axes, four threefold axes, six twofold axes, and a center. This is the highest symmetry found in any crystal.

Tetragonal model: This model should possess one axis of fourfold symmetry, four twofold axes, five planes, and a center.

Orthorhombic model: You should be able to find three twofold axes, three planes of symmetry intersecting in the twofold axes and a center.

Monoclinic model: There is but one axis of twofold symmetry and one plane of symmetry perpendicular to it.

Triclinic model: You will find no planes nor axes of symmetry, but there is a center. Prove to your own satisfaction that planes parallel to the opposite faces cutting the model into two pieces are not planes of symmetry.

Hexagonal model: A single axis of sixfold symmetry, six axes of twofold symmetry, seven planes, and a center characterize the hexagonal model.

After you have found and marked all the symmetry on your models, note how symmetry elements affect each other. Whenever two planes of symmetry meet at right angles, there is a twofold axis at their intersection. Wherever two planes of symmetry meet at 30°, a sixfold axis lies at their intersection and four more planes of symmetry come into being. What new symmetry is produced when two planes meet at 45°?

When a fourfold axis and a threefold axis intersect, as in the cube, note that there must be four threefold axes to satisfy the requirements of the fourfold axis, and there must be three fourfold axes to satisfy the requirements of the threefold axis. No other arrangement is possible. It is the interplay of symmetry elements that reduces the total number of possible ways the symmetry elements can be combined to a modest 32.

The models you have made represent not only the shapes of the building units in each of the six crystal systems but also the symmetry found in six of the 32 crystal classes. We can by making certain assumptions see how other symmetry classes can be based on the same shaped units. For example, let us assume that the fourfold axis in the tetragonal unit is polar with different properties at opposite ends. There would thus be no symmetry plane at right angles to it, and the twofold axes would disappear. We would have the symmetry of another crystal class. Likewise by assuming polar axes for: one twofold axis in the orthorhombic unit, the sixfold axis of the hexagonal unit, and the twofold axis of the monoclinic unit, the symmetry of three other crystal classes would result. All of these classes have less symmetry than your models, which represent the highest symmetry possible for the six crystal systems.

We learned in Chapter 3 that, using identical building units, many different crystal shapes result by varying the stacking arrangement. However, no matter how different the shapes of two crystals of a given mineral, the symmetry remains unchanged, reflecting the symmetry of the unit itself. A careful study of the distribution of faces on two such crystals would lead to assigning them both to the same crystal system.

The building unit for all crystals in the isometric system is a cube. The units vary in size from mineral to mineral, but they are all cubes. It is the stacking arrangement alone that determines crystal shape. Consequently, crystals of isometric minerals with greatly different chemical composition have similar appearance. There are only a small number of common crystal forms in the isometric system: those that result from the stacking of cubes. Some of these are shown in Figure 12a. Note that despite their varied appearance, they all have the same symmetry—that of the cube. Since they all have the same symmetry, two or more can be found in combination on a single crystal as shown in Figure 12a.

Minerals crystallizing in other than the isometric system have different dimensions along different crystallographic axes. In

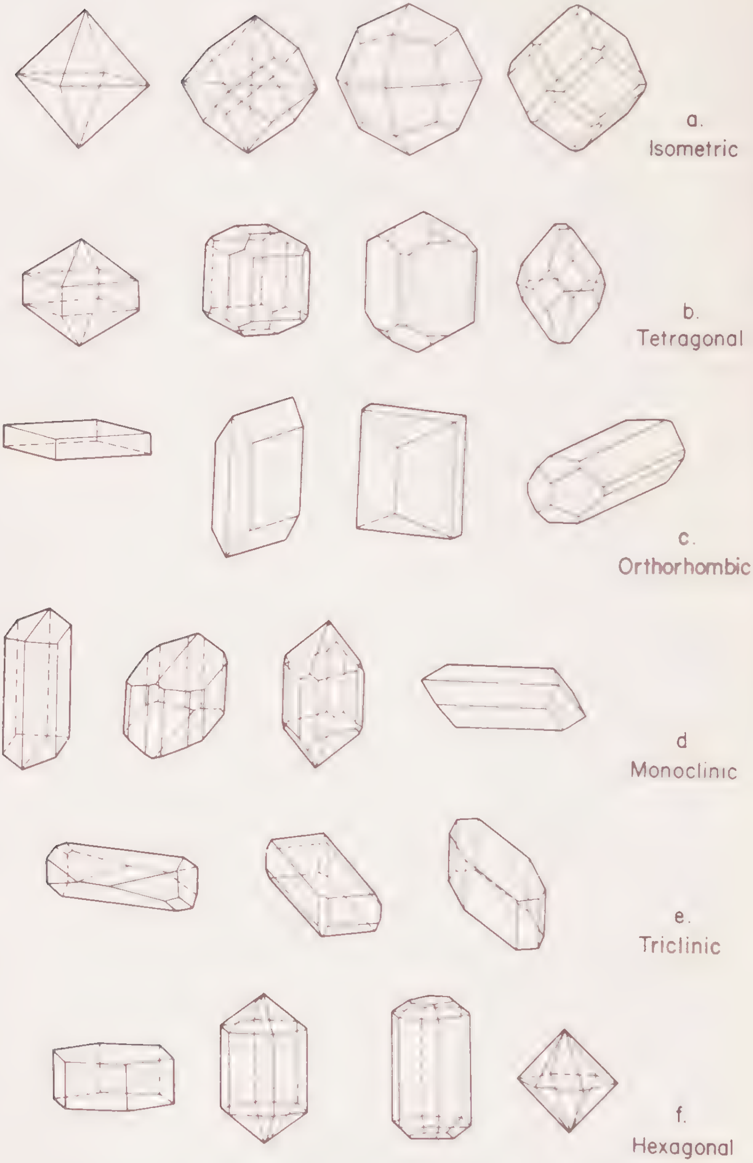


Figure 12. Shapes of crystals in the different crystal systems.

them the shape of the unit as well as the stacking arrangement determines the shape of the crystal and the angles between the faces. Crystals of two tetragonal minerals may have the same stacking of building units, but the angles between corresponding faces will be different because of the unlike dimensions of the unit cells. In spite of this angular difference, the symmetry can be the same. In Figure 12 several drawings of differently appearing crystals of minerals are given for each of the crystal systems. In the drawings for any one system the shapes are different, the angles are different, but the symmetry is the same.

The drawings in Figure 12 all are representative of the crystal classes of highest symmetry in the different crystal systems. More minerals crystallize in these classes than in any others. Moreover, crystals in lower symmetry classes frequently lack their characterizing faces and appear to have higher symmetry. Thus in an elementary study, it is sufficient to assign a crystal merely to its crystal system. To be able to do this is important in mineral identification. To hardness, specific gravity, and the other physical properties is thus added another distinguishing criterion.

As pointed out earlier, the mineralogist can frequently identify a mineral by the characteristic shape of its crystals. But now and then this may lead him astray. The crystal may have the outward shape of one mineral but the chemical composition and internal structure of a completely different one. Such a crystal is called a *pseudomorph* (false form).

We sometimes find quartz having the shape of fluorite crystals or limonite the shape of pyrite crystals. These are called pseudomorphs of quartz after fluorite and limonite after pyrite. Although petrified wood is not a replacement of one mineral by another, it is a type of pseudomorph. The mineral matter, frequently quartz, replaces the woody structure of the tree. Nature may carry out the process of replacement so faithfully that the expert can frequently tell the species of the tree that has been turned into stone.

CHAPTER 6

# HOW TO KNOW THE MINERALS

ON A COLD AFTERNOON in late autumn in the year 1820 two boys were searching for minerals in the hills east of Paris, Maine. They were about to return home empty-handed when the eye of one of them was caught by a flash of green from an object held in the roots of an upturned tree. On close examination they discovered the object to be a transparent green crystal of gem quality. Their excited search for other gems was soon ended by the deepening twilight, but the boys resolved to return the following day. However, during the night a storm covered the hills with a thick blanket of snow which remained until spring and the mineralogical nature of their discovery remained a mystery for many months. When the winter's snow had melted the continued search was rewarded by the finding of many crystals on the bare ledges of rock near the original find. Although all the crystals were the same shape, some were white, others green, red, and yellow of different hues. The ledge itself presented a fascinating mineralogical display with large masses of pink lepidolite, snow-white feldspar, glassy quartz (Figure 13), and broad flakes of glistening white mica. Thus was the discovery of the now world-famous pegmatite of Mount Mica, Maine.

Heavily laden with the choicest of the specimens, the boys returned with their mineral treasures to the village where their elders recognized the lepidolite, quartz, feldspar, and mica. However, no one in the vicinity could identify the crystals. Accordingly, a few of the smaller crystals were sent to Professor Silliman of Yale College requesting that he identify them. His prompt reply told the boys that they had found crystals of fine quality of the relatively rare mineral tourmaline (Figure 13).

Figure 13. Tourmaline (dark), quartz (light). Small platy crystals, feldspar. Pala, California.

Excitement in the small town of Paris was great, for well-colored, flawless tourmaline is a gem mineral. Within a year mining for tourmaline began at Mount Mica and continued almost without interruption for nearly 100 years.

