Definition of a mineral.

A mineral, which by definition must be formed through natural processes, is distinct from the synthetic equivalents produced in the laboratory. Man−made versions of minerals, including emeralds, sapphires, diamonds, and other valuable gemstones, are regularly produced in industrial and research facilities and are often nearly identical to their natural counterparts. By its definition as a homogeneous solid, a mineral is composed of a single solid substance of uniform composition that cannot be physically separated into simpler compounds. Homogeneity is determined relative to the scale on which it is defined. A specimen that megascopically appears homogeneous, for example, may reveal several mineral components under a microscope or upon exposure to X−ray diffraction techniques. Most rocks are composed of several different minerals; e.g., granite consists of feldspar, quartz, mica, and amphibole. In addition, gases and liquids are excluded by a strict interpretation of the above definition of a mineral. Ice, the solid state of water (H_2O), is considered a mineral, but liquid water is not; liquid mercury, though sometimes found in mercury ore deposits, is not classified as a mineral either. Such substances that resemble minerals in chemistry and occurrence are dubbed mineraloids and are included in the general domain of mineralogy. Since a mineral has a definite composition, it can be expressed by a specific chemical formula. Quartz (silicon dioxide), for instance, is rendered as SiO_2, because the elements silicon (Si) and oxygen (O) are its only constituents and they invariably appear in a 1:2 ratio. The chemical makeup of most minerals is not as well defined as that of quartz, which is a pure substance. Siderite, for example, does not always occur as pure iron carbonate ($FeCO_3$); magnesium (Mg), manganese (Mn), and, to a limited extent, calcium (Ca) may sometimes substitute for the iron. Since the amount of the replacement may vary, the composition of siderite is not fixed and ranges between certain limits, although the ratio of the metal cation to the anionic group remains fixed at 1:1. Its chemical makeup may be expressed by the general formula $(Fe, Mn, Mg, Ca)CO_3$, which reflects the variability of the metal content. Minerals display a highly ordered internal atomic structure that has a regular geometric form (see Figure 1). Because of this feature, minerals are classified as crystalline solids. Under favourable conditions, crystalline materials may express their ordered internal framework by a well−developed external form, often referred to as crystal form or morphology (see Figure 2). Solids that exhibit no such ordered internal arrangement are termed amorphous. Many amorphous natural solids, such as glass, are categorized as mineraloids. Traditionally, minerals have been described as resulting exclusively from inorganic processes; however, current mineralogic practice often includes as minerals those compounds that are organically produced but satisfy all other mineral requirements. Aragonite ($CaCO_3$) is an example of an inorganically formed mineral that also has an organically produced, yet otherwise identical, counterpart; the shell (and the pearl, if it is present) of an oyster is composed to a large extent of organically formed aragonite. Minerals also are produced by the human body: hydroxylapatite [$Ca_5(PO_4)_3(OH)$] is the chief component of bones and teeth, and calculi are concretions of mineral substances found in the urinary system.

Mineral nomenclature

While minerals are classified in a logical manner according to their major anionic (negatively charged) chemical constituents into groups such as oxides, silicates, and nitrates, they are named in a far less scientific or consistent way. Names may be assigned to reflect a physical or chemical property, such as colour, or they may be derived from various subjects deemed appropriate, as, for example, a locality, public figure, or mineralogist. Some examples of mineral names and their derivations follow: albite ($NaAlSi_3O_8$) is from the Latin word (albus) for "white" in reference to its colour; goethite ($FeO{\times}OH$) is in honour of Johann Wolfgang von Goethe, the German poet; manganite ($MnO{\times}OH$) reflects the mineral's composition; franklinite ($ZnFe_2O_4$) is named after Franklin, N.J., U.S., the site of its occurrence as the dominant zinc (Zn) mineral; and sillimanite (Al_2SiO_4) is in honour of the American chemist Benjamin Silliman. Since 1960, an international committee of nomenclature has reviewed descriptions of new minerals and proposals for new mineral names and has attempted to remove inconsistencies.

Occurrence and formation of minerals.

Minerals form in all geologic environments and thus under a wide range of chemical and physical conditions, such as varying temperature and pressure. The four main categories of mineral formation are (1) igneous, or magmatic, in which minerals crystallize from a melt; (2) sedimentary, in which minerals are the result of the processes of weathering, erosion, and sedimentation; (3) metamorphic, in which new minerals form at the expense of earlier ones owing to the effects of changingusually increasingtemperature or pressure or both on some existing rock type (metamorphic minerals are the result of new mineral growth in the solid state without the intervention of a melt, as in igneous processes); and (4) hydrothermal, in which minerals are chemically precipitated from hot solutions within the Earth. The first three processes generally lead to varieties of rocks in which different mineral grains are closely intergrown in an interlocking fabric. Hydrothermal solutions, and even solutions at very low temperatures (e.g., groundwater), tend to follow fracture zones in rocks that may provide open spaces for the chemical precipitation of minerals from solution. It is from such open spaces, partially filled by minerals deposited from solutions, that most of the spectacular mineral specimens have been collected. If a mineral that is in the process of growth (as a result of precipitation) is allowed to develop in a free space, it will generally exhibit a well−developed crystal form (see Figure 2), which adds to a specimen's aesthetic beauty. Similarly, geodes, which are rounded, hollow, or partially hollow bodies commonly found in limestones, may contain well−formed crystals lining the central cavity. Geodes form as a result of mineral deposition from solutions such as groundwater.

