

# Chapter 2

## Properties of Minerals

### 2.1 Mineral Chemistry

Mineral chemistry as a science was established in the early years of the nineteenth century by Joseph-Louis Proust's proposal of the Law of Constant Composition in 1799, John Dalton's Atomic Theory in 1805, and the development of accurate methods of chemical analysis. By definition, a mineral has a characteristic composition expressed by its formula, e.g., halite (NaCl) or quartz (SiO<sub>2</sub>).

Atoms are the basic building blocks of all matter, including minerals. Atoms are extremely small, about 10<sup>-8</sup> cm, and are themselves composed of smaller particles: electrons, protons, and neutrons. Only the electron portion of atoms will concern us in this book. Because mineral color was so critical in many ancient uses of minerals, the relevant electronic structure of atoms is presented and related to color variation in Sect. 2.3.

A basic understanding of archaeomineralogy requires knowledge of 38 of the 92 naturally occurring chemical elements, including their chemical symbols, because mineral formulas use these symbols. Many symbols are derived from their ancient (often Latin) name rather than their modern name. Examples are: Au, gold from the Latin *aurum*; Ag, silver from the Latin *argentum*; and Na, sodium from the Latin *natrium*. Table 2.1 is a list of the chemical elements and their symbols. Those in italics are important for an understanding of archaeomineralogy.

### 2.2 Mineral Structure

A mineral species is defined by two distinct properties: (1) its chemical composition and (2) its crystal structure. Each mineral has a distinct three-dimensional array of its constituent atoms. This regular geometry affects its physical properties such as cleavage and hardness.

How the atoms are held together in a mineral is governed by the nature of the chemical bonds formed between elements in the structure. An advanced

**Table 2.1** Elements of the Periodic Table

Actinium	Ac	<i>Gold</i>	<i>Au</i>	Praseodymium	Pr
<i>Aluminum</i>	<i>Al</i>	Hafnium	Hf	Promethium	Pm
Americium	Am	Helium	He	Protactinium	Pa
<i>Antimony</i>	<i>Sb</i>	Holmium	Ho	Radium	Ra
Argon	Ar	<i>Hydrogen</i>	<i>H</i>	Radon	Rn
<i>Arsenic</i>	<i>As</i>	Indium	In	Rhenium	Re
Astatine	At	<i>Iodine</i>	<i>I</i>	Rhodium	Rh
<i>Barium</i>	<i>Ba</i>	Iridium	Ir	Rubidium	Rb
Berkelium	Bk	<i>Iron</i>	<i>Fe</i>	Ruthenium	Ru
<i>Beryllium</i>	<i>Be</i>	Krypton	Kr	Samarium	Sm
Bismuth	Bi	Lanthanum	La	Scandium	Sc
Boron	B	<i>Lead</i>	<i>Pb</i>	Selenium	Se
Bromine	Br	Lithium	Li	<i>Silicon</i>	<i>Si</i>
<i>Cadmium</i>	<i>Cd</i>	Lutetium	Lu	<i>Silver</i>	<i>Ag</i>
<i>Calcium</i>	<i>Ca</i>	<i>Magnesium</i>	<i>Mg</i>	<i>Sodium</i>	<i>Na</i>
Californium	Cf	<i>Manganese</i>	<i>Mn</i>	<i>Strontium</i>	<i>Sr</i>
<i>Carbon</i>	<i>C</i>	Mendelevium	Md	<i>Sulfur</i>	<i>S</i>
Cerium	Ce	<i>Mercury</i>	<i>Hg</i>	Tantalum	Ta
Cesium	Cs	<i>Molybdenum</i>	<i>Mo</i>	Technetium	Tc
<i>Chlorine</i>	<i>Cl</i>	Neodymium	Nd	Tellurium	Te
<i>Chromium</i>	<i>Cr</i>	Neon	Ne	Terbium	Tb
<i>Cobalt</i>	<i>Co</i>	Neptunium	Np	Thallium	Tl
<i>Copper</i>	<i>Cu</i>	<i>Nickel</i>	<i>Ni</i>	Thorium	Th
Curium	Cm	Niobium	Nb	Thulium	Tm
Dysprosium	Dy	<i>Nitrogen</i>	<i>N</i>	<i>Tin</i>	<i>Sn</i>
Einsteinium	Es	Nobelium	No	<i>Titanium</i>	<i>Ti</i>
Erbium	Er	Osmium	Os	<i>Tungsten</i>	<i>W</i>
Europium	Eu	<i>Oxygen</i>	<i>O</i>	<i>Uranium</i>	<i>U</i>
Fermium	Fm	Palladium	Pd	Vanadium	V
<i>Fluorine</i>	<i>F</i>	<i>Phosphorus</i>	<i>P</i>	Xenon	Xe
Francium	Fr	Platinum	Pt	Ytterbium	Yb
Gadolinium	Gd	Plutonium	Pu	Yttrium	Y
Gallium	Ga	Polonium	Po	<i>Zinc</i>	<i>Zn</i>
Germanium	Ge	<i>Potassium</i>	<i>K</i>	<i>Zirconium</i>	<i>Zr</i>

understanding of crystal structures and bonding is unnecessary in the context of this book, so only a brief introduction is provided.

There are three basic types of chemical bonds: metallic, covalent, and ionic. The metallic bond is responsible for the cohesion of a metal. Metals readily lose their outer electrons, so the geometry of crystal structures is determined by the manner in which the positively charged atoms can be “packed” in space. The detached electrons dispersed among the atoms are freely mobile. This mobility is responsible for the good electrical and thermal conductivity of metals.

The most stable configuration for an atom is one in which the outer shell of electrons is completely filled (see Sect. 2.3 for a description of the structure of atoms). One way to achieve this stable configuration is for two or more atoms to share electrons in their outer shells. The best mineralogical example is diamond, in which every carbon atom is surrounded by four other carbon atoms, each sharing one electron with the central atom. This arrangement is repeated throughout the structure. This type of bond is called covalent.

Another way for an atom to achieve a completely filled outer shell of electrons is for it to gain or lose the precise number of electrons required to reach this configuration. A neutral chlorine atom lacks one electron for a filled outer shell. By accepting one additional electron it becomes a stable, negatively charged ion with a filled outer shell. Sodium has only one electron in its outermost shell. By giving up this electron sodium has its outermost shell filled and becomes a stable positively charged ion. Sodium and chlorine ions combine readily to give an ionic structure, bonded by electrostatic attraction. Each ion is surrounded by ions of opposite charge, the number being determined by their relative sizes. This ionic bonding is the most common bonding in minerals. Practically all minerals, except native elements (such as gold or copper) and sulfides, are predominantly ionic.

The hardness of a mineral is defined as its resistance to scratching. Hardness was quantified by the Austrian mineralogist Friedrich Mohs, who proposed the following scale of relative hardness in 1922: (1) talc, (2) gypsum, (3) calcite, (4) fluorite, (5) apatite, (6) orthoclase, (7) quartz, (8) topaz, (9) corundum, (10) diamond. Each of the minerals lower in the scale can be scratched by those higher in the scale. The scale is not linear; in absolute hardness, diamond is three orders of magnitude harder than talc. Hardness does vary with crystallographic direction in a mineral.

Hardness is an important diagnostic property in the field identification of minerals. In addition to the minerals in the scale, the following materials serve as handy references for the hardness (on the Mohs scale): fingernail: 2–2.5; copper coin: approximately 3; pocket knife: 5–5.5; window glass: 5.5; steel file: 6.5.

Because there is a general link between hardness and chemical composition, the following generalizations can be made: (1) most hydrous minerals are relatively soft ( $H < 5$ ), (2) halides, carbonates, sulfates, and phosphates are also relatively soft ( $H < 5.5$ ), (3) most sulfides are relatively soft ( $H < 5$ ) with pyrite being an exception ( $H < 6$  to 6.5), (4) most anhydrous oxides and silicates are hard ( $H > 5.5$ ).

Rock hardness is a very different matter. Rather than based on the Mohs hardness of its constituent minerals rock hardness as used in geology denotes the cohesiveness of a rock and usually is expressed in terms of compressive fracture strength. Geologists also use the qualitative terms “hardrock” to refer to igneous and metamorphic rocks and “softrock” to refer to sedimentary rocks. These terms originated as mining terms indicating how difficult it was to mine a given rock type. The fracture strength of rocks varies from “weak” in poorly cemented **clastic** sedimentary rocks, through “medium” in competent sedimentary rocks, through “strong” in most igneous and metamorphic rocks, to “very strong” in quartzites and dense fine-grained igneous rocks.