Although Professor Silliman was a chemist and minerals are chemical compounds, it was not by chemical analysis that he identified the tourmaline. It was by those features of a mineral that can be recognized at sight or by simple tests. These include luster, color, crystal form, cleavage and fracture, hardness, and specific gravity, and are called the physical properties of a mineral.

Since each mineral has a characteristic set of physical properties, they are very important in distinguishing one mineral from another. However, their importance is not confined to mere identification. Many a mineral has a useful purpose resulting from one or more of its physical properties.

### LUSTER

We see objects because some of the light that falls upon them is reflected to our eyes. *Luster* is the name given to the way in which a mineral reflects light. Since the first thing a person does in examining a mineral is to look at it, luster is usually the first property observed. Some minerals are shining and brilliant and have the appearance of a metal. This appearance arises from the fact that such minerals are completely opaque and thus reflect a large part of the light that falls upon them. These minerals, of which copper, silver, galena, and pyrite are examples, are said to have a *metallic luster*.

On the other hand, those minerals which are transparent or translucent and either absorb or transmit most of the light that falls upon them have *nonmetallic luster*. The luster of those few minerals lying on the borderline between metallic and nonmetallic is called *submetallic*.

Some nonmetallic minerals are often quite transparent. Quartz, calcite, and fluorite are examples of common minerals through which one can often see the shapes of objects clearly. Other nonmetallic minerals transmit light, but the shapes of objects cannot be seen clearly through them. Still others, as much rutile and cassiterite, transmit light only through the thinnest edges. If no light passes through the thinnest edges, the mineral is metallic; if any light passes, it is nonmetallic.

There is a close connection between luster and the property called *streak*. The streak of a mineral is the color of its powder, usually observed by drawing a corner of the specimen across an unglazed porcelain tile. The tile is hard and slightly rough and so grinds a little powder from the specimen. The color of the powder is then clearly visible against the white background.

If a mineral gives a black or very dark-colored streak, its luster is metallic. If the streak is light colored, white or uncolored, the mineral is nonmetallic. The streak, together with examination of a thin edge to see if light is transmitted, helps to place a doubtful specimen in the proper group as to luster.

Since this property is often so characteristic, nonmetallic minerals are further subdivided on the basis of the quality of their luster. Thus clay has a *dull* or earthy luster. Quartz and olivine have the appearance of broken glass and hence have a *glassy* or *vitreous* luster. A large number of nonmetallic minerals have vitreous luster. A few minerals have a brilliant, almost oily, luster characteristic of diamond and thus called *adamantine*. This high luster is found in very hard minerals whose component atoms are linked tightly together. It is also characteristic of minerals containing a heavy metal such as lead or tin. Thus cerussite (lead carbonate) and cassiterite (tin oxide) have an adamantine luster.

Some minerals have a *pearly* luster, that shown by mother-of-pearl. This luster usually is seen on faces parallel to a cleavage that has permitted the mineral to partially separate into many thin layers. One can easily illustrate with cellophane how pearly luster develops. Take a small, transparent sheet of cellophane and fold it over and over on itself. After folding four times, resulting in 16 layers, the aggregate is no longer transparent and it has a pearly luster.

Some minerals, as asbestos, are in fibers arranged in parallel aggregates. The parallel arrangement imparts a sheen to the aggregate known as *silky* luster. This silky appearance is found in the variety of gypsum called satin spar.

## Color

In some minerals color is constant and so characteristic that it alone may serve to identify them. This is particularly true of the minerals with metallic luster. Little variation is seen in the brass-yellow of pyrite, the bronzy color of pyrrhotite, or the black of magnetite. However, the surfaces of these minerals may tarnish so that one should be sure a clean fresh surface is examined. The tarnish itself may be a characteristic property. Such an example is the brilliant-hued peacock tarnish that forms rapidly on a broken surface of bornite.

In some nonmetallic minerals the color is related to chemical composition and is always characteristic. Examples are the yellow of sulfur, green of malachite, the blue of azurite, and the pink of rhodonite. These colors are unmistakable. However, other minerals may have a great variety of colors resulting from small amounts of chemical impurities. Thus the color of tourmaline not only differs from one crystal to the next, it also may differ from one end of an individual crystal to the other. Likewise quartz, usually colorless, is purple in amethyst, yellow in citrine, and pink in rose quartz. Some impurities that color minerals are mechanical rather than chemical. Quartz may be colored red by inclosing finely divided particles of red hematite, or it may be colored green by inclosing tiny flakes of chlorite.

Thus we see that although color is easily determined, it must be used with caution in mineral determination and in a systematic study one must learn in which minerals color is always the same and diagnostic and in which it cannot be relied upon for identification.

Although different specimens of a mineral may be differently colored, the color of the powdered mineral or streak remains nearly constant. Thus, all the varieties of the mineral hematite, whether black and crystalline or earthy and red, give the same brownish-red streak. This color is often called "Indian red" because of its wide use as a face paint by American Indians.

Color is an important factor in minerals used for ornamental purposes and in gem stones. Many minerals in which the color is not constant are colorless when chemically pure. This is true of corundum, quartz, beryl, tourmaline, chrysoberyl, and many other lesser gem minerals. As colorless stones they are of little value, but minute amounts of chemical impurities may render them extremely valuable. Thus the presence of less than one per cent of chromium may transform colorless corundum into the highly prized ruby. Colorless beryl cut as a gem is worth little more than the cost of cutting, \$2–\$3 a carat. If a slight chemical impurity is present, making it a blue-green aquamarine, it is five to ten times as valuable. If, however, the presence of a minute amount of vanadium or chromium results in a deep green beryl, emerald, it may have a value as much as \$1000 a carat! The diamonds we are accustomed to see in jewelry are colorless, but unlike colorless beryl they are highly valued because of their brilliant luster and high hardness. If we were to see a group of rough diamonds, as they come from the mine we would find that more than half were not colorless. Most of these would be yellow and brown and some even black. The color in this case makes the diamond less attractive, and most of them will be used for industrial purposes. However, once in a long while a diamond is found that is a rich golden color or deep red, pink, or blue. These in the trade are called "fancies" with a value far greater than colorless stones. The famous blue Hope diamond is an example.

The ruby, sapphire, and emerald are valued as gems not only because of color but also because they are hard and durable and have a high luster. A few minerals have only color to make them attractive as gem stones. Since the time of the Egyptian Pharaohs, lapis lazuli has been valued as a gem and ornamental stone only because of its rich blue color. Likewise, the turquoise used so extensively by the American Indians in jewelry has its sky-blue color alone to make it attractive as a gem. Both these semiprecious gem materials are soft and lack the durability of diamond, ruby, and emerald.

Some of the colors observed in minerals are not directly traceable to coloring impurities. For instance, the dark color of smoky quartz can be produced by exposing the quartz to X rays, or radiation from radioactive elements. Very dark smoky quartz (Figure 14) is often found in nature closely associated with minerals of radioactive elements like thorium and uranium. This indicates that the coloring of minerals by radiation damage goes on in nature as well as in the laboratory.

**Figure 14.** Smoky quartz (dark) and feldspar, Florissant, Colorado. (Photograph courtesy of Ward's Natural Science Establishment, Inc.)

## FRACTURE AND CLEAVAGE

Some minerals break in a very characteristic manner which serves to aid in their identification. When tourmaline breaks, it presents a surface much like that of broken glass. This is a *conchoidal* fracture and is characteristic of tourmaline, quartz, and other hard minerals that have no preferred directions of breaking. Terms used to explain other types of fracture are self-explanatory such as *rough*, *irregular*, or *splintery*.

We have seen in Chapter 4 that the ions of which minerals are made are held together by electrical forces. If these forces are acting equally in all directions, the mineral breaks as glass does with a conchoidal fracture. If, however, the binding forces are much greater in certain directions than in others, the mineral will break at right angles to the weaker forces and yield smooth plane surfaces. Such surfaces, reflecting the regular internal structure, are called *cleavage*.

Examine a few grains of table salt, the mineral halite, under a magnifying glass. It will be seen that most grains are bounded by six plane surfaces forming little cubes (Figure 15c). Now crush a single grain and examine it again. It will be observed that each tiny particle is also a cube formed by the mineral cleaving equally well in three directions at right angles to each other. Cleavage is not confined to definite planes but will develop anywhere through the crystal parallel to a given set of atomic planes. Thus the "cubes" of salt may or may not be geometrical cubes. The important thing is that they, the cleavage surfaces, are similar in appearance and at right angles to each other.

The mica and feldspar associated with the tourmaline at Mount Mica were identified by the local people largely by the cleavage. They had learned that mica can be separated into extremely thin sheets along cleavage planes (Figure 15a). This property is so striking that it alone serves to identify the mineral. The feldspar also was identified by cleavage, but in this mineral the cleavage is less easily developed than in the mica and furthermore there are two directions at right angles to each other (Figure 15b).

Many minerals have cleavage, but it differs from mineral to mineral in the number of directions, the angles between them, the ease of development, and the perfection of the surface.