MINERALS: THEIR NATURE, CLASSIFICATION,AND ASSOCIATIONS

The nature of minerals MORPHOLOGY

Nearly all minerals have the internal ordered arrangement of atoms and ions that is the defining characteristic of crystalline solids (see Figure 1). Under favourable conditions, minerals may grow as well−formed crystals, characterized by their smooth plane surfaces and regular geometric forms. Development of this good external shape is largely a fortuitous outcome of growth and does not affect the basic properties of a crystal. Therefore, the term crystal is most often used by material scientists to refer to any solid with an ordered internal arrangement, without regard to the presence or absence of external faces. The external shape, or morphology, of a crystal is perceived as its aesthetic beauty, and its geometry reflects the internal atomic arrangement (see Figure 2). The external shape of well−formed crystals expresses the presence or absence of a number of symmetry elements. Such symmetry elements include rotation axes, rotoinversion axes, a centre of symmetry, and mirror planes. A rotation axis is an imaginary line through a crystal around which it may be rotated and repeat itself in appearance one, two, three, four, or six times during a complete rotation. A sixfold rotation axis is illustrated in Figure 3A. When rotated about this axis, the crystal repeats itself each 60° (six times in a 360° rotation). A rotoinversion axis combines rotation about an axis of rotation with inversion. Rotoinversion axes are symbolized as 1, 2, 3, 4, and 6. 1 is equivalent to a centre of symmetry (or inversion, i), 2 is equivalent to a mirror plane, 3 is equivalent to a threefold rotation axis plus a centre of symmetry, 4 is not composed of other operations and is unique, and 6 is equivalent to a threefold rotation axis with a mirror plane perpendicular to the axis. The morphological expression of a fourfold rotoinversion axis is illustrated in Figure 3B. A centre of symmetry exists in a crystal if an imaginary line can be extended from any point on its surface through its centre and a similar point is present along the line equidistant from the centre (see Figure 3C). This is equivalent to 1, or inversion. There is a relatively simple procedure for recognizing a centre of symmetry in a well−formed crystal. With the crystal (or a wooden or plaster model thereof) laid down on any face on a tabletop, the presence of a face of equal size and shape, but inverted, in a horizontal position at the top of the crystal proves the existence of a centre of symmetry. A mirror plane is an imaginary plane that separates a crystal into halves such that, in a perfectly developed crystal, the halves are mirror images of one another. A single mirror in a crystal, also called a symmetry plane, is illustrated in Figure 3D. Morphologically crystals can be grouped into 32 crystal classes that represent the 32 possible symmetry elements and their combinations. These crystal classes, in turn, are grouped into six crystal systems. In decreasing overall symmetry content, beginning with the system with the highest and most complex crystal

symmetry, they are isometric, hexagonal, tetragonal, orthorhombic, monoclinic, and triclinic. The systems may be described in terms of crystallographic axes used for reference. The c axis is normally the vertical axis. The isometric system exhibits three mutually perpendicular axes of equal length (a1, a2, and a3). The orthorhombic and tetragonal systems also contain three mutually perpendicular axes; in the former system, all the axes are of different lengths (a, b, and c), and, in the latter, two axes are of equal length (a1 and a2) while the third (vertical) axis is either longer or shorter (c). The hexagonal system contains four axes: three equal−length axes (a1, a2, and a3) intersect one another at 120° and lie in a plane that is perpendicular to the fourth (vertical) axis of a different length. Three axes of different lengths (a, b, and c) are present in both the monoclinic and triclinic systems. In the monoclinic system, two axes intersect one another at an oblique angle and lie in a plane perpendicular to the third axis; in the triclinic system, all axes intersect at oblique angles. The grouping of the 32 possible crystal classes among the crystal systems is shown in Table 1. Column 1 of the table lists the six crystal systems; column 2 gives the total symmetry content of each of the 32 crystal classes; and column 3 gives a symbolic representation for each of the 32 combinations of symmetry elements known as the Hermann−Mauguin, or international, notation. This compact and very useful notation is discussed in professional literature, such as the references given in the Bibliography. Three different crystals with distinctively dissimilar symmetry contents, as expressed by their external morphology, are given in Figure 4. Figure 4A shows a well−formed monoclinic crystal with symmetry content i, 1A2, and 1m (2/m); Figure 4B features a crystal in the tetragonal system with symmetry content i, 1A4, and 1m (4/m); and Figure 4C shows a crystal in the isometric system having the highest possible symmetry content of 3A4, 4A3, 6A2, and 9m (4/m32/m). (See Table 1.) Photographs of some well−formed crystal groups are given in Figure 5. If two or more crystals form a symmetrical intergrowth, they are referred to as twinned crystals. A new symmetry operation (called a twin element), which is lacking in a single untwinned crystal, relates the individual crystals in a twinned position. There are three twin elements that may relate the crystals of a twin: (1) reflection by a mirror plane (twin plane), (2) rotation about a crystal direction common to both (twin axis) with the angular rotation typically 180°, and (3) inversion about a point (twin centre). An instance of twinning is defined by a twin law that specifies the presence of a plane, an axis, or a centre of twinning. If a twin has three or more parts, it is referred to as a multiple, or repeated, twin. Examples of various twin types are shown in Figure 6.

INTERNAL STRUCTURE

The external morphology of a mineral is an expression of the fundamental internal architecture of a crystalline substancei.e., its crystal structure. The crystal structure is the three−dimensional, regular (or ordered) arrangement of chemical units (atoms, ions, and anionic groups in inorganic materials; molecules in organic substances); these chemical units (referred to here as motifs) are repeated by various translational and symmetry operations (see below). The morphology of crystals can be studied with the unaided eye in large well−developed crystals and has been historically examined in considerable detail by optical measurements of smaller well−formed crystals through the use of optical goniometers. The internal structure of crystalline materials, however, is revealed by a combination of X−ray, neutron, and electron diffraction techniques, supplemented by a variety of spectroscopic methods, including infrared, optical, Mössbauer, and resonance techniques. These methods, used singly or in combination, provide a quantitative three−dimensional reconstruction of the location of the atoms (or ions), the chemical bond types and their positions, and the overall internal symmetry of the structure. The repeat distances in most inorganic structures and many of the atomic and ionic motif sizes are on the order of 1 to 10 angstroms (1 angstrom [Å] is equivalent to 10−8 centimetre [cm] or 3.94 X 10−9 inch) or 10 to 100 nanometres (nm; 1 nm is equivalent to 10−7 cm or 10 Å). Symmetry elements that are observable in the external morphology of crystals, such as rotation and rotoinversion axes, mirror planes, and a centre of symmetry, also are present in their internal atomic structure. In addition to these symmetry elements, there are translations and symmetry operations combined with translations. (Translation is the operation in which a motif is repeated in a linear pattern at intervals that are equal to the translation distance [commonly on the 1 to 10 Å level].) Two examples of translational symmetry elements are screw axes (combining rotation and translation) and glide planes (combining mirroring and translation). The internal translation distances are exceedingly small and can be seen directly only by very