For metals and alloys, in particular, a group of properties called *tenacity* are important. These are:

- malleability*: capable of being flattened under the blows of a hammer into thin sheets without breaking or crumbling in fragments. Malleability is conspicuous in gold, silver, and copper. Most of the native elements show some degree of malleability.
- sectility*: capable of being severed by the smooth cut of a knife. Copper, silver, and gold are sectile.
- ductility*: capable of being drawn into the form of a wire. Gold, silver, and copper are ductile.
- flexibility*: bending easily and staying bent after the pressure is removed. Talc is flexible.
- brittleness*: showing little to no resistance to breakage; separating into fragments under the blow of a hammer or with the cut of a knife. Most silicate minerals are brittle.
- elasticity*: capable of being bent or pulled out of shape but returning to the original form when relieved. Mica is elastic.

*Specific gravity* (G) is a number that expresses the ratio between the mass of a substance and the mass of an equal volume of water at 4°C. The specific gravity of a mineral depends on (1) the atomic weights of all the elements of which it is composed, and (2) the manner in which the atoms are packed together. If two minerals, e.g., graphite and diamond, have the same chemical composition, the differences in specific gravity reflect the difference in internal packing of the atoms or ions (diamond with  $G=3.51$  has a much more densely packed structure than graphite with  $G=2.23$ ).

Minerals may break by fracturing or cleaving. *Cleavage* and *fracture* are two separate phenomena. Cleavage is planar rupture, controlled by the atomic arrangement in the mineral’s crystal structure. For example, mica cleaves into sheets because of the sheet structure of mica. Cleavage planes are symmetrically disposed within minerals, and different minerals have from zero to six directions of cleavage.

Those without cleavage break by fracturing along **parting** surfaces not related to cleavage planes. Different kinds of fracture are designated as follows. Conchoidal fracture is curved and resembles the interior surface of most shells. This is the

type of fracture observed in glass and the mineral quartz. Some minerals exhibit a fibrous or splintery fracture. A hackly fracture results in jagged and sharp edges. Fractures producing rough and irregular surfaces are called irregular fractures. The most common fracture for the production of lithics is the conchoidal fracture exhibited by obsidian, chert, quartz, and quartzite.

The term luster refers to the appearance of a mineral surface in reflected light. Metallic luster is that of a shiny metal. Minerals with a metallic luster are opaque. Galena and pyrite are common minerals with a metallic luster. A metallic luster has also been added artificially to give decorative effects to glazed ceramics. This technique was created by Arab ceramists in the ninth century (Darque-Ceretti et al. 2005) and spread over the Mediterranean basin especially to Spain and Italy. This technique is based on firing of the glazed pottery in a reducing atmosphere in the presence of metallic salts. This produced a metallic-appearing surface with a gold, brown, or red luster. The luster was a result of metal particles of nanometer size dispersed in a glassy matrix.

Minerals with a nonmetallic luster are generally light-colored and transmit light, at least through thin edges. The following are the important types of nonmetallic luster:

<i>Vitreous:</i>	The luster of glass. Example: quartz.
<i>Pearly:</i>	An iridescent pearl-like luster, usually observed on mineral surfaces that are parallel to cleavage planes. Example: cleavage surface of talc.
<i>Greasy:</i>	Appears as if covered with a thin layer of oil, resulting from light scattered by a microscopically rough surface. Examples: some specimens of sphalerite and massive quartz.
<i>Silky:</i>	Silk-like, caused by the reflection of light from a fine fibrous parallel aggregate. Examples: fibrous gypsum and serpentine.
<i>Adamantine:</i>	A hard, brilliant luster like that of a diamond, due to the mineral's high index of refraction. Example: the transparent lead mineral cerussite.

See Sect. 2.4 for further information about the causes of luster in minerals.

## 2.3 Mineral Identification Methods

### 2.3.1 *Element Analyses*

Modern instrumental techniques are all capable of multi-element analysis. These techniques can be used to determine well over half of the elements in the Periodic Table. They provide high precision and accuracy over a range of elemental concentrations. However, each technique has one or more limitations, so one must evaluate the relative merits of the competing systems. Most are destructive so not applicable to museum specimens. Detailed explanations of these instruments and instrumental techniques are readily available in all libraries (for example, see Ewing 1997).

The dominant techniques used by geologists for multi-element analyses are atomic absorption spectrometry (AA), inductively coupled plasma spectrometry (ICP), X-ray fluorescence spectrometry (XRF), and instrumental neutron activation analysis (INAA). Although analysts conducting archaeological provenance studies have favored INAA, this technique is best for trace elements.

Since the mid-1950s, atomic absorption spectroscopy (AA) has developed rapidly and is now a convenient and rapid “work horse” analytical method in most geology and biology departments in universities and major museums. Atomic absorption spectroscopy developed from emission spectroscopy, to gain more sensitivity. This method requires that the sample be put into solution that is then aspirated into a flame. The absorption spectra are compared with standards with curves of absorbency plotted against concentration. For mineral analyses, the primary problem is getting a small sample into solution. Whatever technique is used for this digestion, there is a real danger of contamination.

In the author’s view, the major utility of AA is determining of which metal or metals an artifact is composed when one has only a few milligrams of sample. This is most often the case with museum artifacts that are subjected to destructive analysis. INAA can also identify small metal samples but is not available to most researchers, whereas AA should be. Inductively coupled plasma emission spectroscopy (ICP) is an efficient technique for multi-element analyses, but the instrumentation is quite expensive. Like AA, it suffers from possible contamination as the artifact sample is dissolved.

X-ray fluorescence spectrometry achieved prominence in the 1960s and has been used widely ever since. In this technique, a sample irradiated by an X-ray beam emits a secondary X-ray fluorescence spectrum characteristic of the elements in the sample. The principal advantage of XRF is that it is a bulk technique and, like INAA, can be applied to the raw sample. This overcomes concerns about sample homogeneity and resistance to dissolution. XRF systems can be highly automated, provide high precision analyses for many elements, and can be designed to be both nondestructive and portable—extremely desirable when dealing with museum artifacts. The principal disadvantages of XRF are (1) matrix and interference problems, and (2) an instrument cost perhaps four times as great as AA.

Neutron activation analysis is a physical method of analysis where a wide range of elements can be measured simultaneously with no loss in precision. Neutron activation analysis requires only a small sample (50 mg for metals, 200 mg for silicates), no complex sample preparation, and no extraction techniques. A sample analyzed by this technique is subjected to irradiation by slow (thermal) neutrons in a nuclear reactor. Various constituent atoms capture these neutrons producing unstable daughter elements. These unstable **isotopes** emit gamma rays characteristic of the original element present in the sample, and the gamma ray intensity is a measure of the concentration of each original element present. The gamma ray spectrum from the decay is measured in a multichannel gamma-ray spectrometer.

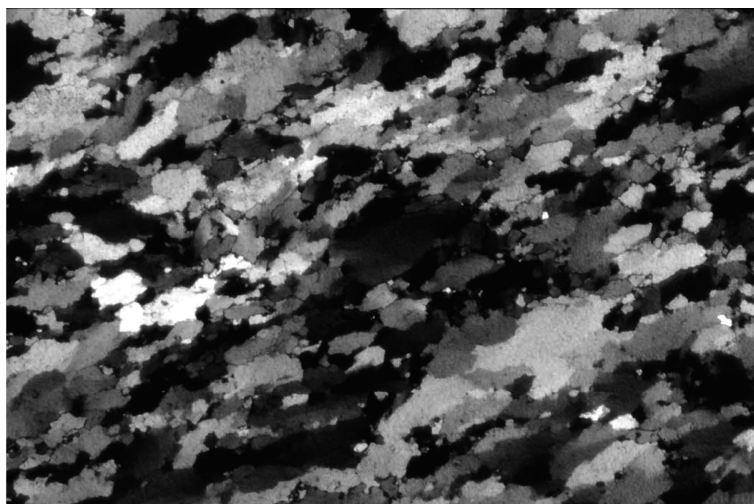
Neutron activation methods can achieve high accuracy and precision for some elements but only moderate or poor results for others. As a technique, neutron activation has a different sensitivity (detection limit) for each chemical element.

Sensitivities vary with irradiation time and intensity, delay time, counting conditions, and composition of the sample. Where a reactor is accessible and set up for automated INAA, the per sample cost is very competitive. A major advantage of INAA is the lack of matrix interference, which is a major problem with AA and ICP. The principal disadvantage for most investigators is the need for access to a reactor. Other disadvantages include the need for compromises when setting the counting routine and the need to monitor the neutron flux. Neutron activation analysis is one of the prominent means used to find the geologic sources of raw materials used by prehistoric human groups. It has often been employed by those interested in trading patterns, population territories, and migration.

Nondestructive activation analyses using isotopic neutron sources may also be appropriate in many cases. The author has not used this technique because of limited sensitivity compared to INAA. However, it has the major advantage of being nondestructive. For example, for the determination of the precious metal content of ancient coins, see Cosma et al. (1988).