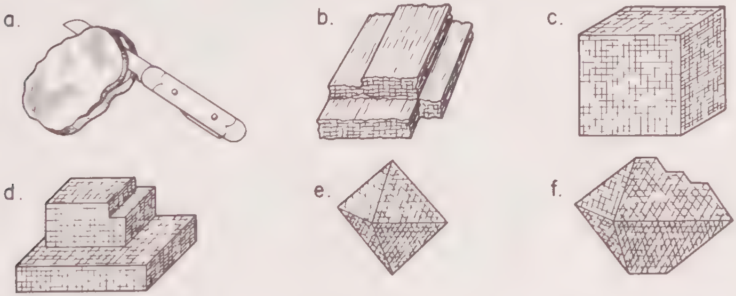


**Figure 15.** Cleavage. **a.** One cleavage direction (mica). **b.** Two cleavage directions (feldspar). **c.** and **d.** Three cleavage directions (halite). **e.** and **f.** Four cleavage directions (fluorite and diamond).

Cleavage is always parallel to a possible crystal face and is consistent with the crystal symmetry. Since cleavage is a fundamental property reflecting the internal structure, it is not subject to change with minor impurities as is color, and is a very important determinative property.

Although the diamond is a very hard mineral, it is at the same time brittle. If you were to put a diamond on an anvil and tap it with a hammer, it would shatter into many pieces. This is because it has four directions of perfect cleavage (Figure 15c). If, however, the force from the blow can be directed along a single plane the diamond can be split into two parts. This is frequently the first step in diamond cutting. However, even the skilled cutter will study a stone most carefully to make sure his blow will split the diamond along only one of its four directions of cleavage.

## HARDNESS

The stronger the electrical bonding forces holding the atoms together, the more difficult it is to separate them from one another and thus the harder the mineral. In some minerals the forces are so weak that in handling them, the skin of the fingers

Figure 16. Calcite crystals. Cumberland, England. (Photograph by B. M. Shaub.)

is hard enough to slide one layer of atoms over another. As a result such minerals, as talc or graphite, feel slippery or greasy. At the other extreme is diamond, which is so hard that it can be scratched by nothing except another diamond. The ease or difficulty with which these electrical bonds can be broken is a measure of the *hardness* (designated **H**) of a mineral. One can determine hardness in a qualitative way by scratching the mineral with the knife blade or another mineral.

Early in the 19th century the Austrian mineralogist Friedrich Mohs proposed a series of minerals numbered from one (the softest) to ten (the hardest) as standards of hardness. This list given below, known as the Mohs Hardness Scale, has been the standard of reference for over 150 years.

### MOHS HARDNESS SCALE

10. diamond
9. corundum
8. topaz
7. quartz
6. feldspar
5. apatite
4. fluorite
3. calcite
2. gypsum
1. talc

Each mineral is harder than and can scratch any other mineral below it in the scale. Thus calcite (3) can scratch gypsum (2) and talc (1); and topaz (8) can scratch quartz (7). On this scale window glass is 6, the knife blade 5½, a copper cent 3, and the fingernail 2½. Although testing hardness in this way is not a precision measurement, hardness is an important physical property and a complete description of any mineral includes it.

We have seen that hardness is related to the internal forces holding the mineral together. Since these forces frequently differ in different directions, it is reasonable to assume that hardness may be different in different directions. This is true. However, the nonprecise method suggested above of measuring the property is unable to detect subtle differences. It is only when there is a major difference that it can be detected. One example is calcite, number 3 in the scale. Over most of its surface it obviously has a hardness of 3. At one place parallel to a given set of atomic planes, it can be scratched by the fingernail and has a hardness of less than 2½.

The hardness of some minerals leads to their use as abrasives in cutting and polishing. There are pits on the Grecian island of Naxos from which the tough, black material, emery, was quarried by the ancient Greeks. They had discovered that emery was harder than their building materials of granite and marble and that it could be used to grind and polish them. Today emery is quarried from the same island and used for similar purposes.

About one hundred years ago it was learned that emery is a mixture of two minerals—corundum and magnetite—and that the cutting mineral is corundum (**H** = 9). A search for corundum resulted in finding many deposits of it in various parts of the world. It is still one of the standard industrial abrasives, but today much corundum is manufactured synthetically.

Other minerals are also used for cutting and polishing. Garnet (**H** = 6½–7½) and quartz (**H** = 7) are two of the most common and abundant minerals used for this purpose. Although even industrial grade diamond is expensive, it is so much harder than any other material that it is widely used as an abrasive. Diamond drills are used by the miner to sample the rock before mining. Thin metal discs impregnated with diamond are used to saw hard minerals and metals and even other diamonds. Because of its great hardness diamond has become an extremely important industrial mineral, and modern industry would be greatly slowed down without its use. Synthetic diamond is rapidly supplanting natural diamond from Africa as an industrial abrasive.

## SPECIFIC GRAVITY

Which is heavier, a pound of feathers or a pound of lead? Most of us have been guilty of asking this question of an unsuspecting child and occasionally the immediate reply is—"Lead is heavier, of course." The answer would be correct had the question been asked—Which is heavier, a bushel of feathers or a bushel of lead? In order to make comparisons of weights, we must be sure to compare equal volumes of two things. It doesn't matter whether the volumes concerned be pints, quarts, cubic inches, or cubic feet, so long as they are the same. We say lead is heavy only because we tend to compare its weight with the weight of other more familiar things of the same size. A cubic inch of lead would seem light compared with a cubic inch of gold.

Comparative weight is one of the important properties of minerals and is called *specific gravity* (designated Sp.G. or merely **G.**). Specific gravity is defined as the ratio of the weight of a given volume of a mineral to the weight of the same volume of some other substance taken as a standard. For solids the standard is water. Thus if a mineral weighs 3 pounds and an equal volume of water weighs 1 pound, the specific gravity is 3. The specific gravities of some metals are: magnesium, 1.74; aluminum, 2.70; iron, 7.86; lead, 11.34; gold, 19.3. Iron is the commonest metal with which we have daily contact, and we tend to accept its specific gravity as average for a metal. By comparison magnesium and aluminum seem light, and lead and gold heavy.

Unconsciously most of us have established an idea of specific gravity; that is, how much an object of a given size should weigh. If you pick up pebbles on a lake shore to skip on the water, you may throw one after the other without thinking they are either heavy or light for their size. If, however, you pick up a piece of the mineral barite, that looks like the other stones, you probably would look at it twice before throwing it. It seems too heavy; **G.** 4.5. The common stones we are used to handling are dominantly made of quartz (**G.** 2.65), feldspar (**G.** 2.60–2.75) and calcite (**G.** 2.72). Thus another mineral with a much greater or lesser specific gravity we consider unusual. With a little practice anyone can by hefting a specimen judge whether it is heavy, light or about average for its size.

Although barite with specific gravity 4.5 seems heavy for a nonmetallic mineral, we would not consider a metallic object with this specific gravity too heavy for its size. We thus have established another standard for metallic objects—we expect them to be heavier. In general metallic minerals have specific gravities higher than nonmetallic and that of the common mineral pyrite (**G.** 5.0) is average for them.

The chief factor influencing specific gravity is the weight of the atoms of which the mineral is composed. Consequently, if two minerals have the same structure with like bonding forces acting between the ions, the one composed of the heavier atoms usually has the higher specific gravity.

For example, consider the three minerals: rutile, pyrolusite, and cassiterite listed in the table below, all belonging to the same structure type. In each mineral the ratio of cation to anion (metal to oxygen) is 1:2.

CHANGE IN SPECIFIC GRAVITY WITH CHANGE IN CATION

| MINERAL | CHEMICAL COMPOSITION | ATOMIC WEIGHT OF CATION | SPECIFIC GRAVITY |
|---|---|---|---|
| Rutile | Titanium dioxide | 47.9 | 4.2 |
| Pyrolusite | Manganese dioxide | 54.9 | 4.8 |
| Cassiterite | Tin dioxide | 118.7 | 7.0 |

Another factor influencing specific gravity is related, as is hardness, to the type and strength of the bonding forces holding the atoms together. If the forces hold the atoms close together so that more are packed into a given volume, the specific gravity is higher than if the same atoms are held farther apart. Such an example is seen most dramatically in diamond and graphite. Both are made up entirely of atoms of carbon. Yet diamond, the hardest of minerals, has **G.** 3.5; whereas graphite, one of the softest, has **G.** 2.3. The powerful bonds in diamond hold the atoms closely together giving it a high hardness and specific gravity. Identical atoms in graphite are loosely held by weak van der Waal's bonds, giving the mineral a low hardness and specific gravity.