high magnification electron−beam techniques, as used in a transmission electron microscope, at magnifications of about 600,000X. The 32 combinations of the translation−free symmetry elements are the crystal classes listed in Table 1 above. When all possible combinations of translational elements compatible with the 32 crystal classes (also known as point groups) are considered, one arrives at 230 possible ways in which translations, translational symmetry elements (screw axes and glide planes), and translation−free symmetry elements (rotation and rotoinversion axes and mirror planes) can be combined. These translation and symmetry groupings are known as the 230 space groups, representing the various ways in which motifs can be arranged in an ordered three−dimensional array. The symbolic representation of space groups is closely related to that of the Hermann−Mauguin notation of point groups as listed in column 3 of Table 1. A detailed discussion of space groups, their derivation, and notation is beyond the scope of this article. For more specific information, consult the books on mineralogy cited in the Bibliography. As in the case of the illustrations of the external morphology of crystals given above (Figures 2 through 6), the three−dimensional arrangement of crystal structures must be presented on a two−dimensional page. A common method of illustration involves projecting the crystal structure onto a planar surface, as in Figure 7, which portrays the structure of a form of silicon dioxide (SiO_2) known as tridymite. The structural motif units in this case are SiO_4 tetrahedrons composed of a silicon atom surrounded by four oxygen atoms. To further aid the visualization of complex crystal structures, models of such structures can be built or obtained commercially. Models of this sort reproduce the internal atomic arrangement on an enormously enlarged scale (e.g., one angstrom might be represented by one centimetre).

POLYMORPHISM Polymorphism is the ability of a specific chemical composition to crystallize in more than one form. This generally occurs as a response to changes in temperature or pressure or both. The different structures of such a chemical substance are called polymorphic forms, or polymorphs. For example, the element carbon (C) occurs in nature in two different polymorphic forms, depending on the external (pressure and temperature) conditions. These forms are graphite, with a hexagonal structure, and diamond, with an isometric structure. The composition FeS_2 occurs most commonly as pyrite, with an isometric structure, but it is also found as marcasite, which has an orthorhombic internal arrangement. The composition SiO_2 is found in a large number of polymorphs, among them quartz, tridymite, cristobalite, coesite, and stishovite. The stability field (conditions under which a mineral is stable) of these SiO_2 polymorphs is expressed in a stability diagram in Figure 9, with the external parameters of temperature and pressure as the two axes. In the general quartz field, there is additional polymorphism leading to the notation of high quartz and low quartz, each form having a slightly different internal structure. The diagram clearly indicates that cristobalite and tridymite are the high−temperature forms of SiO_2, and indeed these SiO_2 polymorphs occur in high−temperature lava flows. The high−pressure forms of SiO_2 are coesite and stishovite, and these can be found in meteorite craters, formed as a result of high explosive pressures upon quartz−rich sandstones, and in very deep−seated rock formations, as from the Earth's upper mantle. CHEMICAL COMPOSITIONThe chemical composition of a mineral is of fundamental importance because its properties greatly depend on it. Such properties, however, are determined not only by the chemical composition but also by the geometry of the constituent atoms and ions and by the nature of the electrical forces that bind them. Thus, for a complete understanding of minerals, their internal structure, chemistry, and bond types must be considered. Various analytical techniques may be employed to obtain the chemical composition of a mineral. Quantitative chemical analyses conducted prior to 1947 mainly utilized so−called wet analytical methods, in which the mineral sample is first dissolved. Various compounds are then precipitated from the solution, which are weighed to obtain a gravimetric analysis. Since 1947 a number of analytical procedures have been introduced that provide faster but somewhat less accurate results. Most analyses performed since 1960 have made use of instrumental methods such as optical emission, X−ray fluorescence, atomic absorption spectroscopy, and electron microprobe analysis. Relatively well−established error ranges have been documented for these methods, and samples must be prepared in a specific manner for each technique. A distinct advantage of wet analytical procedures is that they make it possible to determine quantitatively the oxidation states of positively charged atoms, called cations (e.g., Fe^{2+} versus Fe^{3+}), and to ascertain the amount of water in hydrous minerals. Instrumental techniques, on the other hand, cannot provide this type of information. To ensure an accurate chemical analysis, the selected sample must contain only one mineral species (i.e., the one for which the analysis is

being done) and must not have undergone alteration processes. Since it is frequently difficult, and at times impossible, to obtain as much as 0.1 to 1 gram of "clean" material for analysis, the results should be accompanied by specifications on the amount of impurities present. To reduce the effect of the impurities, an instrumental technique, such as electron microprobe analysis, is often employed. In this method, quantitative analysis in situ may be performed on mineral grains only 1 micrometre (10−4 centimetre) in diameter.