### ***2.3.2 Petrographic Analyses***

Rock and mineral specimens can be examined using polarized light microscopy in two different ways; either by making a thin transparent section 0.03 mm thick, or by crushing to a convenient size to be examined as grains. Thin sections reveal the mineralogy, texture, grain size, and relative proportions of different minerals in a rock. Figure 2.1 is a photomicrograph of a thin section of a quartzite tool from the Lower Paleolithic of France.



**Fig. 2.1** Petrographic thin-section of a quartzite used as a lithic tool in Paleolithic France

Grain mounts have the advantage of more easily identifying minerals by their most diagnostic optical property, refractive indices. In my view, microscope methods are woefully underutilized in archaeological investigations. Most lithic and ceramic materials and products are composed of minerals (obsidian—a volcanic glass—is an exception). Minerals are crystalline, so **petrography** is based on crystal symmetry and crystal chemistry. The coarsest categorization of crystal symmetry classifies minerals into seven crystal systems: isometric, hexagonal, tetragonal, trigonal, orthorhombic, monoclinic, and triclinic. For petro-graphic analysis it is the optical symmetry and optical parameters of minerals that allow identification and interpretation.

Isometric minerals are optically isotropic, i.e., they have only one index of refraction. Hexagonal, tetragonal, and trigonal minerals are uniaxial—they have one optical axis and two indices of refraction. Orthorhombic, monoclinic, and triclinic minerals are biaxial. They have two optical axes and three indices of refraction. Uniaxial and biaxial crystals are said to be **anisotropic** (i.e., not isotropic). Mineral grains can be immersed in oils of known indices of refraction to measure the refractive indices and other optical characteristics and thereby be identified. Clay minerals are too fine-grained to be studied by the methods of optical mineralogy.

In grain mounts the grains should be of approximately the same size, between 0.10 and 0.15 mm. This can be done by passing the crushed material through a 100-mesh screen and retained on a 150-mesh screen. The useful grain size limits for this technique are from 0.01 to 0.2 mm. If refractive indices are to be determined, one needs a set of refractive index oils in which the grains can be immersed and compared.

When a polarizing microscope is available, microdebitage can be studied, and chert and obsidian are easily distinguished because obsidian is a glass with only one index of refraction. There are dozens of standard textbooks on optical mineralogy and petrography for those who would find this method to be useful. Thin sections of rocks or ceramics when studied under polarized light allow investigation of textures and chemical alteration as well as mineral identification. A note on nomenclature—petrology is the study of the origin of rocks, petrography is the description of rocks. American usage follows the strict definition. The description of rocks or ceramics in thin section is *petrography*. British usage is to call thin-section analysis *petrology*.

Thin-section petrography requires the use of a polarizing microscope. The polarizing microscope has two functions: (1) to provide an enlarged image of an object placed on the microscope stage, and (2) to provide plane and crossed polarized light and convergent light. The *polarizing lens* below the rotating microscope stage constrains light to vibrate only in a front-back (north-south) direction. A converging lens is also mounted in the substage. Above the microscope stage (and above the object under study) is a second polarizer called an *analyzing lens* that constrains light to vibrate only left-right (east-west). The substage polarizing lens is fixed in place, but the analyzer can be moved in or out of position. Minerals exhibit a host of distinguishing characteristics in plane and crossed (both lenses in position) polarized light and in convergent polarized light. As with other compound microscopes, polarizing microscopes contain a variety of other lenses and devices that can modify the transmission of light for specialized studies.

Thin sections of rocks allow identification of mineral constituents, their relative abundances, associations and states of alteration; grain orientations and related fabric features; the size, shape, and orientation of voids; and post-use **diagenetic** recrystallization. The mineral grains exhibit distinct size, shape, sorting, roundness, and sphericity characteristics. All these parameters can provide diagnostic data.

Those using the thin-section method of rock identification and characterization will find the following volumes very helpful: for igneous rocks MacKenzie et al. (1982), and for metamorphic rocks Yardley et al. (1990). Each of these volumes has large numbers of colored photographs of rock thin sections.

### ***2.3.3 Physical Methods of Identification***

To go very deeply into X-ray diffraction methods (XRD) would require that the reader be familiar with the fundamentals of crystallography and the physics of electromagnetic radiation. This section will only outline what XRD seeks to do and a segment concerning how one goes about it. In archaeomineralogy, the primary use of XRD is to identify crystalline materials. Glassy or amorphous substances are not amenable to diffraction techniques.

XRD encompasses two distinct recording methods: film and diffractometry. Both methods require that the specimens be in powdered form. The main advantage of using the camera/film technique is that one can obtain a strong pattern with very little material, much less than with diffractometry. The diffractometer technique has the advantages of getting better angular resolution, and the low-angle limit is much lower than with an ordinary powder camera. The latter advantage is quite important when identifying minerals with large spacings between planes of atoms. Clays and other sheet silicates have one, very large, spacing.

Once an X-ray diffraction pattern is obtained, one can identify the mineral or minerals by comparing the pattern with the known patterns of all mineral species. As part of recent powder diffractometer instruments, a computer will do the matching. Otherwise one can do the matching “by hand” using the American Society for Testing Materials (ASTM) powder data file and the ASTM index. XRD works because each mineral has a unique structure.

Density is a fundamental and characteristic property of each mineral and, as such, is an important determinative property. Specific gravity is a number, the ratio of the mass of a substance to the mass of an equal volume of water at 4°C. Density is defined as the ratio of the mass of any quantity of a substance to its volume normally expressed in g/cm<sup>3</sup>. If you look up the density or the specific gravity of a mineral, you will normally find its specific gravity recorded. For small artifacts, density can be used to distinguish the two jade minerals. Nephrite has a specific gravity of 3.0, whereas jadeite is denser (heavier) at 3.3.

Although there are many methods of density determination, only four types will be introduced briefly here. The first is the displacement method. This method is based on direct weighing of the mineral followed by measuring the volume of liquid displaced

when the mineral is immersed in it. In its simplest form, the volume is determined by immersing the mineral in a graduated cylinder, and the volume increase read off. All laboratories will have both weighing scales and graduated cylinders.

The second method is called pycnometry. The principle underlying this method requires that the weight of the mineral is measured directly, and the volume obtained by weighing the volume of the liquid displaced from the pycnometer by the minerals. This method entails the successive weighing of the empty pycnometer, the pycnometer with the sample alone, the pycnometer with the sample and liquid and the pycnometer with liquid only. Water can be used if it is not absorbed by, nor reacts with, the mineral. N.H. Winchell (1938) modified the basic technique to achieve accuracies of  $\pm 1.0\%$ . The primary disadvantage of this method is that most universities and major museums might not have a pycnometer. The major advantage is that one can use many small fragments when a larger sample is not available.

The third method is based on hydrostatic weighing. For most small artifacts, less than 50 g or so, the well-known Jolly balance (Fig. 2.2) is quite suitable. This is the technique preferred by the author. The mineral is first weighed in air and then reweighed in a liquid of known density. From the apparent loss in weight, the volume of the mineral may be computed and hence its density. Most geoscience departments should have a Jolly balance. The fourth, most accurate, method is based on comparison of the mineral or metal artifact with heavy liquids (many of which are toxic). All of these density methods are valuable in small artifact identification because they are nondestructive.

Geologists use a 10- or 20-power hand lens as an aid in identifying rocks and minerals in hand specimens. Use of a hand lens is valuable in seeing the relict sand



**Fig. 2.2** The author using a Jolly balance

grains that identify quartzite; the cleavage or fracture diagnostic of many minerals; and fine-grained textural features common in some rocks. Specimens that are polished by geologic or human action are much harder to identify than those showing natural features of cleavage, fracture, crystallinity, and color.

## 2.4 Color of Minerals

Color has always been important to the human psyche, from protecting against evil spirits to attracting the opposite sex. In the modern Western world black is the symbol of mourning, white of purity, and red of passion or danger. To some groups in East Africa black is the color of joy. In ancient times purple pigment was rare and expensive, so it was a royal color.

For thousands of years humans have marveled at the variety of colors found in “stones” and have attributed magical, curative, and protective powers to certain minerals, especially the varicolored gems. The beauty of amethyst was secondary to its value as a safeguard against intoxication; hematite, from the Greek word for blood, was believed to cure all manner of blood diseases, and beryl to promote conjugal love. Even today certain colors are considered appropriate on some occasions and inappropriate on others. Colors as symbols, magic or otherwise, have retained their authority: brides wear white, priests black; red signals stop, and so on.

Alchemists, in many ways forerunners of modern experimental scientists, equated color with the essence or true nature of a substance. They tried to find a way to dye, tinge, alloy, or otherwise color metal, believing that such an alteration would indeed transform one substance into another. If their “synthetic gold” tarnished, they knew they had failed. The alchemists’ lack of understanding of the structure of matter was matched, and in some measure governed, by their ignorance of the nature of the color of light. If there is no light, there is no color.