In order to find the specific gravity, one divides the weight of the mineral by the weight of an equal volume of water. Although it is easy to weigh the mineral fragment, it is much more difficult to determine the weight of a like volume of water. One, therefore, makes use of the well-known principle, that a substance immersed in water is buoyed up and weighs less than in air; and that the weight lost is equal to the weight of water displaced. Thus in making a specific gravity determination, one must weigh the mineral fragment first in air and then in water. The difference in the two readings is the weight of the equal volume of water. Specific gravity can thus be stated as:

$$\frac{\text{Weight in air}}{\text{Loss of weight in water}} = \text{specific gravity}$$

For example, suppose a small tourmaline crystal weighs 7.12 grams in air and 4.86 grams when immersed in water. The specific gravity can be calculated:

$$\frac{7.12}{7.12-4.86} = \frac{7.12}{2.26} = 3.15^{+}, \text{ the specific gravity}$$

Since specific gravity expresses merely a ratio, it is not necessary that the actual weights in air and in water be known but only the relative weights. A *beam balance*, such as shown in Figure 17, can be easily constructed to determine the relative weights. The beam *a b*, made of a thin piece of wood, is graduated into inches and tenths of inches with the zero point at *c*. The distance from *a* to *c* is about 4 inches. A heavy needle pressed through the beam at *c*, exactly at the zero graduation

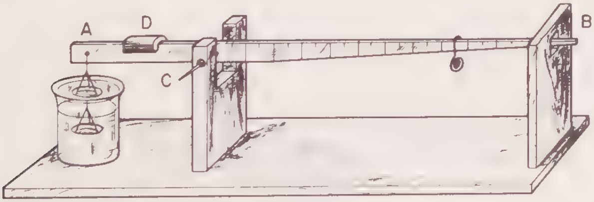


Figure 17. Beam balance.

serves as the axis. A fine wire is passed through a small hole at the *a* end of the beam from which two pans are suspended. Watch glasses with wires crisscrossing beneath them for support make good pans. The lower pan is immersed in water. A small piece of lead *d* is placed on the beam between *a* and *c* to counterbalance the long arm and bring it to a horizontal position as indicated on the upright at the *b* end. Make two or three counterbalances of different weights of soft copper wire or wire solder by forming a hook at one end and a small coil of wire at the other. These counterbalances need have no definite weight; the larger weights are used with the heavier specimens. Now you are ready to make a specific gravity determination.

Place a small mineral fragment in the upper pan. Now select the counterbalance which when placed near the *b* end of the balance restores the beam to a horizontal position. Note the position of the weight ($R_1$) which might be 8.4. Transfer the specimen to the pan immersed in water and *using the same weight* again restore the beam to a horizontal position. Because the specimen is now buoyed up and has lost weight equal to the weight of the water displaced, this reading will be smaller than the first. This position ($R_2$) might be 5.3. Although these numbers are not weights they are proportional to the weight first in air and then in water. The specific gravity is obtained by dividing the first number by the difference of the two numbers as:

$$\text{Specific gravity} = \frac{R_1}{R_1 - R_2} \quad \text{for the numbers given:} \quad \frac{8.4}{8.4 - 5.3} = 2.65^{+}$$

## OTHER PROPERTIES

Many other properties of minerals are of occasional importance in mineral recognition. The salty taste of halite, the strong and characteristic odor of clay, the response of magnetite and pyrrhotite to a magnet are such properties. Simple chemical tests are also used in practical mineral identification. Thus, the fact that calcite will "fizz" with cold dilute hydrochloric acid, whereas magnesite is unaffected, readily separates these similar species. However, mineral recognition and identification are a relatively minor part of modern mineralogy. It is those properties that lead to industrial and technologic applications that are most carefully studied by modern mineralogists.

Some of the most interesting properties of minerals cannot be detected readily with simple equipment and hence are seldom used in mineral identification. There are, however, examples in which the use of these properties has led to the development of multimillion-dollar industries. The fascinating story of the use of quartz for radio oscillator plates is an example.

You have no doubt come to rely on finding your favorite radio stations always at exactly the same places on the radio dial, but have never stopped to wonder how this is accomplished. As a matter of fact, the Federal Communications Commission requires radio broadcast stations to maintain their transmitted frequency within 50 cycles of their assigned frequency. At 1,500 kilocycles (1,500,000 cycles) this is a precision of one part in 30,000. Such close control of frequency can be attained only by the use of a radio oscillator plate cut from quartz. Vibrating mechanically one and a half million times a second, year in and year out, the pulsing quartz plate is truly the beating heart of the broadcast transmitter. The story of that dependable heartbeat begins more than 80 years ago.

In 1881 Pierre and Jacques Curie discovered an interesting property in quartz. They found that if pressure were applied to certain edges of a crystal (Figure 13), a positive electric charge appeared at one edge and a negative electric charge at the opposite edge. Electricity generated in this way is called *piezoelectricity* (pressure electricity). The Curies also found this phenomenon in crystals of certain other minerals. At first it appeared that there was no correlation between this property and the type of crystal, since representatives were found in each of the six crystal systems. On further study it was determined that a piezoelectric mineral crystallized in a symmetry class which lacks a center of symmetry. Quartz is one of these. It has a threefold symmetry axis and three twofold symmetry axes which emerge at the edges of the crystal where the electric charges are developed. The twofold axes are thus polar and sometimes called the "electric axes."

It was reasoned that if quartz generates an electric current when it is squeezed or mechanically deformed, might not the converse be true? That is, would not quartz become mechanically deformed if subjected to an electric field? Experiments carried out by the Curies proved this to be indeed the situation. However, interesting as this property of piezoelectricity was, it remained merely a laboratory curiosity for many years. It was not until World War I that any attempt was made to use it.

At that time the submarine menace to ship convoys crossing the Atlantic was great. The only way to tell of the presence of a submarine was to observe it when it surfaced—frequently this was too late. The solution to the problem of detecting and locating a submerged submarine was most urgent. Among the many suggestions put forth to solve the problem was the use of quartz and its piezoelectric property. The sound waves generated by the engines of a submarine might be detected if they had sufficient force on impinging on a submerged quartz plate to generate a piezoelectric current. Experiments carried out using quartz plates cut perpendicular to the polar axes were successful. It was found that the sound waves not only could be "picked up" by the quartz but also, since the electric current generated was proportional to the deforming force, a rough estimate of the distance could be made. Although these devices were developed too late to be of great value during the war, they pointed the way to many future applications.

It was not until 1921 that the piezoelectric property of quartz was used for the precise control of radio frequencies. This has proved to be its most important application. Used in this way, a properly cut, dimensioned, and mounted plate of quartz is subjected to the electrical field generated by a radio circuit. The alternating electrical current causes the quartz to vibrate, that is, to be mechanically deformed or flexed first one way and then the other. The thicker the quartz plate, the lower the frequency of vibration. If the frequency of the quartz plate coincides with the oscillations of the circuit, the frequency of radio transmission and reception can be precisely controlled. Thus almost from the time of the discovery of this use, quartz plates were used in radio transmitting stations to enable them to maintain their assigned frequencies.

The use of quartz oscillators gradually increased, but it was not until 1941 when the United States entered World War II that the demand became great. Then almost over night the requirements for the Armed Services rose from a few thousand a year to as many millions. It was essential that radio communication between ships, tanks, aircraft, and their command posts be controlled precisely. The quartz radio oscillator was the only means of doing this. As a result by war's end in 1945 over 55,000,000 oscillators had been manufactured!

To do this required a tremendous effort by many people. A supply of thousands of tons of quartz was required. Machines to cut the crystals had to be developed and manufactured. Frequency-measuring equipment had to be designed and produced as well as X-ray apparatus for the orientation of the quartz crystals.

It was a relatively easy problem to cut a quartz plate to certain dimensions and grind it to a given thickness. It was a far more difficult task to cut it in such a way that it made a precise angle with invisible atomic planes. This exactness of angular control was necessary, for it was discovered that as the temperature of the quartz plate changed, the frequency at which it oscillated also changed. Only if the plate were cut accurately in reference to the atomic structure of quartz could the variation of frequency with temperature change be held to a minimum. The problem of poorly cut crystals was of great concern during the early part of the war for "drift" of frequency with changing temperature meant uncertain communication. The temperature of an airplane radio could vary in a few minutes from 120°F on the ground to —50°F at an altitude of 20,000 feet. An improperly cut quartz oscillator could mean the complete loss of communication. Because of their specialized knowledge of crystallography, mineralogists were drawn into the program to help with the problems of crystal orientation. Of the 100 plants cutting quartz and manufacturing radio oscillators during the war, nearly half of them drew on the services of mineralogists.

Since the days of the experiments of the Curies tourmaline has also been known to be piezoelectric. When squeezed in the proper direction, tourmaline, like quartz, generates a measurable electric current. But it was early shown to be less effective as a radio oscillator than quartz. Moreover, compared to quartz, it is an extremely rare mineral, found in high quality in only small amounts. Nevertheless, tourmaline, because of its piezoelectric property, has played an interesting and important role in the measurement of high pressures.

With the first explosion of the atomic bomb in 1945, it was realized that the blast pressures developed were far greater than any previously experienced. No equipment was available capable of either withstanding or recording the pressures. Some completely new kind of pressure-recording instrument was necessary. The problem of developing such equipment was given to the Aberdeen Proving Ground, Maryland. Perhaps the piezoelectric response of tourmaline could be called upon. To test this possibility a plate was cut from a tourmaline crystal furnished by the Mineralogical Museum of Harvard University. The plate was cut at right angles to the "electric" axis and coated with metallic electrodes from which wires led to the recording equipment. Initial experiments showed that with certain refinements, tourmaline could be used to construct a satisfactory gauge for testing the atomic bomb.