MINERAL FORMULASElements may exist in the native (uncombined) state, in which case their formulas are simply their chemical symbols: gold (Au), carbon (C) in its polymorphic form of diamond, and sulfur (S) are common examples. Most minerals, however, occur as compounds consisting of two or more elements; their formulas are obtained from quantitative chemical analyses and indicate the relative proportions of the constituent elements. The formula of sphalerite, ZnS, reflects a one−to−one ratio between atoms of zinc and those of sulfur. In bornite (Cu5FeS4), there are five atoms of copper (Cu), one atom of iron (Fe), and four atoms of sulfur. There exist relatively few minerals with constant composition; notable examples include quartz (SiO2) and kyanite (Al2SiO5). Minerals of this sort are termed pure substances. Most minerals display considerable variation in the ions that occupy specific atomic sites within their structure. For example, the iron content of rhodochrosite (MnCO3) may vary over a wide range. As ferrous iron (Fe2+) substitutes for manganese cations (Mn2+) in the rhodochrosite structure, the formula for the mineral might be given in more general termsnamely (Mn, Fe)CO3. The amounts of manganese and iron are variable, but the ratio of the cation to the negatively charged anionic group remains fixed at one Mn2+ or Fe2+ atom to one CO3 group.
COMPOSITIONAL VARIATIONAs stated above, most minerals exhibit a considerable range in chemical composition. Such variation results from the replacement of one ion or ionic group by another in a particular structure. This phenomenon is termed ionic substitution, or solid solution. Three types of solid solution are possible, and these may be described in terms of their corresponding mechanismsnamely, substitutional, interstitial, and omission. Substitutional solid solution is the most common variety. For example, as described above, in the carbonate mineral rhodochrosite (MnCO3), Fe2+ may substitute for Mn2+ in its atomic site in the structure. The degree of substitution may be influenced by various factors, with the size of the ion being the most important. Ions of two different elements can freely replace one another only if their ionic radii differ by approximately 15 percent or less. Limited substitution can occur if the radii differ by 15 to 30 percent, and a difference of more than 30 percent makes substitution unlikely. These limits, calculated from empirical data, are only approximate. The temperature at which crystals grow also plays a significant role in determining the extent of ionic substitution. The higher the temperature, the more extensive is the thermal disorder in the crystal structure and the less exacting are the spatial requirements. As a result, ionic substitution that could not have occurred in crystals grown at low temperatures may be present in those grown at higher ones. The high−temperature form of KAlSi3O8 (sanidine), for example, can accommodate more sodium (Na) in place of potassium (K) than can microcline, its low−temperature counterpart. An additional factor affecting ionic substitution is the maintenance of a balance between the positive and negative charges in the structure. Replacement of a monovalent ion (e.g., Na+, a sodium cation) by a divalent ion (e.g., Ca2+, a calcium cation) requires further substitutions to keep the structure electrically neutral. Simple cationic or anionic substitutions are the most basic types of substitutional solid solution. A simple cationic substitution can be represented in a compound of the general form A+X− in which cation B+ replaces in part or in total cation A+. Both cations in this example have the same valence (+1), as in the substitution of K+ (potassium ions) for Na+ (sodium ions) in the NaCl (sodium chloride) structure. Similarly, the substitution of anion X− by Y− in an A+X− compound represents a simple anionic substitution; this is exemplified by the replacement of Cl− (chlorine ions) with Br− (bromine ions) in the structure of KCl (potassium chloride). A complete solid−solution series involves the substitution in one or more atomic sites of one element for another that ranges over all possible compositions and is defined in terms of two end−members. For example, the two end−members of olivine [(Mg, Fe)2SiO4], forsterite (Mg2SiO4) and fayalite (Fe2SiO4), define a complete solid−solution series in which magnesium cations (Mg2+) are replaced partially or totally by Fe2+. In some instances, a cation B3+ may replace some A2+ of compound A2+X2−. So that the compound will remain neutral, an equal amount of A2+ must concurrently be replaced by a third cation, C+. This is given in equation form as 2A2+ {arrows, left & righ} B3+ + C+; the positive charge on each side is the same. Substitutions such as this are termed coupled substitutions. The plagioclase feldspar series exhibits complete solid solution, in the form of coupled

substitutions, between its two end−members, albite (NaAlSi3O8) and anorthite (CaAl2Si2O8). Every atomic substitution of Na+ by Ca2+ is accompanied by the replacement of a silicon cation (Si4+) by an aluminum cation (Al3+), thereby maintaining electrical neutrality: Na+ + Si4+ {arrows, left & righ} Ca2+ + Al3+. The second major type of ionic substitution is interstitial solid solution, or interstitial substitution. It takes place when atoms, ions, or molecules fill the interstices (voids) found between the atoms, ions, or ionic groups of a crystal structure. The interstices may take the form of channellike cavities in certain crystals, such as the ring silicate beryl (Be3Al2Si6O18). Potassium, rubidium (Rb), cesium (Cs), and water, as well as helium (He), are some of the large ions and gases found in the tubular voids of beryl. The least common type of solid solution is omission solid solution, in which a crystal contains one or more atomic sites that are not completely filled. The best−known example is exhibited by pyrrhotite (Fe1 − xS). In this mineral, each iron atom is surrounded by six neighbouring sulfur atoms. If every iron site in pyrrhotite was occupied by ferrous iron, its formula would be FeS. There are, however, varying percentages of vacancy in the iron site, so that the formula is given as Fe6S7 through Fe11S12, the latter being very near to pure FeS. The formula for pyrrhotite is normally written as Fe1 − xS, with x ranging from 0 to 0.2. It is one of the minerals referred to as a defect structure, because it has a structural site that is not completely occupied. CHEMICAL BONDINGElectrical forces are responsible for binding together the atoms, ions, and ionic groups that constitute crystalline solids. The physical and chemical properties of minerals are attributable for the most part to the types and strengths of these binding forces; hardness, cleavage, fusibility, electrical and thermal conductivity, and the coefficient of thermal expansion are examples of such properties. On the whole, the hardness and melting point of a crystal increase proportionally with the strength of the bond, while its coefficient of thermal expansion decreases. The extremely strong forces that link the carbon atoms of diamond, for instance, are responsible for its distinct hardness. Periclase (MgO) and halite (NaCl) have similar structures; however, periclase has a melting point of 2,800° C (5,072° F), whereas halite melts at 801° C (1,474° F). This discrepancy reflects the difference in the bond strength of the two minerals: since the atoms of periclase are joined by a stronger electrical force, a greater amount of heat is needed to separate them. The electrical forces, called chemical bonds, can be divided into five types: ionic, covalent, metallic, van der Waals, and hydrogen bonds. Classification in this manner is largely one of expediency; the chemical bonds in a given mineral may in fact possess characteristics of more than one bond type. For example, the forces that link the silicon and oxygen atoms in quartz exhibit in nearly equal amount the characteristics of both ionic and covalent bonds. As stated above, the electrical interaction between the atoms of a crystal determine its physical and chemical properties. Thus, classifying minerals according to their electrical forces will cause those species with similar properties to be grouped together. This fact justifies classification by bond type.

Ionic bonds.

Atoms have a tendency to gain or lose electrons so that their outer orbitals become stable; this is normally accomplished by these orbitals being filled with the maximum allowed number of valence electrons. Metallic sodium, for example, has one valence electron in its outer orbital; it becomes ionized by readily losing this electron and exists as the cation Na+. Conversely, chlorine gains an electron to complete its outer orbital, thereby forming the anion Cl−. In the mineral halite, NaCl (common, or rock, salt), the chemical bonding that holds the Na+ and Cl− ions together is the attraction between the two opposite charges. This bonding mechanism is referred to as ionic, or electrovalent (see Figure 10A). Ionically bonded crystals typically display moderate hardness and specific gravity, rather high melting points, and poor thermal and electrical conductivity. The electrostatic charge of an ion is evenly distributed over its surface, and so a cation tends to become surrounded with the maximum number of anions that can be arranged around it. Since ionic bonding is nondirectional, crystals bonded in this manner normally display high symmetry (see Table 2).