Although it is the color of individual minerals that has attracted nearly all of the scientific study, some rocks have been investigated. An example of a study where a rock has been studied carefully to account for its color is that of the color changes in purple-green slate from North Wales (Borradaile et al. 1991). The normally purple slate changes to green in patches parallel to the bedding. The green color is seen where there is a diffusion of  $\text{Fe}^{3+}$  away from the green material leading to a replacement of hematite (red) with magnetite (black). The green material also has twice as much **chlorite** (green). Mineral and compound descriptions in Chaps. 5, 6, 7, 8, and 9 often describe color and its role in defining the value of the material.

**The Nature of Light and Color.** Information gathered by the human eye as it perceives light governs the way we think about the material world. As knowledge of the nature of light increased, so, correspondingly, has knowledge of the materials and forces that make up the universe.

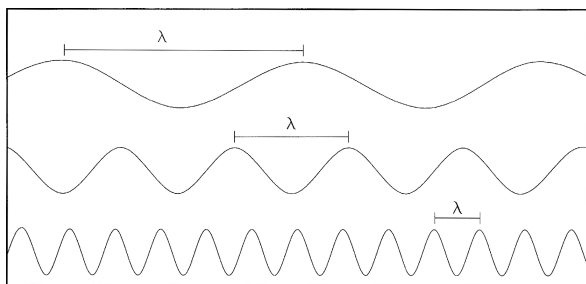
Beginning in the seventeenth century, when scientists first devised experiments to check their ideas on the nature of the physical world, a running controversy developed on the nature of light. Experiments like those showing that light could be made to

go around corners, that it could interact to produce “beats” similar to those produced by sound waves, and that sunlight could be separated into colors and then recombined seemed to indicate that light traveled in “waves.” However, Sir Isaac Newton proposed that light consisted of a series of particles, which, because they traveled in straight lines, could be considered “rays”. Experiments conducted from Newton’s time until the beginning of the twentieth century gave ever-increasing support to the wave theory as opposed to the particle theory. In fact, it became the custom in science to designate a particular color in terms of its “wavelength.” This system is still used.

In the latter part of the nineteenth century, James Clerk-Maxwell showed that visible light as well as infrared and ultraviolet radiation are forms of *electromagnetic radiation* (Fig. 2.3). All forms of electromagnetic radiation travel at a constant speed in empty space, approximately  $3 \times 10^{10} \text{ cms}^{-1}$ . Types of radiation differ only in their wavelengths ( $\lambda$  in Fig. 2.3).

Shortly after Clerk-Maxwell’s work, radio waves (with wavelengths longer than infrared radiation) and X-rays (with wavelengths much shorter than ultraviolet) were discovered. Thus the “electromagnetic spectrum” was greatly extended at both ends of the range of visible light, and today it is known that visible light occupies only a very narrow portion of that spectrum (Fig. 2.4). The only other portion of the electromagnetic spectrum that humans can sense is the infrared, the region of heat radiation. We feel the warmth of infrared radiation generated by particles colliding in the hot gases of the sun, as well as the infrared radiation from a hot stove, electric iron, and similar heat-producing implements.

At about the time radio waves and X-rays were discovered, Albert Einstein created a “new physics” by relating electromagnetic energy to the mass concept of matter and the velocity of light. We were back to light consisting of particles. According to this concept, radiation comes in discrete packets, later called *photons*. The more energetic photons correspond to radiation with short wavelengths; the less energetic, to radiation with long wavelengths. Light, then, can be considered either an electromagnetic wave with a specific wavelength or a stream of light particles called photons, each possessing a specific amount, or quantum, of energy. The narrow band of the electromagnetic spectrum occupied by visible light, or light that registers on the average human eye, can be further broken down by wavelength into colors (Fig. 2.5). The longest waves in the visible spectrum form the color we call red; the shortest waves produce blue or violet; the remainder of the rainbow hues falls in-between. Wavelengths of light recognized by the human eye range from



**Fig. 2.3** The wave nature of light

Fig. 2.4 Types of electromagnetic radiation

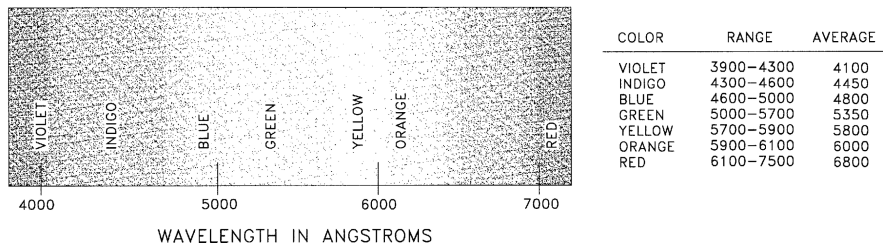
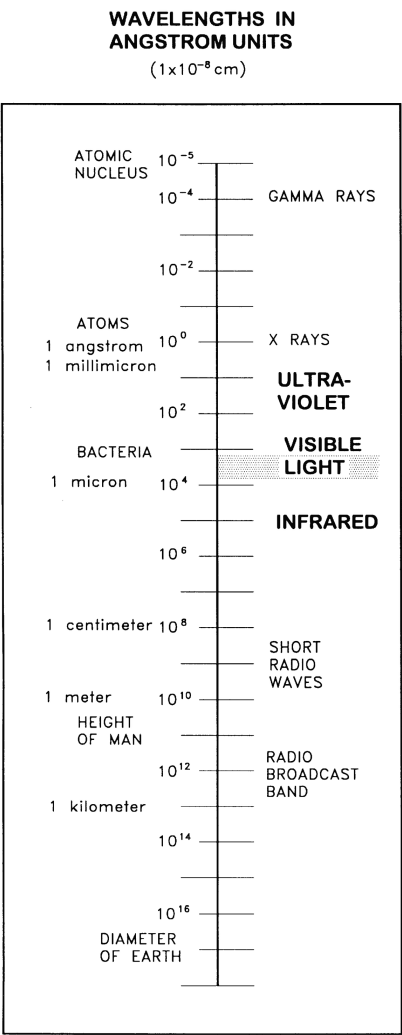


Fig. 2.5 Wavelengths of light in the visible spectrum

about 4000 to 7500 angstrom units. *One angstrom equals one hundred-millionth of a centimeter* ( $10^{-8}$  cm), about the diameter of an atom.

The possibility of separating sunlight into its different wavelengths or colors was first recognized by Sir Isaac Newton, who allowed a narrow circular beam of light to pass through a glass prism and fall onto a white surface. The individual colors contained in sunlight were spread out in a rainbow-like display, recorded by Newton as red, orange, yellow, green, blue, indigo, and violet. Thus sunlight, or *white light*, which appears to have no color, is really a mixture of all colors.

**Interaction of Light with Crystals.** For color to be perceived, light waves must interact with the object. Light striking the surface of a crystal undergoes reflection, refraction, scattering, and absorption. Reflection is the return to the original medium, normally air, of a portion of the light striking a surface. The amount of light reflected depends on the composition and structure of the solid object. Metals reflect a high percentage of the incident light. If the metal is colored, the reflection will also be colored. Light reflected from the surface of a transparent substance, on the other hand, is generally not colored even if the substance is colored.

Refraction is the change in direction of a light ray when it enters a material of a different optical density at an angle (other than  $90^\circ$ ). Differential refraction causes the color spectrum seen by Newton in his experiment with a prism. Each wavelength (color) of light has a different angle of refraction, so the colors separate as they emerge from the prism. Blue light is bent the most; red, the least.

Scattering arises from imperfections or flaws in the regular arrangement of atoms in a crystal. In this process, light energy is taken from the light beam and re-radiated as spherical light waves from each "scattering center." Thus, an amount of energy is lost by the beam as it travels in an altered direction. Solids that transmit light scatter and reduce it to such an extent that transmitted patterns that cannot be seen are *translucent*; solids that transmit light with no appreciable loss in clarity are *transparent*; solids that transmit no light are *opaque*.

Absorption in crystalline substances is the process by which certain wavelengths in the visible spectrum are neither transmitted nor reflected. If some portions of the spectrum are absorbed and others transmitted or reflected, the wavelengths that are reflected combine to make the apparent color of the substance. For some substances the absorption is general, or approximately the same for all wavelengths. If the absorption is general and complete, or nearly so, we see the object as black—a complete lack of color. The object is seen as white if there is little or no absorption and all wavelengths are reflected or scattered, so the whole visible spectrum is contained in the reflected light. The difference between a white material and one that is clear or colorless is that the white material reflects or scatters all wavelengths without selective absorption, while a colorless substance transmits the light without appreciably altering anything but the path of the light as it enters and leaves the substance.