One of the first problems that plagued the people at Aberdeen was to find a sufficient supply of high-quality tourmaline. Where should they look? Letters requesting information were sent out to many people, one of which went to the United States Geological Survey in Washington. This letter came to the attention of the mineralogist, Dr. Waldemar T. Schaller. Schaller remembered that several years earlier Martin Ehrman, a mineral dealer, had brought some fine tourmaline crystals into the country from Madagascar. He noted this in a letter to the Commanding General at Aberdeen. Shortly thereafter Ehrman received a letter from the General asking his help in locating a supply of tourmaline. The letter reached Ehrman, not at his address in Rockefeller Center, New York, but at Aberdeen, where as a Lieutenant Colonel he was in charge of the bomb-disposal school!

Ehrman immediately was relieved of his duties at Aberdeen and sent on a special mission with the hope of locating the stock of tourmaline that before the war had been brought from Madagascar to France. He discovered the shop in Paris was closed and the proprietor vanished. By good fortune he was able to locate a woman who had worked in the shop. She told him that the tourmaline was owned by the Companie Général de Grande Ile in Bordeaux. Arriving in Bordeaux Colonel Ehrman discovered that the Germans had vacated the city only the previous week. The company officials told him the Germans knew of the existence of the tourmaline and had made efforts to find it but were unsuccessful. It had been long buried in the Cognac forest, a district still occupied by the Germans.

With the aid of the French underground several wagons were assembled and under cover of night they drove to the farm on which the tourmaline was buried. While evading the watchful eye of the patrolling Germans, they dug up many tons of tourmaline, and drove it out of the hostile territory. The following day Ehrman sorted out three tons of the best tourmaline and started it on its way to America.

The bulk of this tourmaline has been cut and manufactured into piezoelectric gauges. These gauges have been used to measure the blast pressure of every atomic bomb test by the United States since 1945. The small amount of this tourmaline not cut is now at the National Museum, Washington, D.C.

CHAPTER 7

# MAN–MADE MINERALS

One of the goals of the mineralogist is to draw conclusions regarding the origin of minerals and answer such questions as, "Was this mineral formed at the earth's surface and if not, how deep below the surface? Was it the result of crystallization from a melt or did it precipitate from a watery solution? What chemical elements were present in the melt or solution? What were the temperature and pressure at the time of formation?" These questions are usually answered by inference and speculation. But there is a more direct approach. Why not try to duplicate the conditions of formation of the mineral in the laboratory? This has been done for many minerals. If the experiment is successful and the mineral has been formed in the laboratory, the experimenter can then infer that the conditions under which it was produced in nature may have been similar. Thus mineral synthesis is an important phase of mineralogical research and has brought about a much better understanding of the conditions under which minerals formed in nature. Of course, the natural environment in all its complexity can never be wholly reproduced in the laboratory.

Although much mineral synthesis is directed toward the production of sizable crystals for technologic or commercial purposes, most mineral synthesis carried out by mineralogists has no such purpose. The material produced, far from being beautiful or valuable, is usually a fine-grained powder whose identity must be established by X-ray methods. Furthermore, the substances synthesized are often the commonest and most prosaic of mineral substances—the rock-making minerals. Feldspar, pyroxene, and olivine, for example, have been the subject of much experimentation. These minerals make up basalt and gabbro, the rocks which are thought to constitute the larger part of the earth's crust. Basalt is known to underlie the ocean basins, and the more diversified rocks of the continental masses are thought to "float" on a substratum of denser basaltlike rock. Hence, these common and commercially almost worthless materials are the most frequently studied by petrologists and mineralogists who wish to learn more of the earth's structure.

An important means of carrying on such studies is the simple but effective technique called the quenching method. Suppose we wish to find out the temperature at which a mixture of pyroxene and feldspar will crystallize. We can weigh out the oxides of the elements—calcium, magnesium, aluminum, and silicon in the correct proportions. These chemicals would then be mixed together, put into a crucible and melted in a furnace. After solidifying, the reaction mixture is ground and placed in a small platinum envelope which is suspended by a thin wire in the furnace. The furnace is brought to a carefully measured temperature and held there until any reaction is probably complete. By burning out the tiny suspension wire the envelope is then caused to fall into a dish of mercury below the furnace. The mercury "quenches" the contents of the envelope; that is, cools them so quickly as to preserve their conditions at the temperature of the experiment. The contents of the envelope is then examined under the polarizing microscope. If the material is found to consist entirely of glass, the charge was completely liquid at the temperature of the experiment.

Another similar sample is now placed in the furnace, but the temperature is adjusted to a lower value. After a suitable time, the charge is quenched and examined. Perhaps now, tiny crystals of pyroxene are seen surrounded by glass. This means that at the temperature of the experiment, pyroxene had crystallized but all else was liquid. Another experiment at a still lower temperature may reveal crystals of pyroxene in a matrix of smaller crystals of both pyroxene and feldspar with little or no glass. At the temperature of this experiment we may then say that crystallization was complete. Now another composition is made up and the process repeated. After hundreds of runs, the experimenter can prepare what is called a *phase equilibrium diagram* showing what minerals, or *phases*, are formed at any temperature for any composition within the range of chemical composition he covered. This range he calls his *system*.

Thus, we may hear of a mineralogist writing about his work in the system $CaO\text{-}MgO\text{-}SiO_2$. This means he has studied combinations of these three chemical constituents at a variety of temperatures and has worked out, in whole or in part, a phase equilibrium diagram. This laborious and exacting work is the foundation upon which much of modern knowledge of rocks rests. The method is an old one. It was largely developed into a powerful tool for mineralogical research in the United States by the late N. L. Bowen and co-workers at the Geophysical Laboratory of the Carnegie Institute.

The quenching method has one very serious weakness; it cannot be used in systems containing water. Rocks always contain some water, and hence the quenching method cannot fully represent their condition of origin. For this and other reasons, the *hydrothermal method* of mineral synthesis, in which minerals are made in sealed bombs or autoclaves with water and volatiles present, is supplementing and aiding the results from quenching experiments.

No samples are available from deep within the earth. But we know that the temperatures and pressures there are extremely high; higher than the temperature of the quenching method or the pressure of the hydrothermal. To try to reproduce in part the conditions that exist at great depths, presses are used. In these, very small samples are crowded between the hammer and anvil to such an extent that in some presses pressures of 1,500,000 pounds per square inch are reached. This is equivalent to a depth of 250 miles beneath the earth's surface! In such presses diamond is synthesized. The very highest pressures and temperatures are achieved in *shock tubes*. In these, hot gases from an explosion generate a shock wave in a tube like a gun barrel. Momentarily both pressure and temperature rise to very high levels.

Although many of the techniques used for mineral synthesis are new, experiments have been going on for over 150 years. The early experimenters, however, were more interested in practical results than in gathering scientific data. As the alchemists were interested in transmuting base metals into gold; so the early efforts in mineral synthesis were directed to produce minerals of great value. These were the gem stones: diamond, ruby, sapphire, and emerald. See Figure 18. Of greatest interest of all was diamond since it had the greatest value.

There is a great difference between an imitation and a synthetic gem stone. The imitation is not the same thing chemically or physically as the stone it is made to imitate. It may be a common mineral of similar color or even colored glass. A synthetic gem stone is one that differs from a natural one only in that man has made it. Chemically and physically it is the same. A good mineralogist or gemologist, therefore, has little difficulty in detecting the imitation but may be hard put to distinguish the synthetic from the natural.

**Figure 18.** Synthetic sapphires and rubies before cutting. The "boule" on the extreme right is 350 carats. (Photograph courtesy of Union Carbide and Carbon Corp.)

In any experiment of mineral synthesis, it is of course necessary to know the chemical composition of the mineral. The next step is to determine as closely as possible the conditions under which the mineral forms in nature and try to duplicate them in the laboratory.

The word *diamond* comes from the Greek, *adamas*, meaning indestructible. This name is well given, for it was early discovered that diamond could not be destroyed by ordinary means. In the flame of an ordinary fire it remained unchanged, and the strongest chemical reagents had no effect on it. To be sure, if struck by a hammer, it would shatter, but this merely made smaller fragments. How then was it possible to tell the chemical composition of the diamond? This was done in Florence, Italy, in 1694.

Although diamond would not burn at the temperature of an ordinary fire, it was believed that it might burn or melt at a higher temperature. At that time there was no electric furnace or other easy means of getting temperatures higher than given by burning wood or coal. It was known, however, that the sun's rays focused by a lens on a small area gave a high temperature and that the larger the lens the higher the temperature. It was in Florence that a burning-mirror of great size was constructed at the order of Cosimo III, Grand Duke of Tuscany. When used to collect the sun's rays, it gave at the focal spot an exceeding high temperature, one that seemingly would melt anything. Would it melt diamond? The rays from the hot Italian sun were focused by this great mirror on a diamond; surely it would melt as other materials had melted under the same intense heat. But no. At first there was no apparent change and then it was noted that the diamond was becoming smaller, merely wasting away. Finally the diamond completely disappeared, leaving no residue! What was the composition of such material that could vanish into the air?

More diamonds were sacrificed in repeated experiments. A great burning-lens four feet in diameter was constructed at Tschirnhaus. Finally, in the late 18th century, under the guidance of Lavoisier, arrangements were made to recover any gaseous products that resulted. After the experiment the gas that had formed was analyzed and found to be carbon dioxide and nothing else. It was thus realized that the diamond must be pure carbon which under the intense heat had reacted with the oxygen of the air; that is, it had burned, forming only the colorless gas carbon dioxide. In this way it was established that diamond is composed of nothing but the element carbon. Here then had been determined the chemical composition, information that was essential before there could be any hope of synthesis. But what were the pressure and temperature conditions under which diamond formed in nature?