Covalent bonds.

In the discussion of the ionic bond, it was noted that chlorine readily gains an electron to achieve a stable electron configuration. An incomplete outer orbital places a chlorine atom in a highly reactive state, so it attempts to combine with nearly any atom in its proximity. Because its closest neighbour is usually another

chlorine atom, the two may bond together by sharing one pair of electrons. As a result of this extremely strong bond, each chlorine atom enters a stable state. The electron−sharing, or covalent, bond is the strongest of all chemical bond types. Minerals bonded in this manner display general insolubility, great stability, and a high melting point. Crystals of covalently bonded minerals tend to exhibit lower symmetry than their ionic counterparts because the covalent bond is highly directional, localized in the vicinity of the shared electrons (see Table 2). The Cl2 molecules formed by linking two neighbouring chlorine atoms are stable and do not combine with other molecules. Atoms of some elements, however, have more than one electron in the outer orbital and thus may bond to several neighbouring atoms to form groups, which in turn may join together in larger combinations. Carbon, in the polymorphic form of diamond, is a good example of this type of covalent bonding. There are four valence electrons in a carbon atom, so that each atom bonds with four others in a stable tetrahedral configuration (see Figure 10B). A continuous network is formed by the linkage of every carbon atom in this manner. The rigid diamond structure results from the strong localization of the bond energy in the vicinity of the shared electrons; this makes diamond the hardest of all natural substances. Diamond does not conduct electricity, because all the valence electrons of its constituent atoms are shared to form bonds and therefore are not mobile (see Table 2).

Metallic bonds.

Bonding in metals is distinct from that in their salts, as reflected in the significant differences between the properties of the two groups. In contrast to salts, metals display high plasticity, tenacity, ductility, and conductivity. Many are characterized by lower hardness and have higher melting and boiling points than, for example, covalently bonded materials. All these properties result from a metallic bonding mechanism that can be envisioned as a collection of positively charged ions immersed in a cloud of valence electrons (see Figure 10C). The attraction between the cations and the electrons holds a crystal together. The electrons are not bound to any particular cation and are thus free to move throughout the structure. In fact, in the metals sodium, cesium, rubidium, and potassium, the radiant energy of light can cause electrons to be removed from their surfaces entirely. (This result, known as the photoelectric effect, is utilized in light meters.) Electron mobility is responsible for the ability of metals to conduct heat and electricity. The native metals are the only minerals to exhibit pure metallic bonding (see Table 2).

Van der Waals bonds

Neutral molecules may be held together by a weak electric force known as the van der Waals bond. It results from the distortion of a molecule so that a small positive charge develops on one end and a corresponding negative charge develops on the other (see Figure 10D). A similar effect is induced in neighbouring molecules, and this dipole effect propagates throughout the entire structure. An attractive force is then formed between oppositely charged ends of the dipoles. Van der Waals bonding is common in gases and organic liquids and solids, but it is rare in minerals. Its presence in a mineral defines a weak area with good cleavage and low hardness. In graphite, carbon atoms lie in covalently bonded sheets with van der Waals forces acting between the layers (see Figure 11).

Hydrogen bonds.

In addition to the four major bond types described above, there is an interaction called hydrogen bonding. This takes place when a hydrogen atom, bonded to an electronegative atom such as oxygen, fluorine, or nitrogen, is also attracted to the negative end of a neighbouring molecule. A strong dipole−dipole interaction is produced, forming a bond between the two molecules. Hydrogen bonding is common in hydroxides and in many of the layer silicatese.g., micas and clay minerals.

Metals

Gold, silver, and copper are members of the same group (column) in the periodic table of elements (see

CHEMICAL ELEMENTS: Periodic law and table) and therefore have similar chemical properties. In the uncombined state, their atoms are joined by the fairly weak metallic bond. These minerals share a common structure type, and their atoms are positioned in a simple cubic closest−packed arrangement. Gold and silver both have an atomic radius of 1.44 angstroms (Å), which enables complete solid solution to take place between them. The radius of copper is significantly smaller (1.28 Å), and as such copper substitutes only to a limited extent in gold and silver. Likewise, native copper contains only trace amounts of gold and silver in its structure. Owing to their similar crystal structure, the members of the gold group display similar physical properties. All are rather soft, ductile, malleable, and sectile; gold, silver, and copper serve as excellent conductors of electricity and heat and exhibit metallic lustre and hackly fracture. These properties are attributable to their metallic bonding. The gold−group minerals crystallize in the isometric system and have high densities as a consequence of cubic closest packing. In addition to the elements listed above, the platinum group also includes the rarer mineral alloys platiniridium and iridosmine. The members of this group are harder than the metals of the gold group and also have higher melting points. The iron−group metals are isometric and have a simple cubic packed structure (see Figure 17A). Its members include pure iron, which is rarely found on the surface of the Earth, and two species of nickel−iron (kamacite and taenite), which have been identified as common constituents of meteorites. The atomic radii of iron and nickel are both approximately 1.24 Å, and so nickel is a frequent substitute for iron. The terrestrial core is thought to be composed largely of such iron−nickel alloys.

Regional metamorphic rocks.