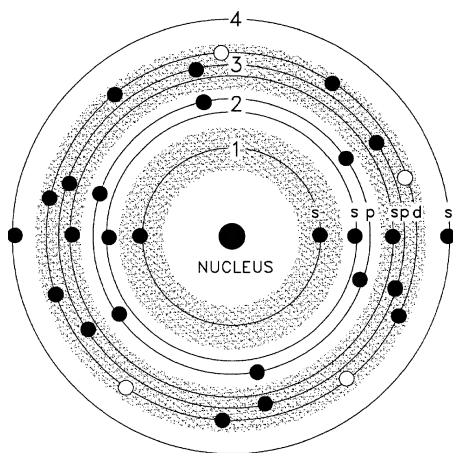
When a board that has been painted red is viewed in sunlight, it appears red because pigment in the paint selectively absorbs all the wavelengths shorter than red. However, if this same "red" board is viewed in light from a light source containing only the shorter (bluer) wavelengths, the board appears black because all the

blue light is absorbed and there is no incident red light to be reflected. An otherwise “white” board appears red if illuminated by exclusively red light.

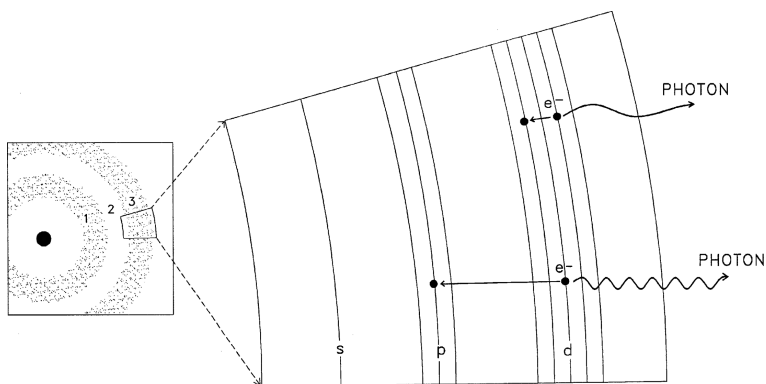
**Color Development in Crystals.** The following sections relating to atomic structure use the convenient diagrammatic approach that allows one comprehend physical interactions. Although physicists would say this does not adequately describe the underlying physics it is quite sufficient for our purposes. To understand how electrons can absorb electromagnetic energy in the visible light region, one must understand the electronic structure of atoms. The element iron contributes heavily to the color of many minerals. Figure 2.6 shows a highly simplified diagram of its electron shells. These shells are more or less spherical and concentric with the nucleus. Within the shell each electron is restricted to a certain energy level called an *orbital*. The orbitals, designated *s*, *p*, *d*, and *f*, each have a certain number of “positions” for electrons. The *s* orbital electrons have the lowest energy, and the energy increases through the *p*, *d*, and *f* orbitals. Not all shells have all types of orbitals. In some atoms the electron positions in the orbitals are not all filled. It is in these atoms with partially filled orbitals that mechanisms exist to develop many of the colors observed in minerals.

For every distinct quantity of energy contained by Einstein’s photons or light packets, there is one, and only one, associated wavelength. When light of a specific wavelength enters a crystal and encounters an electron that can accept the amount of energy associated with that particular wavelength, the light is absorbed. A given electron is able to accept and absorb the amount of energy stored in the light photon if the energy corresponds exactly to the amount necessary for the electron to “jump” from its normal position to a position of higher energy.

Conversely, when an electron drops to a lower energy level, a photon is emitted containing energy equivalent to the energy difference between the new and old positions of the electron (Fig. 2.7). The whole field of spectroscopic analysis is based on this principle. Each chemical element has a unique set of energies associated with its particular set of electron orbitals and, therefore, has its own distinguishing emission wavelengths. For example, common table salt (sodium chloride) placed in a



**Fig. 2.6** Atomic structure of iron



**Fig. 2.7** Electron jumps producing light rays (photons)

nonluminous flame will emit a strong yellow color. This color is due to the photons of light emitted when electrons in sodium, having been “excited” by the heat, return from a higher to a lower energy level. At ordinary temperatures electrons lack the energy to jump from one type of orbital to another. However, electron jumps from one orbital to another orbital of the same type within the same shell require only a small amount of energy, and the associated wavelength often lies in the visible region.

**Sources of Color in Minerals: Transition Elements.** It takes two electrons to fill the *s* orbital of a shell in an atom, six to fill the three *p* orbitals, ten to fill the five *d* orbitals, and fourteen to fill the seven *f* orbitals. See Table 2.2 for electronic configuration in the chemical elements. Whenever an atom with a partially filled *d* or *f* orbital is present in a mineral, there is a good chance that the electrons will jump between the various *d* or *f* orbitals, absorbing energy in the visible region. Because the energy differences between electron positions in these orbitals correspond to the wavelengths of visible light, the mineral will be colored. The *transition elements* (Fig. 2.8) have such partially filled orbitals and play the major role in mineral color.

Elements like iron, manganese, chromium, and vanadium have partially filled *d* orbitals. Elements in the so-called lanthanide and actinide series have partially filled *f* orbitals.

A given element does not always cause the same color, however. This is because the energy required for an electron jump from one position to another is influenced by the environment of the atom – the types and number of nearby atoms – and also by its *oxidation state* – the number of electrons it has in excess or in deficit of its atomic number *Z* (the number of protons). Some elements, notably the transition metals, can assume more than one oxidation state. For example, manganese can assume oxidation states +2, +3, +4, and +7, corresponding to a deficit of 2, 3, 4, or 7 electrons.

The large majority of highly colored minerals contain transition metals. Iron, the most abundant transition metal, is the coloring agent in a great variety of minerals. In addition to having unfilled *d* orbital positions, iron can exist in two oxidation states (+2 and +3); this leads to further complexities that result in the absorption

**Table 2.2** Electronic configuration of the first 36 elements (transition elements are in capital letters; *s, p, d, f* are orbital designations)

Atomic number	Name of element	Symbol	First shell	Second shell	Third shell	Fourth shell
			s	s p	s p d	s p d f
1	Hydrogen	H	1			
2	Helium	He	2	Inert gas		
3	Lithium	Li	2	1		
4	Beryllium	Be	2	2		
5	Boron	B	2	2 1		
6	Carbon	C	2	2 2		
7	Nitrogen	N	2	2 3		
8	Oxygen	O	2	2 4		
9	Fluorine	F	2	2 5		
10	Neon	Ne	2	2 6 Inert gas		
11	Sodium	Na	2	2 6	1	
12	Magnesium	Mg	2	2 6	2	
13	Aluminum	Al	2	2 6	2 1	
14	Silicon	Si	2	2 6	2 2	
15	Phosphorus	P	2	2 6	2 3	
16	Sulfur	S	2	2 6	2 4	
17	Chlorine	Cl	2	2 6	2 5	
18	Argon	Ar	2	2 6	2 6 Inert gas	
19	Potassium	K	2	2 6	2 6	1
20	Calcium	Ca	2	2 6	2 6	2
21	SCANDIUM	Sc	2	2 6	2 6 1	2
22	TITANIUM	Ti	2	2 6	2 6 2	2
23	VANADIUM	V	2	2 6	2 6 3	2
24	CHROMIUM	Cr	2	2 6	2 6 5	1
25	MANGANESE	Mn	2	2 6	2 6 5	2
26	IRON	Fe	2	2 6	2 6 6	2
27	COBALT	Co	2	2 6	2 6 7	2
28	NICKEL	Ni	2	2 6	2 6 8	2
29	COPPER	Cu	2	2 6	2 6 10	1
30	Zinc	Zn	2	2 6	2 6 10	2
31	Gallium	Ga	2	2 6	2 6 10	2 1
32	Germanium	Ge	2	2 6	2 6 10	2 2
33	Arsenic	As	2	2 6	2 6 10	2 3
34	Selenium	Se	2	2 6	2 6 10	2 4
35	Bromine	Br	2	2 6	2 6 10	2 5
36	Krypton	Kr	2	2 6	2 6 10	2 6 Inert gas

of light. A given iron ion, say **ferric** iron ( $\text{Fe}^{3+}$ ), does not have a characteristic color since the specific absorption will be modified by the environment of the ion. The colors of compounds where the same ion is surrounded by a nearly identical arrangement of other ions are quite similar. For instance, the two iron silicates olivine,  $(\text{FeMg})_2\text{SiO}_4$ , and tremolite-actinolite,  $\text{Ca}_2(\text{MgFe})_3\text{Si}_8\text{O}_{22}(\text{OH})_2$ , are both green since the **ferrous** ion ( $\text{Fe}^{2+}$ ) has a similar environment. Consider also the

I																VIII											
1																2											
H																He											
3	4															5	6	7	8	9	10						
Li	Be															B	C	N	O	F	Ne						
11	12															13	14	15	16	17	18						
Na	Mg															Al	Si	P	S	Cl	Ar						
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36										
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr										
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54										
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe										
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86										
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn										
87	88	89	LANTHANIDE SERIES																								
Fr	Ra	Ac																									
			58	59	60	61	62	63	64	65	66	67	68	69	70	71											
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu											
			90	91	92	93	94	95	96	97	98	99	100	101	102	103											
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw											
			ACTINIDE SERIES																								

Fig. 2.8 Periodic Table of the elements

coloring effect caused by varying amounts of the transition metal iron in these two minerals. Both olivine and tremolite-actinolite are magnesium-iron silicates, which means that magnesium and iron may substitute for one another at the same site in the crystal structure. The magnesium ion (+2) has all orbitals and shells filled (an inert gas configuration) and does not contribute to absorption in the visible region. Therefore, as the transition metal iron replaces magnesium in the structure of these minerals, the minerals range from white to dark greens.