It was believed that diamonds originate deep beneath the earth's surface where both the pressure and the temperature are extremely high. Therefore, to synthesize diamond one must subject pure carbon to these same conditions. It was 260 years after the experiment in Florence before apparatus was constructed that could create the pressure necessary and at the same time withstand the high temperature. In the interval many workers were busy on the problem. Several reported success only to be proved later they were wrong. Some workers apparently issued false reports; others truly believed they had synthesized diamond when in fact it was another material. But today there are man-made diamonds.

With modern steel to withstand high pressure and yet not weaken under high temperature, new attempts were made by several companies to manufacture diamond. Using carbon from different sources, different materials such as nickel metal as fluxes, and strengthening the equipment to withstand ever-increasing temperature and pressure, workers conducted thousands of experiments. Laboratory workers eagerly subjected the product of each experiment to tests. After failures without number, imagine the joy of one experimenter when, under the microscope, he saw tiny crystals that looked like diamond. A co-worker agreed they appeared to be diamond, but how hard are the crystals? They scratch glass and sapphire, as diamond should. But is this proof? An X-ray examination will tell if the tiny crystals have the atomic structure of diamond. An hour to record the X-ray diffraction on photographic film was an impatient one. When the film was developed, the lines on it showed with complete certainty it was indeed diamond that had been synthesized. This successful experiment was performed by the General Electric Company late in 1954. Unlike the efforts of earlier workers, these experiments received no public mention until they could be repeated and the products tested and retested. In February 1955 the announcement was made that diamonds had been made by man at temperatures up to 5000 F and pressures up to 1,500,000 pounds per square inch.

Although the diamonds were small, no greater in diameter than the dot of an i, it was the fulfillment of man's dream of hundreds of years. Since then, improved techniques have enabled somewhat larger diamonds to be produced, and today millions of carats of diamond are manufactured each year for industrial purposes. Large clear stones that we see in jewelry have not yet been made by man, but with advancing technology it is conceivable that they will be soon.

## Synthetic Corundum

Except for a small amount of "impurities" which make the ruby red and the sapphire blue, these two gems are the same both chemically and physically. They are the best known of many color varieties of the mineral corundum, aluminum oxide. Without coloring "impurities" corundum is clear and colorless.

Since ruby has always been the most highly prized of the corundum gems, efforts to synthesize it have been many. The first successful attempt was in 1837, but the stones were only microscopic in size. During the next 65 years many other experiments were carried out, mostly in France, but none produced cuttable stones. In 1902 Auguste Victor Louis Verneuil announced that he had developed a process whereby not only ruby but sapphire and corundum of other colors could be manufactured.

In this method of synthesis, known as the Verneuil process, the corundum is grown at a high temperature, 3800–4000°F. A small stream of fine powder of aluminum oxide, the composition of the corundum, is allowed to fall through a hot flame produced by a mixture of oxygen and hydrogen. In the brief passage through the flame the powder melts and tiny molten droplets fall to a plate below where there has been placed a small fragment of crystallized corundum. Here where the temperature is lower, the atoms of each droplet arrange themselves on the "seed" of corundum in a manner to extend the crystal lattice upward and outward. Gradually a carrot-shaped mass with the broad end toward the flame is built up. This is called a *boule* and may be as much as an inch in diameter and three to four inches long. If all conditions have been properly controlled, this boule is a flawless single crystal but without crystal faces.

By adding chemical impurities to the powdered aluminum oxide, workers can cause the synthetic corundum to take on various colors. Chromium oxide colors the boules red, and the product is *synthetic ruby.* Iron and titanium oxide give a blue color to produce *synthetic sapphire.* Oxides of various other elements yield other colors.

Synthetic corundum grown in this way is so nearly like the natural mineral that it is difficult to tell the two apart once they are cut into gem stones. The chemistry, the hardness, the specific gravity are the same and only the expert with aid of his microscope can distinguish them by observing tiny irregularities and impurities. Frequently the synthetic is more perfect than the natural. In spite of this fact most purchasers of gem stones are quite willing to pay more for the natural. For a fine quality natural ruby the cost is nearly 1000 times that of a synthetic stone of similar size!

Corundum is not only synthesized to be sold by the carat as a gem, but it is also manufactured by the ton for abrasive purposes. About the time the Verneuil process was being perfected, abrasive manufacturers were busy trying to make synthetic abrasives for grinding and polishing to take the place of those found in nature. From the time of the ancient Egyptians until about 1900 A.D., corundum was the major abrasive material, first used as a mixture with magnetite in emery and later as crystals of corundum. These were expensive as mined in out-of-the-way places in Greece, Turkey, South Africa, Canada, and the United States.

For such an inexpensive product as abrasives, making a chemically pure powder of aluminum oxide as a starting material was much too costly. Something had to be found in nature that contained aluminum oxide sufficiently pure, which on fusion might recrystallize as corundum. The ore of aluminum, bauxite, seemed to answer these requirements. It is a mixture of several minerals containing essentially aluminum, oxygen, and water. In the high temperature of the electric furnace the water present in the minerals of bauxite was driven off and the remaining material fused to a molten mass. On cooling slowly it formed a polycrystalline mass of aluminum oxide, corundum.

This was one of the first great triumphs in mineral synthesis. Man had made and was able to make in vast quantities a useful substance from abundant natural materials. Today synthetic corundum has almost completely replaced the natural abrasives, and in the United States it is sold under the names of *alundum* and *aloxite*. The first is named in allusion to its physical and chemical identity to corundum, and the second in reference to the starting material, bauxite. The first two letters of both, *al*, refer to the metal aluminum.

## SYNTHETIC EMERALD

Emerald is a variety of the mineral beryl (beryllium aluminum silicate). It owes its deep green color to the presence of small amounts of either chromium or vanadium. Most large stones have come from one of two old localities, either the Ural Mountains, U.S.S.R., or the Muso district in Colombia, South America. In the Ural Mountains they are associated with schist, a layered metamorphic rock and in Colombia with metamorphic limestones. Emeralds are also found at numerous other localities and occur in a variety of geologic environments. The most recent in 1956, are the Sandawanda emeralds from Southern Rhodesia, found in a schist.

Synthetic emeralds, too small for gem purposes, were reported in 1848 and again in 1885 as crystallized from a melt with fluxes. In 1930 the German chemical trust, I. G. Farben, marketed a few synthetic emeralds of gem size and quality. The process they used has never been disclosed. Shortly after this, Carol Chatham, of San Francisco, produced large stones, over one carat in weight. Although this process remains a secret, it probably is similar to the original experiments, crystallization from a melt with fluxes. Chatham synthetic emeralds, produced now for over 25 years, are in almost every way identical with natural stones. They are emeralds in the chemical and crystallographic sense and are of a fine color. The Smithsonian Institution displays a Chatham emerald crystal of 1014 carats! Synthetic emeralds display a red fluorescence in ultraviolet light which natural stones do not. In other regards they are practically identical.

## Quartz Synthesis

When minerals are abundant and accessible as found in the rocks, man through the years understandingly has shown little interest in synthesizing them. Only when they are rare or costly do the rewards for synthesis become attractive. Such is the case with diamond, ruby, sapphire, and emerald. Why then in recent years has there been a great effort to synthesize quartz, one of the most common and abundant minerals on the surface of the earth?

Although quartz is common, even as well-formed crystals, Brazil is the only country in the world where it is found in large enough and flawless enough crystals to be used for radio oscillators and in optical equipment. During World War II there were times of inadequate supply due both to lack of production and difficulties of transportation. At that time efforts were made in several countries to grow quartz. Successful synthesis of quartz required that it not only be flawless but that it be in large crystals. The war had ended before usable crystals had been produced, but the experimentation continued. Today many tons of flawless quartz crystals are being synthesized each year, whose individual weights are measured in pounds rather than in carats or ounces.

Many different methods have been used in growing quartz, but the hydrothermal process has proved most successful. In this process the temperature is high (750°F) and the pressure also is high (up to 25,000 pounds per square inch). To withstand such pressures and temperature the vessels in which the crystals are grown, called autoclaves, are made of special steel, and resemble huge rifle barrels. They are about 10 feet long with walls 3 inches thick and when in operation are placed vertically.

In the bottom of this long tube are placed broken fragments of quartz and in the top half arranged in racks are "seed" plates of quartz. The autoclave is then filled about 80% full of a solution of sodium hydroxide and the open upper end sealed securely. Heaters are arranged around the autoclave in such a way that the bottom is kept hotter than the top. As the temperature rises the liquid inside expands until it completely fills the cavity; with additional heat, the liquid, unable to expand further, builds up a high pressure. At the high temperature and pressure the solution dissolves the nutrient quartz in the bottom of the autoclave and convection carries it toward the top. Here at a lower temperature the solution deposits the dissolved material on the seed plates, slowly building up larger and larger crystals. At the end of a three-week period when the autoclave is opened, most of the nutrient quartz is gone and "seeds" have grown into crystals 5 to 6 inches long, weighing 1 to 2 pounds.