Many different amphiboles may be contained in regional metamorphic rocks. Commonly several amphiboles may coexist with one another in the same sample, depending on the bulk chemistry of the rock and on the pressure and temperature of metamorphism. The amphiboles typically occur with plagioclase feldspar, quartz, and biotite, as well as with chlorite and oxide minerals. In magnesium−rich rocks, tremolite, anthophyllite, and hornblende may exist together. Gedrite and cummingtonite coexist with garnet in rocks enriched in aluminum and iron. Rocks containing cummingtonite or grunerite are characteristic of metamorphosed iron formations associated with iron oxides, iron−rich sheet silicates, carbonates, and quartz. Glaucophane occurs only in such metamorphic rocks as schist, eclogite, and marble. Glaucophane associated with jadeite, lawsonite, and calcite or aragonite is the characteristic assemblage found in high−pressure, low−temperature metamorphic rocks called blueschists, which have a blue colour imparted by the glaucophane. Blueschists have basaltic bulk compositions and may also contain riebeckite. The latter also may occur in regional metamorphic schists. Tremolite−actinolite and the sheet−silicate chlorite are the principal minerals in the low−to−moderate temperature and pressure greenschist metamorphic rocks. Hornblende is characteristic of some medium−grade metamorphic rocks known as amphibolites, in which hornblende and plagioclase are the major constituents. Dehydration of amphiboles in the lower crust or mantle may be an important source of water that aids in the generation of magmas from partial melting processes.

Pyroxenes

GENERAL CONSIDERATIONSPyroxenes are the most significant and abundant group of rock−forming ferromagnesian silicates. They are found in almost every variety of igneous rock and also occur in rocks of widely different compositions formed under conditions of regional and contact metamorphism. The name pyroxene is derived from the Greek pyro, meaning "fire," and xenos, meaning "stranger," and was given by Haüy to the greenish crystals found in many lavas which he considered to have been accidentally included there. Pyroxenes crystallize in both the orthorhombic and monoclinic crystal systems. Typically pyroxenes occur as stubby prismatic crystals. They are chemically analogous to the amphiboles except that, as discussed above, hydroxyls are absent in the pyroxene structure. They are similar in colour, lustre, and hardness to the amphiboles but have slightly higher densities owing to the absence of hydroxyls. Pyroxenes have two distinctive planes of cleavage with intersecting angles of about 87° and 93°. Perpendicular to their cleavage planes, pyroxenes have nearly square cross sections, which, together with the cleavage directions, are diagnostic properties. CHEMICAL COMPOSITIONThe chemical composition of minerals of the pyroxene

group can be expressed by the general formula XYZ2O6, in which X = Na+, Ca2+, Mn2+, Fe2+, Mg2+, Li+; Y = Mn2+, Fe2+, Mg2+, Fe3+, Al3+, Cr3+, Ti4+; and Z = Si4+, Al3+. The range of possible chemical substitutions in pyroxene is constrained by the sizes of the available sites in the structure and the charge of the substituting cations. The X cation sites in general are larger than the Y cation sites. Extensive atomic substitution occurs between the ideal end−member compositions. Most pyroxenes have only limited substitution of aluminum for silicon in the Z (tetrahedral) site. When a substituting ion differs in charge, electrical neutrality is maintained by coupled substitutions. For example, the pair consisting of Na+ and Al3+ substitutes for 2 Mg2+. Table 21 shows the five major chemical subdivisions of pyroxenes. The most common pyroxenes can be represented as part of the chemical system CaSiO3 (wollastonite, a pyroxenoid), MgSiO3 (enstatite), and FeSiO3 (orthoferrosilite; see Figure 49). Since no true pyroxenes exist with calcium contents greater than that of the diopside−hedenbergite join, the part of this system below this join is known as the pyroxene quadrilateral. Ferrous iron and magnesium substitute freely since they have similar ionic sizes and identical charges. Complete substitution exists between enstatite (Mg2Si2O6) and orthoferrosilite (Fe2Si2O6), and complete solid solution of iron for magnesium exists between diopside (CaMgSi2O6) and hedenbergite (CaFeSi2O6). Augite, subcalcic augite, and pigeonite lie within the interior of the pyroxene quadrilateral. Compositionally, augite is related to members of the diopside−hedenbergite series with limited substitution of Na+ for Ca2+, Al3+ for Mg2+ and Fe2+, and Al3+ for Si4+ in the Z (tetrahedral) site. Augites with substantial aluminum or sodium cannot be strictly represented in the quadrilateral plane. Monoclinic pigeonite encompasses a field of magnesium−iron solid solution with a slightly higher calcium content than the orthorhombic enstatite−orthoferrosilite series. The nomenclature for the orthopyroxene series is based on the percentage of MgSiO3: enstatite, 90−100; bronzite, 70−90; hypersthene, 50−70; ferrohypersthene, 30−50; eulite, 10−30; and orthoferrosilite, 0−10. Coupled substitutions involving Na+, Li+, or Al3+ for Mg2+ in the enstatite structure yield pyroxenes that lie outside the quadrilateral compositional field. The coupled substitution of Na+ and Al3+ for 2 Mg2+ in enstatite produces the pyroxene jadeite. The coupled substitution of Na+ and Fe3+ for 2 Mg2+ produces the pyroxene aegirine (acmite). Substitution of Li+ and Al3+ for 2 Mg2+ yields spodumene. The substitution of Al3+ for Mg2+ and Al3+ for Si4+ yields the ideal tschermakite component MgAlSiAlO6. Other less common pyroxenes with compositions outside the pyroxene quadrilateral include johannsenite [CaMnSi2O6], a variety of augite called fassaite [Ca(Mg, Fe2+, Fe3+, Al)(Si, Al)2O6], and kosmochlor (ureyite) [NaCrSi2O6]. Johannsenite involves the substitution of manganese for iron in hedenbergite. Kosmochlor has chromium (Cr) in place of iron or aluminum in a sodic pyroxene. The fassaite variety of the calcium pyroxene group has a variable but high aluminum content and a high Fe3+:Fe2+ ratio. The nature of aluminum substitution in pyroxenes varies significantly from one pyroxene to another. In the magnesium−iron pyroxene group, aluminum is usually present in only small amounts. In both jadeite and spodumene, which contain essential aluminum in the Y site, the substitution of silicon by aluminum in the Z tetrahedral site is almost negligible. In augite there can be extensive substitution of aluminum for tetrahedral silicon. At high temperatures, pyroxenes have more extensive fields of solid solution than they do at lower ones. Consequently, as temperatures decrease, the pyroxene adjusts its composition in the solid state by exsolving a separate phase in the form of lamellae within the host pyroxene grain. The lamellae are exsolved along specific crystallographic directions, producing oriented intergrowths with parallel and herringbone texture. There are five principal combinations of exsolution pairs: (1) augite with hypersthene lamellae, (2) augite with pigeonite lamellae, (3) augite with both pigeonite and hypersthene lamellae, (4) pigeonite with augite lamellae, and (5) hypersthene with augite lamellae. The pyroxenes differ compositionally from the amphiboles in two major respects. Pyroxenes contain no essential water in the form of hydroxyls in their structure, whereas amphiboles are considered to be hydrous silicates. The second key chemical difference between the two is the presence of the A site in amphiboles which contains the large alkali elements, typically sodium and at times potassium; the pyroxenes do not have an equivalent site that can accommodate potassium. Hydroxyl groups in the amphibole structure decrease their thermal stability relative to the more refractory pyroxenes. At high temperatures amphiboles decompose to anhydrous minerals.