The intensity of the color seems to increase when the transition element in the mineral is present in more than one oxidation state, a situation made possible by a process called charge transfer. Many minerals containing only the ferrous ion ( $\text{Fe}^{2+}$ ) or only the ferric ion ( $\text{Fe}^{3+}$ ) are relatively pale in color, whereas iron-containing silicates like **pyroxenes** and **amphiboles** that contain both ions are dark green to black. This feature is shown dramatically by the mineral vivianite,  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ . The fresh mineral is usually colorless, but exposure to air, with the accompanying partial oxidation of ferrous to ferric iron as the ferrous ion gives up an electron to an oxygen atom, causes vivianite to turn bluish-black.

*Charge transfer* among atoms, a mechanism related to light absorption, may also take place when an element capable of more than one oxidation state is present. Since an electron is a charged particle, a transfer of an electron from one ion to another is a charge transfer. This transfer is possible when the energy difference between the different oxidation states of the same element is small. Under these circumstances, an electron may transfer or jump from one ion to another, thus

changing the oxidation state of both. The small energy difference between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  causes the deep color of magnetite,  $\text{Fe}_3\text{O}_4$ , and is a contributing factor in the color of biotite,  $\text{K}(\text{MgFe})_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2$ , and tourmaline,  $(\text{Na,Ca})(\text{AlFe,Li,Mg})_3\text{B}_3\text{Al}_2(\text{AlSi}_2\text{O}_9)_3(\text{O,OH,F})_4$ . A broad and intense band of optical absorption spectra in ferrous and ferric iron garnets is attributed to charge-transfer transitions. (Taran et al. 2007) Charge transfers can also occur between ions of different chemical elements. The  $\text{Fe}^{2+} \rightleftharpoons \text{Ti}^{2+}$  charge transfer gives sapphire its blue color.

When a small amount of chromium, another transition element, is present in corundum ( $\text{Al}_2\text{O}_3$ ), a red color develops and the corundum is called ruby. Both natural and synthetic rubies are colored in this manner. However, if a large amount of chromium is forced into the corundum structure, the resulting color is green. The same phenomenon occurs in chrome spinel,  $\text{Mg}(\text{Al,Cr})_2\text{O}_4$ . Minor amounts of chromium produce a red color; larger amounts, green. This may be interpreted as follows: placing the chromium ion, which is larger than the aluminum ion, in the aluminum position results in a squeezing of the chromium. The strain energy from the squeezing causes the red color by absorption of the blue-green portions of the spectrum. When sufficient chromium replaces aluminum to expand and distort the structure, the strain energy changes and the absorption shifts, producing the green. Chromium is also the green coloring agent in uvarovite garnet,  $\text{Ca}_2\text{Cr}_2(\text{SiO}_4)_3$ , chromium muscovite,  $\text{K}(\text{Al,Cr})_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ , and emerald,  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ .

Manganese usually lends a pink, lavender, or violet color to silicates and carbonates such as lepidolite,  $\text{K}(\text{LiAl})_3(\text{Si,Al})_4\text{O}_{10}(\text{OH,F})_2$ ; rhodonite,  $\text{MnSiO}_3$ ; rhodochrosite,  $\text{MnCO}_3$ ; and thulite (zoisite),  $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$ . The prefix “rhodo-” is used to indicate a rose color. Manganese oxides such as manganite,  $\text{MnO}(\text{OH})$ , and pyrolusite,  $\text{MnO}_2$ , however, develop a deep black color as a result of charge transfer in the manganese.

Copper minerals occur in a variety of colors. When copper is bonded to oxygen in minerals such as malachite,  $\text{Cu}_2\text{CO}_3(\text{OH})_2$ , and azurite,  $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ , the resulting colors are green and blue, respectively. The copper sulfides, however, display a variety of colors due to the interaction of the copper ion with loosely held electrons of the sulfur atoms. Different structures and different copper/sulfur ratios produce absorption in different portions of the visible spectrum. Exposure to a moist atmosphere causes oxidation and tarnishes the metallic gray of chalcocite,  $\text{Cu}_2\text{S}$ , and the metallic pink of bornite,  $\text{Cu}_5\text{FeS}_4$ , to an iridescent purple. These color changes are in response to the chemical change on the surface of the mineral. The material beneath the surface does not change color.

Some transition metal ions whose *d* orbitals are either empty or completely filled do not cause coloring. An example is  $\text{Ti}^{4+}$ , which, when in its neutral state, has two *d* electrons in the third shell. However, in becoming a +4 ion, titanium loses these two *d* electrons, along with the two *s* electrons in its fourth shell. Therefore, no electrons are present in the *d* orbitals to jump around from one *d* orbital to another. The intense absorption observed in rutile,  $\text{TiO}_2$ , is due to an excess of titanium over the Ti/O ratio of 1: 2. The excess titanium results in the development of  $\text{Ti}^{3+}$  with one electron in a *d* orbital. There may also be charge transfer between  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$ .

Zinc minerals display a variety of colors, depending on their impurities, because zinc is not a transition element and does not contribute to color in

minerals. Sphalerite,  $\text{ZnS}$ , is colorless when pure and assumes its typical honey-brown color when iron substitutes for zinc in the structure. Willemite,  $\text{Zn}_2\text{SiO}_4$ , is also colorless when pure but develops a variety of colors through chemical substitution of other elements in the structure. The following transition elements produce the color indicated in parentheses when introduced into willemite: copper (light green), iron (gray), manganese (yellow), chromium (gray), and cobalt (intense blue).

It is often difficult to determine completely the cause of color when transition metals are present, because effects arising from partially filled  $d$  orbitals may be masked by the strong absorbing power of charge-transfer phenomena also common in minerals containing transition metals.

**The Effects of Chemical Bonding.** “Free” electrons give metals their characteristic opacity (by absorption), their high reflecting power (“metallic” luster), and, in many cases, their color. Two distinct mechanisms, both dependent on the different manner in which the electrons in metals respond to different parts of the visible spectrum, are important in defining the optical properties of metals. One is *selective reflection*, and the other is *selective absorption*. Selective reflection may be the dominant mechanism in highly reflecting minerals such as metals. Gold exhibits a yellow color due to selective reflection of yellow light, not selective absorption. Light transmitted through thin gold foil is bluish green; the yellow has been reflected and the red absorbed.

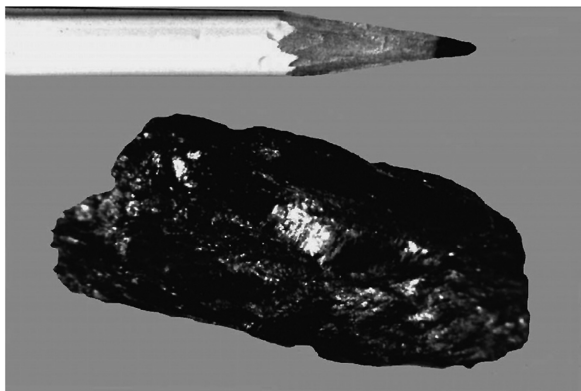
Finely powdered metals show a strong general absorption and appear black due to the large number of small light traps between the particles. Light is continually reflected back and forth among the small metal grains. On each contact with a metal surface a little more light is absorbed, ultimately resulting in total absorption and extinction of the light.

The color absorption characteristics of covalently bonded minerals depend on how tightly the bonding electrons are held in the elements. In diamond these electrons are held securely, resulting in electromagnetic wave absorption only in the ultraviolet region; therefore, a diamond crystal appears colorless and transparent. In silicon the electrons are not as tightly held, so absorption occurs in the visible spectrum, and the material is colored or opaque. Tin has the same crystal structure as diamond and silicon, but the electrons are so loosely held that pure tin is opaque and has properties we normally associate with metals, although it is not a true metal.

The element carbon illustrates well the color variations due to different bond strengths in the same element. In diamond the strong bonding results in a dense, very hard mineral that is transparent and colorless. The mineral graphite, however, is also composed solely of carbon. Here a different type of bonding produces a large number of loosely bonded electrons that absorb almost the entire visible spectrum, resulting in a deep black opaque mineral (Fig. 2.9).