Although a pound of synthetic quartz costs more than a pound of natural quartz, the synthetic crystals may prove to be less expensive. Natural quartz is usually flawed, making much of it unusable, whereas synthetic quartz is flawless and completely usable. As methods of growth become more perfected, it is quite probable that most, if not all, of the requirements of quartz crystals can be met with synthetic material.

## CONCLUSION

The few examples chosen from the field of mineral synthesis suggest the many and varied activities of the modern mineralogist. Numerous cases could also be cited in which mineralogical research has supported and aided mining and metallurgy. Ores cannot be efficiently extracted from the ground, nor metals from their ores, without some knowledge of the minerals of which the valuable metals form a part. Some ores are very complex and metal values are dispersed among numerous minerals, all having different properties. Mineralogists, studying polished sections of ores with the reflecting microscope, contribute the vital information as to minerals present, grain size and mode of intergrowth, so that proper recovery techniques may be used. Further, mineralogical study of ores leads to knowledge of the conditions under which the ores formed, and hence to reasonable inferences as to the quantity and quality of ore to be found at greater depth.

Although mineralogists cooperate with many specialists in solving industrial problems, it is also true that most mineralogists study minerals primarily because they are curious about them. Exhaustive and highly detailed work has been done again and again on the structure, chemistry, physical properties and conditions of origin of rare minerals of no great economic importance. Mineralogists investigate minerals for the same reason that mountain climbers climb mountains; because they are there. It is not right to say that such studies are useless or that such curiosity is idle: so complex is the world in which we live that almost no information that is true will ever be wholly useless. Nevertheless, the significant point is the motivation of the scientist. It is not an ultimate application, but the gaining of the knowledge itself, that is his goal.

So mineralogy, like every true science, has an inner life of its own, transcending and outlasting the material benefits that accrue from its findings. Like all science, it has continuity, in that every generation builds on the work of preceding generations, so that nothing is lost. And like every true science, mineralogy is a living growth, looking to an unimaginable future. In that future, whatever it contains, mineralogists will continue with the task of interpreting the world we live in and shaping the world of more distant tomorrows.

# APPENDIX

## PROPERTIES OF SOME COMMON MINERALS

| NAME | LUSTER | CRYSTAL SYSTEM | SPECIFIC GRAVITY | HARDNESS | REMARKS |
|---|---|---|---|---|---|
| Albite | vitreous | Tricl. | 2.62 | 6 | 2 cleavages |
| Andalusite | vitreous | Orth. | 3.16–3.20 | 7½ | in crystals |
| Anglesite | adamantine | Orth. | 6.2–6.4 | 3 | 2 cleavages |
| Anhydrite | vitreous | Orth. | 2.9–3.0 | 3–3½ | 3 cleavages |
| Anorthite | vitreous | Tricl. | 2.76 | 6 | 2 cleavages |
| Apatite | vitreous | Hex. | 3.15–3.20 | 5 | 1 poor cleavage |
| Aragonite | vitreous | Orth. | 2.95 | 3½–4 | 2 cleavages |
| Arsenopyrite | metallic | Mon. | 6.07 | 3½ | silvery |
| Augite | vitreous | Mon. | 3.2–3.4 | 5–6 | black, 2 cleavages |
| Azurite | vitreous | Mon. | 3.77 | 3½–4 | blue |
| Barite | vitreous | Orth. | 4.5 | 3–3½ | 3 cleavages |
| Bauxite | earthy | — | 2.0–2.5 | 1–3 | a mixture |
| Beryl | vitreous | Hex. | 2.75–2.8 | 7½–8 | green |
| Biotite | vitreous | Mon. | 2.8–3.2 | 2½–3 | 1 cleavage, black |
| Bornite | metallic | Iso. | 5.07 | 3 | purple-tarnish |
| Calcite | vitreous | Hex. | 2.72 | 3 | 3 cleavages |
| Cassiterite | adamantine | Tet. | 6.8–7.1 | 6–7 | tin ore |
| Celestite | vitreous | Orth. | 3.96 | 3–3½ | 3 cleavages |
| Cerussite | adamantine | Orth. | 6.55 | 3–3½ | good cleavage |
| Chalcopyrite | metallic | Tet. | 4.1–4.3 | 3½–4 | yellow |
| Chlorite | vitreous | Mon. | 2.6–2.9 | 2–2½ | green, 1 cleavage |
| Chromite | submetallic | Iso. | 4.6 | 5½ | black |
| Chrysoberyl | vitreous | Orth. | 3.65–3.8 | 8½ | in crystals |
| Cinnabar | earthy | Hex. | 8.1 | 2½ | red |
| Copper | metallic | Iso. | 8.9 | 2½–3 | red |
| Corundum | vitreous | Hex. | 4.02 | 9 | various colors |
| Diamond | adamantine | Iso. | 3.5 | 10 | in crystals |
| Dolomite | vitreous | Hex. | 2.85 | 3½–4 | 3 cleavages |
| Emery | metallic | — | — | 9 | corundum + magnetite |
| Epidote | vitreous | Mon. | 3.3–3.4 | 6–7 | green |
| Feldspar | vitreous | Mon., Tri. | 2.57–2.74 | 6 | 2 cleavages |
| Fluorite | vitreous | Iso. | 3.18 | 4 | 4 cleavages |
| Franklinite | metallic | Iso. | 5.15 | 6 | Franklin, N. J. |
| Galena | metallic | Iso. | 7.4–7.6 | 2½ | 3 cleavages |
| Garnet | vitreous | Iso. | 3.5–4.3 | 6½–7½ | in crystals |
| Goethite | metallic | Orth. | 2.37 | 5–5½ | brown streak |
| Gold | metallic | Iso. | 19.3 | 2½–3 | yellow |
| Graphite | metallic | Hex. | 2.3 | 1–2 | black |

| NAME | LUSTER | CRYSTAL SYSTEM | SPECIFIC GRAVITY | HARDNESS | REMARKS |
|---|---|---|---|---|---|
| Gypsum | vitreous | Mon. | 2.32 | 2 | 3 cleavages |
| Halite | vitreous | Iso. | 2.16 | 2½ | 3 cleavages, salty |
| Hematite | metallic | Hex. | 5.26 | 5½–6½ | red |
| Hornblende | vitreous | Mon. | 3.2 | 5–6 | black, 2 cleavages |
| Ilmenite | metallic | Hex. | 4.7 | 5½–6 | black |
| Kaolinite | earthy | Mon. | 2.6 | 2–2½ | clay |
| Lepidolite | vitreous | Mon. | 2.8–3.0 | 2½–4 | purple mica |
| Limonite | earthy | — | 3.6–4.0 | 5–5½ | brown streak |
| Magnesite | vitreous | Hex. | 3.0 | 3½–5 | 3 cleavages |
| Magnetite | metallic | Iso. | 5.18 | 6 | magnetic |
| Malachite | vitreous | Mon. | 3.9–4.0 | 3½–4 | green |
| Marcasite | metallic | Orth. | 4.89 | 6–6½ | brassy |
| Mica | vitreous | Mon. | 2.8–3.2 | 2–4 | 1 cleavage |
| Monazite | vitreous | Mon. | 5.0–5.3 | 5–5½ | small crystals |
| Muscovite | vitreous | Mon. | 2.76–3.1 | 2–2½ | 1 cleavage, mica |
| Olivine | vitreous | Orth. | 3.3–4.4 | 6½–7 | green |
| Opal | vitreous | — | 1.9–2.2 | 5–6 | noncrystalline |
| Orthoclase | vitreous | Mon. | 2.57 | 6 | 2 cleavages |
| Pyrite | metallic | Iso. | 5.02 | 6–6½ | yellow |
| Pyrolusite | sooty | Tet. | 4.75 | 1–2 | black |
| Pyrrhotite | metallic | Hex. | 4.6 | 4 | magnetic |
| Quartz | vitreous | Hex. | 2.65 | 7 | no cleavage |
| Rhodonite | vitreous | Tri. | 3.6–3.7 | 5½–6 | 2 cleavages |
| Rutile | adamantine | Tet. | 4.2 | 6–6½ | red |
| Serpentine | vitreous | Mon. | 2.2 | 2–5 | green |
| Siderite | vitreous | Hex. | 3.85 | 3½–4 | brown |
| Silver | metallic | Iso. | 10.5 | 2½–3 | usually tarnished |
| Sodalite | vitreous | Iso. | 2.2–2.3 | 5½–6 | blue, 6 cleavages |
| Sphalerite | adamantine | Iso. | 3.9–4.1 | 3½–4 | 6 cleavages |
| Spinel | vitreous | Iso. | 3.6–4.0 | 8 | in crystals |
| Spodumene | vitreous | Mon. | 3.1–3.2 | 6½–7½ | 2 cleavages |
| Staurolite | vitreous | Orth. | 3.6–3.7 | 7–7½ | brown |
| Stibnite | metallic | Orth. | 4.5–4.6 | 2 | 1 cleavage |
| Sulfur | vitreous | Orth. | 2.0 | 1½–2½ | yellow |
| Talc | pearly | Mon. | 2.7–2.8 | 1 | greasy feel |
| Topaz | vitreous | Orth. | 3.4–3.6 | 8 | 1 cleavage |
| Tourmaline | vitreous | Hex. | 3.0–3.2 | 7–7½ | in crystals |
| Turquoise | vitreous | Tri. | 2.6–2.8 | 6 | blue-green |
| Uraninite | submetallic | Iso. | 9.0–9.7 | 5½ | radioactive |
| Wolframite | metallic | Mon. | 7.0–7.5 | 5–5½ | black, 1 cleavage |
| Zircon | adamantine | Tet. | 4.68 | 7½ | in crystals |

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## GLOSSARY

**abrasive:** a substance used for cutting and polishing.

**actinides:** radioactive elements, atomic numbers 89–103

**adamantine luster:** diamondlike luster.

**alchemy:** a pseudoscience of medieval times having as its purpose the transmutation of base metals to gold, the attainment of perpetual youth, etc.