CRYSTAL STRUCTURE

The pyroxene group includes minerals that form in both the orthorhombic and monoclinic crystal systems. Orthorhombic pyroxenes are referred to as orthopyroxenes, and monoclinic pyroxenes are called clinopyroxenes. The essential feature of all pyroxene structures is the linkage of the silicon−oxygen (SiO_4) tetrahedrons by sharing two of the four corners to form continuous chains. The chains, which extend indefinitely parallel to the c crystallographic axis, have the composition of $(SiO_3)_n$ (Figure 50). A repeat distance of approximately 5.3 Å along the length of the chain defines the c axis of the unit cell. The SiO_3 chains are bonded to a layer of octahedrally coordinated cation bands which also extend parallel to the c axis. The octahedral layer contains two distinct cation sites called M1 and M2. The size and charge of the cations that occupy the M2 site chiefly determine the structural type of a pyroxene. Large, singly or doubly charged cations give rise to a diopside (monoclinic) structure, whereas small, singly or doubly charged cations result in an enstatite (orthorhombic) structure. In most pyroxenes the chains are not exactly straight as shown in Figure 50, but are rotated or kinked so that more than one type of chain is possible. The diopside, jadeite, augite, protoenstatite, and spodumene structures consist of only one chain type. Pigeonite, clinoenstatite, and omphacite have two symmetrically distinct types of tetrahedral chains. Orthopyroxenes also have two distinct types of tetrahedral chains and an octahedral stacking sequence that leads to a doubling of the a axis. A representative pyroxene structure that illustrates the tetrahedral and octahedral chains in jadeite is shown in Figure 51. The octahedral strips consist of M1 and M2 octahedrons sandwiched between two oppositely pointing tetrahedral chains. The M1 sites are occupied by smaller cations such as magnesium, iron, aluminum, and manganese, which are coordinated to six oxygen atoms to form a regular octahedron. In monoclinic pyroxenes, the M2 site is a large irregular polyhedron occupied by the larger calcium and sodium cations which are in eightfold coordination. In the low−calcium orthorhombic pyroxenes, M2 contains magnesium and iron, and the polyhedron takes on a more regular octahedral shape. The M1 cation strip is bonded to oxygen atoms of two oppositely pointing tetrahedral chains. Together, these form a tetrahedral−octahedral−tetrahedral (t−o−t) strip. A schematic projection of the pyroxene structure perpendicular to the c axis and the relationship of the pyroxene cleavage to the t−o−t strips or I beams is shown in Figure 52. Pyroxenes in the quadrilateral with compositions near the diopside−hedenbergite join exist only in the monoclinic form. Those with compositions near the enstatite−orthoferrosilite join containing less than about 15 percent $CaSiO_3$ can be subdivided into three structural types. Those with approximately 30 percent $FeSiO_3$ are monoclinic at high temperatures (pigeonite) and invert to an orthorhombic structure at low temperatures (hypersthene). Those with less than 30 percent $FeSiO_3$ can exist as clinoenstatite (monoclinic), protoenstatite (orthorhombic), or enstatite (orthorhombic) polymorphic structures. Pyroxenes outside the quadrilateral all have monoclinic pyroxene structures similar to that of diopside. The inversion of high−temperature structures to low−temperature structures is often accompanied by the exsolution of lamellae of either a separate calcium−rich or magnesium−iron−rich phase. For example, as high−temperature monoclinic pigeonite slowly cools, it exsolves calcium ions to form augite lamellae and inverts to the orthorhombic hypersthene structure. Consequently, the presence of the exsolution lamellae is evidence of a previous monoclinic structure.

PHYSICAL PROPERTIES

Within hand specimens, pyroxene can generally be identified by the following characteristics: two directions of cleavage intersecting at roughly right angles (approximately 87° and 93°), stubby prismatic crystal habit with nearly square cross sections perpendicular to cleavage directions, and a Mohs hardness between 5 and 7. Specific gravity values of the pyroxenes range from about 3.0 to 4.0. Unlike amphiboles, pyroxenes do not yield water when heated in a closed tube. Characteristically, pyroxenes are dark green to black in colour, but they can range from dark green to apple−green and from lilac to colourless, depending on the chemical composition. Diopside ranges from white to light green, darkening in colour as the iron content increases. Hedenbergite and augite are typically black. Pigeonite is greenish brown to black. Jadeite is white to apple−green to emerald−green or mottled white and green and is a massive aggregate of compact fibres. Aegirine (acmite) forms long, slender prismatic crystals that are brown to green in colour. Enstatite is yellowish or greenish brown; bronzite has a submetallic bronzelike lustre; and hypersthene and more iron−rich orthopyroxenes range from brown to black. Spodumene is colourless, white, gray, pink, yellow, or

green. The clear lilac−coloured variety is called kunzite, while the clear emerald−green type is known as hiddenite. In thin sections, monoclinic pyroxenes are distinguished by two directions of cleavage at approximately 87° and 93°, eight−sided basal cross sections, and light brown or green colour (Figure 53). Orthorhombic pyroxenes differ from monoclinic pyroxenes in that they have parallel extinction. Microscopically, many igneous pyroxenes show exsolution textures of thin lamellae of one pyroxene in a host of a different composition. The lamellae occur as oriented intergrowths that display parallel and herringbone textures (Figure 54). These lamellae result from the exsolution of a separate pyroxene phase from a host grain due to subsolidus re−equilibration (that occurs while the mineral is in the solid state) during slow cooling.