Pure quartz,  $\text{SiO}_2$ , is transparent and colorless. Crystals of quartz are transparent to wavelengths of electromagnetic radiation ranging all the way from 1800 to 300,000 angstrom units. However, since impurities are often included in the crystal, colored varieties of quartz are common. Some amethystine quartz owes its

**Fig. 2.9** Graphite's *deep black*, opaque appearance is the result of its atomic bonding



color to thin films of iron oxide incorporated in the surface planes of the growing crystal. It has been suggested that the lemon color of citrine quartz is produced either by **colloidally** dispersed particles of hydrous iron oxide too small to be seen with a microscope or by the presence of  $\text{Fe}^{3+}$  in noncrystalline surroundings. Amethyst may be decolorized or changed to the citrine color by heating. Some blue quartz is found in igneous and metamorphic rocks. The blue color of light reflected from this quartz is due to selective scattering of the blue wavelengths by the oriented patterns of needlelike inclusions of rutile within its structure. Milky quartz owes its color to the light scattered by the large number of tiny cavities or flaws in the crystals. Small flakes or bands of mixed material often impart a distinct color to otherwise colorless or pale-colored minerals. For example, the red color of some feldspar,  $\text{KAlSi}_3\text{O}_8$ , is produced by the distribution of small flakes of hematite,  $\text{Fe}_2\text{O}_3$ , within the crystal.

Reflection and refraction of light from layers of dissimilar optical properties near the surface of a mineral produce the play of colors observed in some varieties of opal,  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ , and labradorite,  $(\text{Ca}, \text{Na})(\text{Al}, \text{Si})\text{AlSi}_3\text{O}_8$ .

**Color Centers.** Another mechanism that produces color in crystals is the selective absorption of light by certain imperfections in the crystal structure called *color centers*. An imperfection may be a foreign atom or ion, or it may be a “vacancy” in the structure as, for example, an excess of positive ions accompanied by “negative” vacancies. A negative vacancy would be a site where a negative ion belonged but was missing. Such a negative vacancy may be filled by an electron that has become trapped there through displacement from its normal position by bombardment with X-rays or other high-energy particles.

The energy of an electron trapped in a negative vacancy may be the proper magnitude to absorb light; this energy will depend on the environment of the site in which the electron is located. When a crystal is irradiated with white light, any photon in this light with the appropriate amount of energy will be absorbed by the electron and excite it to jump to a higher energy state. An induced color center is usually easily bleached by exposure to strong light or by heating, since supplying enough energy will release the electron from the color center.

Impurities in a crystal may cause color by:

1. acting as direct absorbers of a portion of the visible spectrum,
2. straining the structure sufficiently to produce imperfections if the impurity is a larger ion than the normal ion, or
3. promoting positive or negative vacancies allowing for color centers if the impurity is an ion of different charge.

The so-called colloidal colors result from the inclusion of colloid-sized impurities in solid material. Glass manufacturers have long added colloidal gold, copper, cadmium, and selenium to glass for color effects. These colloidal particles promote color by direct absorption, *selective scattering* (removing part of the optical spectrum by scattering and thus destroying some colors), and the development of *strain imperfections* (irregularities in the structure similar to impurity or vacancy imperfections).

Crystals of the mineral fluorite,  $\text{CaF}_2$ , commonly exhibit a variety of colors; many, if not most, of these are caused by color centers. Transparent and clear fluorite specimens can be colored blue by radium irradiation. Undoubtedly, the development of imperfections and electron traps by the bombarding radiation imparts new light-absorbing properties to this mineral.

Some fluorite colors have been correlated with the size of the color centers. Small centers develop green, medium-sized centers develop blue, and larger centers produce a violet color. Why? The size of the electron trap or color center is related to the amount of energy holding the electron in the trap. Therefore, since each wavelength of light is associated with a different energy, the size of the color center will control the wavelength absorbed. One portion of the spectrum will have energy just equal to the amount required to cause an electron jump from the color center.

Many colors in minerals are the result of exposure to high-energy radiation from the widespread occurrence of naturally radioactive isotopes of uranium, thorium, and potassium. This radiation damages the structure and may lead to the development of color centers.

In some crystals color centers seem to be stable indefinitely; in others, the centers are unstable. Apparently, impurities help stabilize color centers. Color induced by the formation of color centers may change with time as the electronic environment of the color center is altered. The violet color of some natural fluorites may be a result of radioactive bombardment of blue fluorite.

Not all the colors observed in fluorite crystals are due to the development of color centers. Incorporation of transition metals or rare earths into a fluorite structure in place of some of the calcium will impart a color to the specimen. Lanthanides in fluorite usually give rise to a yellow color. Small amounts of  $\text{Mn}^{4+}$  will produce a violet, and  $\text{Mn}^{3+}$ , a pink fluorite. Most green fluorite contains ferrous iron,  $\text{Fe}^{2+}$ . Many blue fluorites contain a small quantity of  $\text{Fe}^{2+}$  plus  $\text{Fe}^{3+}$ . Is the blue color due to these impurities, or has an earlier irradiation produced blue color centers? Probably, the best test is to see if strong light or heat will bleach out the color by releasing electrons from traps. If so, the specimen probably contains color centers.

Halite is common table salt (sodium chloride), the name comes from the Greek for salt. It is normally colorless and transparent to light over a wide range of wavelengths. This transparency ends, however, in the ultraviolet at about 2000 angstrom units. Radiation with wavelengths shorter than this has sufficient energy to excite electrons in the crystal to higher energy states. A strongly irradiated halite crystal turns yellow, but exposure to the radiation of sunlight turns it blue. This blue is not easily bleached out but can be removed by heating. Many natural halite crystals that have been subjected to heavy X-ray bombardment by nearness to radioactive minerals exhibit a semi permanent blue to purplish-black color.

What is taking place in a halite crystal on an atomic scale? In a perfect sodium chloride crystal each  $\text{Na}^+$  ion is surrounded by six  $\text{Cl}^-$  ions, and each  $\text{Cl}^-$  ion has six  $\text{Na}^+$  ions as its nearest neighbors. However, this picture of a crystal is idealized. In nature, crystals have defects; every so often in a crystal an ion is missing. Half the missing ions will be positive ions, the other half negative, because the overall charge balance must be maintained. This type of defect that contributes to color centers is shown in Fig. 2.10. Some of the negative vacancies in the halite crystal that indicate a missing chloride ion may trap an electron that has been agitated by strong X-rays from outside the crystal. Such trapped electrons form color centers. When a halite crystal containing these trapped electron color centers is exposed to visible light the electron is excited and jumps from the vacancy in which it was trapped, thus destroying the color. Celestite,  $\text{SrSO}_4$ , is commonly blue, a color resulting from natural radioactive bombardment. Pure celestite, however, resists artificial coloring by irradiation. Impure celestite with some sodium ions ( $\text{Na}^+$ ) substituting for strontium ions ( $\text{Sr}^{2+}$ ) will develop radiation-induced colors. Every two sodium ions substituted in the structure may lead to one  $\text{SO}_4^{2-}$  vacancy that could become a color center electron trap. Other materials develop colors in response to different types of radiation. Colorless glass bottles usually become pink or violet

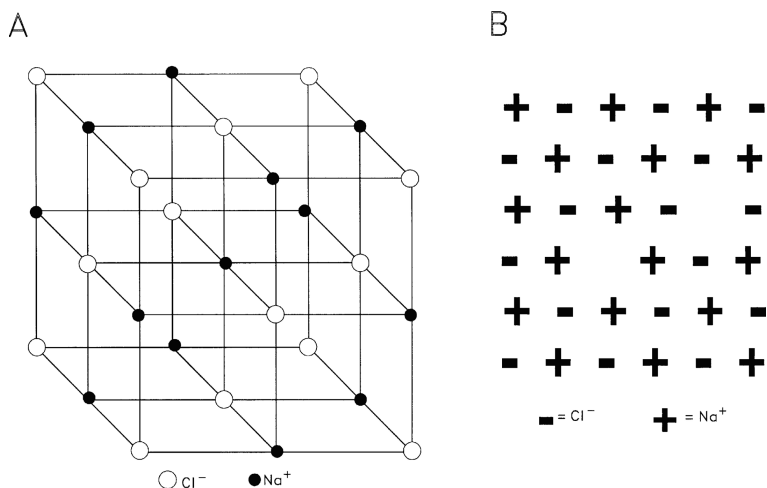


Fig. 2.10 A Structure of halite, NaCl. B Vacancies in halite crystals

from long exposure to the sun's radiation. In other materials, including halite, the sun's rays may have a bleaching effect. In each case, electrons are excited to jump to a different position by the energy contained in a given wavelength of electromagnetic radiation.