**alkali earth:** one of a group of elements forming divalent cations including calcium, strontium, and barium.

**alkali metal:** group of elements which react with water to form "alkalis," or strong bases.

**American Mineralogist:** the journal of the Mineralogical Society of America; the chief periodical about mineralogy in the United States.

**Angstrom unit:** one hundred-millionth of a centimeter.

**anion:** atom with negative charge.

**atom:** the smallest unit of a chemical element.

**atomic number:** number of protons or electrons in an atom.

**atomic weight:** the average weight of the atoms of an element expressed in units of $\frac{1}{12}$th of the weight of a carbon atom.

**axes:** crystallographic directions through a crystal used as lines of reference.

**axial ratio:** the ratio of the unit cell edges to one cell edge taken as unity.

**axis, symmetry:** a direction through a crystal about which the crystal is symmetrical.

**base exchange:** a chemical reaction in which one cation leaves its place in a solid crystal while another cation from the solution takes its place.

**boiling point:** the temperature at which a cooling gas becomes a liquid.

**bomb:** a heavy-walled reaction vessel, or autoclave, used to carry out reactions at high pressure and temperature.

**Bravais lattices:** the 14 frameworks on which crystals are built.

**cation:** atom with positive charge.

**center of symmetry:** a point in a crystal about which the crystal is symmetrical.

**cleavage:** a plane surface produced on breaking a mineral or the property of breaking so as to yield smooth, plane surfaces.

**coordination number:** the number of atoms surrounding a central atom.

**covalent bond:** electrical force holding atoms together, arising from sharing of electrons.

**crystal:** a solid with characteristic internal order bounded by symmetrically arranged plane surfaces.

**crystal chemistry:** science relating the chemistry and crystal structure to the properties of solids.

**crystal class:** one of the 32 combinations of symmetry elements.

**cube:** crystal form having six faces at right angles, ideally square.

**double refraction:** the property of breaking light into two rays, polarized at right angles, which move through the crystal at different speeds.

**economic geology:** the science of locating and processing ores.

**electron:** a negative charge of electricity.

**electron-shared bond:** (see covalent bond)

**element:** one of the 103 fundamental building blocks of matter, not capable of decomposition into simpler substances by chemical means.

**flux:** a substance to reduce melting temperature.

**fracture:** the way a mineral breaks along directions that are not cleavage planes.

**freezing point:** temperature at which a cooling liquid becomes a solid.

**geochemistry:** the science dealing with the abundance and distribution of the elements in the earth.

**geologic thermometer:** a mineral which indicates the temperature of formation of the deposit.

**goniometer:** a device for measuring the interfacial angles on crystals; *contact* and *optical*.

**halogen:** an element that reacts with metals to form salts.

**hardness:** resistance of a substance to being scratched, ground away or indented.

**hexagonal:** the crystal system in which crystals have a sixfold symmetry axis.

**hypo:** sodium thiosulfate, used as a fixer in photography.

**identity period:** the distance between like points in a crystal lattice measured along a crystallographic axis.

**inert gas:** a gas that does not enter into chemical reactions.

**interfacial angle:** angle between the perpendiculars to two crystal faces.

**ionic bond:** electrostatic force holding ions together in a crystal.

**ionic radius:** the radius of an ion measured in Angstrom units.

**isometric:** the crystal system in which crystals have four threefold symmetry axes.

**isotopes:** atoms of a given element differing slightly in weight.

**lanthanides:** rare earth group of elements, with atomic numbers 58–71.

**laser:** a device for light amplification using a crystal, a gas, or a liquid excited or "pumped" from an auxiliary light source.

**luster:** the manner in which a mineral reflects light.

**magnetism:** the property of being affected by a magnet; some materials are attracted, like magnetite; others, such as beryl, are repelled.

**maser:** a device for amplifying microwave radio signals by means of a crystal, a gas, or a liquid excited or "pumped" by an auxiliary radio frequency generator.

**metamorphic rock:** a rock that has undergone changes due to change in pressure and temperature.

**meteorite:** material from outer space consisting of nickel-iron, rock, or a mixture of iron and rock.

**Mohs scale:** series of minerals used as hardness scale.

**molecule:** two or more atoms united by strong chemical bonds into an electrically neutral unit.

**monoclinic:** crystal system in which crystals have one twofold axis, a symmetry plane or both.

**morphological crystallography:** the study of the external shapes of crystals.

**mother-of-pearl:** iridescent portion of mollusk shells, made of the mineral aragonite.

**octahedron:** isometric crystal with eight equivalent faces.

**optical crystallography:** the study of the behavior of light in crystals.

**orthorhombic:** crystal system in which crystals have two or three symmetry planes and twofold symmetry axes at their intersection.

**oscillator plate:** a thin slab of quartz which, by mechanical vibration, controls the frequency of a radio transmitter.

**pearly luster:** luster shown by easily cleavable minerals.

**periodic table:** table in which similar elements are placed one above the other.

**piezoelectricity:** electricity produced in crystals by pressure.

**plane of symmetry:** an imaginary plane dividing a crystal so that one part is the mirror image of the other.

**polycrystalline:** a term describing an aggregate of many interfering crystals.

**polymorphism:** occurrence of a chemical element or compound in two or more different structure types.

**powder photograph:** X-ray diffraction picture of a fine powder.

**proton:** positive charge in the nucleus of an atom.

**pseudomorph:** mineral with the crystal shape of another mineral.

**radius, ionic:** proportionate share of the inter-ionic distance in crystals assigned to one of the bonded ions: has no meaning in free space.

**radius ratio:** the ratio of the radius of the smaller to the larger ion: may not exceed 1.

**refraction:** the bending of light at an interface between two substances in which light moves at different speeds.

**silicate:** mineral or compound with a framework composed of silicon and oxygen atoms.

**solid solution:** substitution of one ion for another in a crystal.

**specific gravity:** weight of a substance compared to weight of an equal volume of water.

**streak:** color of powdered mineral.

**streak plate:** unglazed porcelain to test streak.

**structure, crystal:** the way atoms are arranged in a crystal.

**submetallic luster:** luster between metallic and nonmetallic.

**synthetic mineral:** an artificial substance having all the properties of a mineral.

**tarnish:** surface color due to alteration of a mineral.

**tetragonal:** crystal system in which crystals have one fourfold symmetry axis.

**transistor:** a device for amplifying alternating electrical currents by the controlled movement through a crystal of silicon or germanium of electrons and holes.

**transition elements:** elements with atomic numbers 21–30; 39–48; 57–80.

**triclinic:** crystal system in which crystals have no axes or planes of symmetry.

**ultraviolet:** portion of spectrum having wavelength shorter than visible light and longer than X rays.

**unit cell:** smallest unit of a crystal lattice having all the properties of the crystal.

**valence:** the power of combining with other elements.

**Van der Waal's bond:** weak bonding in crystals.

**vitreous luster:** the reflection of light so as to produce the appearance of broken glass.

**wavelength:** distance between similar points on successive waves.

**X ray:** penetrating radiation of wavelength between 0.01 and 100 Angstrom units.

# INDEX

## THE CHANGING SCIENCE OF MINERALOGY

With the advent of X-ray crystal analysis, mineralogy changed from being a purely descriptive science to an exact, experimental one. The impact of this change resulted in an understanding of the internal structure of minerals. Many of the problems that perplexed earlier mineralogists were solved. In this book Dr. Hurlbut and Dr. Wenden provide the basic chemical theory necessary for understanding this revolution in mineralogical thought and method. They discuss the arrangement of atoms in crystals and the forces which hold the atoms together. They show how the physical properties of minerals result from the internal structure. Through such knowledge materials of the laboratory have become the building blocks of new industries and are contributing to our future civilization.

### THE AUTHORS

Dr. Cornelius S. Hurlbut is Professor of Mineralogy at Harvard University from which he received his Ph.D. in 1933. He has three times revised the MANUAL OF MINERALOGY, a standard college textbook in the field. He is president of the Mineralogical Society of America (1963).

A student of Dr. Hurlbut, Dr. Wenden completed his Ph.D. work at Harvard in 1958. He is Associate Professor of Mineralogy at Ohio State University and was the recipient of the 1962 Neil Miner Award given by the National Association of Geology Teachers for outstanding teaching in the earth sciences.

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