ORIGIN AND OCCURRENCE

Minerals in the pyroxene group are abundant in both igneous and metamorphic rocks. Their susceptibility to both chemical and mechanical weathering makes them a rare constituent of sedimentary rocks. Pyroxenes are classified as ferromagnesian minerals in allusion to their high content of magnesium and iron. Their conditions of formation are almost exclusively restricted to environments of high temperature, high pressure, or both. Characteristically the more common pyroxenes are found in mafic and ultramafic igneous rocks where they are associated with olivine and calcium−rich plagioclase and in high−grade metamorphic rocks such as granulites and eclogites. Enstatite, clinoenstatite, and kosmochlor occur in meteorites.

Igneous rocks.

Magnesium−rich orthopyroxenes and calcium−rich clinopyroxenes are important constituents of basalts, gabbros, peridotites, and norites. They are the major minerals in pyroxenites. Magnesium−rich orthopyroxenes occur in the earlier−formed rocks of layered ultramafic complexes. Uninverted pigeonites (monoclinic) are common as phenocrysts in high−temperature, rapidly cooled lavas and in some intrusives such as diabases. In slowly cooled mafic intrusive rocks, pigeonite inverts to an orthorhombic pyroxene and undergoes exsolution. Augite is the most common pyroxene and is found primarily in mafic igneous rocks. It occurs in basalts, gabbros, andesites, diorites, and peridotites. The augites in layered ultramafic intrusions show compositional trends of increasing iron and decreasing magnesium contents with fractionation. Augite is also known to occur in lunar basalts. Although more common in metamorphic rocks, diopside is found in some mafic and ultramafic rocks. Aegirine (acmite) and aegirine−augite occur most commonly as products of the late crystallization of alkaline magmas. They are found in alkalic rocks such as nepheline syenites and phonolites, wherein they are associated with orthoclase, feldspathoids, augite, and sodium−rich amphiboles. Spodumene is found almost exclusively in lithium−rich granite pegmatites. Some of the world's largest known crystals are spodumene. Single crystals of spodumene exceeding 13 metres (43 feet) in length were mined for their lithium content in the Black Hills of South Dakota, U.S. Spodumene is typically associated with microcline, albite, quartz, muscovite, lepidolite, beryl, and tourmaline.

Metamorphic rocks

Iron−rich orthopyroxenes are found in metamorphosed iron formations in association with the amphibole grunerite. At higher grades of regional metamorphism, the amphibole anthophyllite breaks down to form magnesium−iron orthopyroxenes. The orthopyroxenes hypersthene and enstatite occur in high−temperature and high−pressure granulite facies rocks such as quartz−rich, garnet−bearing granulites. Diopside results from the thermal metamorphism of siliceous limestones or dolomites according to the following decarbonation reaction:$CaMg(CO_3)_2 + 2SiO_2 \rightarrow CaMgSi_2O_6 + 2CO_2$. [See print Britannica for tabular display] dolomite quartz diopside carbon dioxideIn calc−silicate skarns produced by contact metamorphism, diopside is associated with wollastonite, vesuvianite, grossular, and tremolite. Diopside also forms under conditions of regional metamorphism by the breakdown of tremolite. Hedenbergite is a product of thermal metamorphism of iron−rich sediments where its formation is probably due to the breakdown of ferroactinolite with increasing temperature. The variety of augite called fassaite is found in quartz−free, aluminum−rich skarns associated with spinel, calcite, vesuvianite, garnet, clintonite, and diopside. Johannsenite is associated with rhodonite,

bustamite, sphalerite, chalcopyrite, galena, pyrite, and magnetite in metasomatized limestones adjacent to igneous intrusions. Aegirine (acmite) is associated with glaucophane or riebeckite in some metamorphic rocks. Jadeite is found only in metamorphic rocks. It is associated with albite, glaucophane, aragonite, lawsonite, and quartz in high−pressure, low−temperature metamorphic rocks of blueschist facies. In some localities, jadeite is associated with serpentine in glaucophane−bearing metamorphic rocks. Omphacite is restricted in occurrence to the high−pressure and high−temperature rocks called eclogites. Eclogites represent the most deep−seated conditions of metamorphism and are characterized by an assemblage of omphacite and magnesium−rich pyrope garnet. Omphacite−bearing eclogite nodules are associated with peridotites in the kimberlite pipes of South Africa. (W.B.Si.)

Alteration products and weathering.

Olivines gelatinize in even weak acids and offer little resistance to attack by weathering agents and hot mineralizing (hydrothermal) solutions. The forsteritic olivines are altered principally through leaching, which results in the removal of magnesium and the addition of water and some iron. The chemical reactions are usually complex and involve hydration, oxidation, and carbonation. The fayalitic olivines are altered principally through oxidation and the removal of silica. The usual products of alteration are the minerals serpentine, iddingsite, and bowlingite, all of which may occur as pseudomorphs (forms with the outward appearance of the original mineral but which have been completely replaced by another mineral). Serpentine, which is the most common alteration product of olivine in ultramafic rocks, often is accompanied by magnesite. Iddingsite and bowlingite are variable in composition, and, even though they appear optically homogeneous, each actually consists of an intimate mixture of several distinct minerals. X−ray diffraction analyses of iddingsite show that the mineral goethite (FeO×OH) is an important component. Also included with the mixture may be hematite (Fe2O3), as well as a silicate phase related to vermiculite or montmorillonite. Iddingsite develops almost exclusively from the olivines of extrusive or shallow intrusive rocks and practically never from the olivines of plutonic and metamorphic rocks. The process of "iddingsitation" of olivine may set in even before the complete consolidation of the lava or the hypabyssal magma. This is evident from the observation of rock textures in which shells of iddingsite surrounding a core of olivine are, in turn, surrounded by more unaltered olivine. The mechanical weathering of olivine−rich rocks leads to the release of olivine particles that, in the absence of much chemical weathering, may accumulate to produce green or greenish black sands. Conspicuous examples of such sands occur on the beaches of the islands of Oahu and Hawaii, particularly at Diamond Head (Oahu) and South Point (Hawaii). Alluvial sands rich in olivine are also known from Navajo county of Arizona and from New Mexico in the United States; these sands provide the clear olivine (peridot) used in jewelry. (C.E.T./W.B.Si.)

MINERAL

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