**Band Theory in Metals.** Unlike other causes of color which originate in the electronic structure of atoms or in crystal defects, the color of metals can be attributed to what is called band theory. In metals like gold, copper, and silver, and in alloys like brass, each metal atom contributes its outer electrons to a joint pool. These electrons can move freely throughout the metal, hence metals are good conductors of electricity and heat. These free electrons at the surface of a metal also give it the characteristic luster and high reflectivity. One aspect of this "sea of electrons" is that light cannot pass readily through the metal, so it is opaque.

Pleochroism is the characteristic of a mineral to produce different colors in different crystallographic directions. Alexandrite (a variety of chrysoberyl), when rotated, can exhibit red, orange, yellow, and green coloration. Amethyst has a weak dichromism, ranging from purple to gray-purple.

**Reflectivity, Luster, and Luminescence.** Reflectivity is a precise measure of the quantity of light reflected from a surface, usually recorded as a percentage of the incident light of a given wavelength that is reflected. Reflectivity varies with (1) the angle of refraction of the light as it enters the mineral, and (2) the absorption. The governing factor is absorption, since any light absorbed cannot be reflected. Reflectivity of minerals ranges from less than 5% (ice) to approximately 95% (native silver). Most common minerals have a reflectivity of less than 25%. Some light that we think of as purely reflected may be made up of rays that have traveled extensively in a mineral before returning to the air. A good example is snow. The small six-sided snow or ice crystals are minerals with a definite crystal structure. When light falls on a layer of snow, only 3 or 4% is reflected directly, but the random arrangement of billions of tiny crystal faces causes the reflections to be returned in a great variety of directions. Most of the light is refracted into the crystals and travels through them until it strikes their lower faces. The greater part will then be refracted deeper into the snow, but the angle made by the light with the lower faces of many snow crystals will cause reflection back into the mineral and upward toward the air. Light striking the billions of tiny, randomly arranged snow crystals bounces back and forth and in and out of the individual crystals, with most of it finally returning to the air. This gives the snow an appearance of high reflectivity. A thin layer of snow will not appear as white as a thicker layer because in the thin layer more of the light will escape into the ground rather than return and contribute to the twinkling effect.

Luster has been described historically in terms indicating the similarity of mineral luster to the luster of other common objects. A "pearly" luster simulates mother-of-pearl. The luster of glass is described as "vitreous"; "adamantine" luster comes from the Greek word for diamond. Most metals have the typical "metallic" luster.

The property we call luster is related to the manner and intensity of reflection of light from surface and near-surface atomic layers in a mineral. Some minerals have

been named on the basis of luster. Galena (PbS) means “lead glance”. The nature of this optical property is determined by four factors:

1. chemical composition,
2. type of chemical bond (ionic, covalent, metallic),
3. smoothness of surface, and
4. size of the reflecting grains.

A reduction in the smoothness of the surface and a reduction in grain size are really the same, since both give smaller plane reflecting surfaces.

Considering the luster of minerals having reasonably smooth surfaces allows luster to be correlated with chemical composition and type of bonding. Ionic, covalent, and metallic bonds each provide a distinctly different type of electronic interaction with light waves. Many minerals, however, appear to have a combination of ionic and covalent, or of covalent and metallic bonds.

Minerals falling in the ionic-covalent group usually have a luster that is vitreous (at the ionic end) to adamantine (at the covalent end), and a comparatively low index of refraction (ratio of the sine of the angle of incidence to the sine of the angle of refraction) at the ionic end and a high index at the covalent end. In general, the more covalent the bond, the greater the absorption and the greater the index of refraction.

Covalent, adamantine minerals are often compounds combining an element that is a certain number of places to the left of the Group IV elements (C, Si, Ge, Sn) in the Periodic Table (Fig. 2.8) with an element an equal number of places to the right of Group IV. For example: sphalerite, ZnS, cinnabar, HgS, and greenockite, CdS.

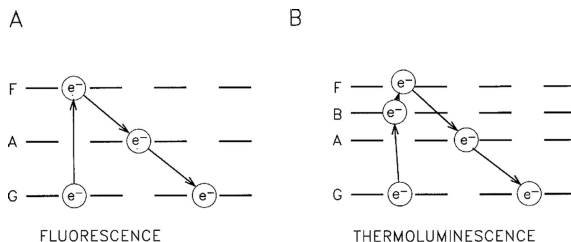
Those minerals with covalent-metallic bonds contain transition elements with *d* orbital electrons or heavy metals with *s* orbital electrons not involved in bonding (e.g., lead). The electronic field of such minerals strongly interferes with the passage of light, and absorption is correspondingly large. The opacity and refractive index in this group depend on the number of loosely bonded electrons or weakly overlapping orbitals. A greater number of loosely held electrons results in a more metallic luster and a greater opacity to light. Opaque minerals have a metallic, black, or at least strongly colored streak (powder of the mineral on a porcelain plate), whereas transparent minerals usually have a white or weakly colored streak.

Whether or not a mineral has a metallic luster depends on the amount of energy necessary to remove an electron from the metal ion and allow it to become a “free” electron. If energy greater than that of visible light is required, the mineral has a luster that is not metallic; if smaller, it has a metallic luster.

Luminescence is a glow some minerals exhibit when they are heated or exposed to light rays. A mineral is said to *fluoresce* if it is luminescent only during the period of thermal or ultraviolet excitation and to *phosphoresce* if the luminescence continues for some time after the excitation has ceased.

Luminescence is illustrated in Fig. 2.11 by picturing the energy changes attending the absorption and emission of radiation. Each atom or molecule begins with its electrons in a stable or ground state, *G*. Fluorescence may be considered as

**Fig. 2.11 A** Fluorescence.  
**B** Thermoluminescence



absorption of radiation moving the electron energy level, F, followed by a drop of the electron to a lower energy state, A, by radiating with a wavelength longer than the stimulating radiation. In practice, fluorescence usually involves the absorption of radiation in the invisible ultraviolet portion of the electromagnetic spectrum, with the simultaneous emission of radiation of a longer wavelength in the region of visible light. The word “fluorescence” was first suggested to describe this mechanism in the brilliant blue luminescence of many specimens of fluorite found in England. The blue fluorescence in fluorites is caused by the lanthanide elements. They fluoresce by electron transitions involving unfilled *f* orbitals. Probably, no other mineral shows so many different fluorescent hues as fluorite.

As with some other light absorption phenomena, fluorescence is due to the presence of foreign ions acting as absorbers. In some minerals the activator or foreign ion is known. Manganese (+2) is the cause of fluorescence in calcite,  $\text{CaCO}_3$ , and willemite,  $\text{Zn}_2\text{SiO}_4$ ; lead and molybdenum generate fluorescence in scheelite,  $\text{CaWO}_4$ . In some instances, a special combination of foreign ions is needed. The bright red fluorescence of halite from California dry lake deposits and from a salt spring in Idaho is due to cooperative activation by minute amounts of manganese and lead. Alone, neither element will generate fluorescence in halite. Apparently,  $\text{Pb}^{2+}$  acts as an absorber,  $\text{Mn}^{2+}$  as an emitter.

There are few minerals of which every specimen is fluorescent. Most minerals, however, have at least one occurrence of fluorescence when activator ions are incorporated into the crystal during its formation, producing fluorescence when it is exposed to radiation at one or more wavelengths. Fluorescent specimens of halite; gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; barite,  $\text{BaSO}_4$ ; apatite,  $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl})$ ; and leucite,  $\text{KAlSi}_2\text{O}_6$ , have been found. The most interesting fluorescent mineral is hackmanite,  $\text{Na}_4(\text{S}, \text{Cl})\text{Si}_3\text{Al}_3\text{O}_{12}$ , which changes color under the influence of different wavelengths of light. A purplish-pink when freshly exposed, hackmanite bleaches rapidly in sunlight, but the color returns when the strong light is removed. With ultraviolet stimulation, the mineral becomes an intense pink or purple. The source of these color changes in hackmanite is thought to be the chemical substitution of  $\text{S}^{2-}$  for  $\text{Cl}^-$ , resulting in the development of color centers.

In a few minerals the color is not a result of electronic properties of transition metals. For example, in lazurite (the main component of lapis lazuli), the sulfur atoms are in  $\text{S}_3^{2-}$  groups. Transitions among the atoms in this grouping produce the deep-blue color.

The fluorescence characteristics of a mineral obtained in one locality will generally not be identical with those of the same mineral from other localities. Minor changes in the quantity or type of activator ion incorporated in the mineral structure will produce different fluorescent properties from locality to locality.

Chermette (1985), Fritsch (1985), and Fritsch and Rossman (1987, 1988 a, b) have presented extensive reviews of the physical and chemical basis for mineral color. Lehmann and Bambauer (1973) and Rossman (1994) explain the basis of the color in silvery minerals, particularly tin.



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