

MINERALS

ROCK AND STONE: PIGMENTS, ABRASIVES, AND GEMSTONES

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The outer crust of earth has provided the solid foundation for the evolution of human beings, who are the prime focus of interest and concern to archaeology. The main components of this crust are *minerals* and *rocks*, some *consolidated* and others occurring as *sediments*, nonconsolidated deposits, created by weathering processes from the minerals and rocks. All these minerals, rocks, and sediments, as well as everything else in the universe, are made up from just over 100 *chemical elements* listed in Appendix I. Most of the elements in the crust of the earth occur in extremely low relative amounts, and only a few, listed in Table 1, make up almost 99% of its total bulk (Bloom 1969).

1.1. THE CHEMICAL ELEMENTS

There are two basic types of *elements*: *metals* and *nonmetals*. The *metals*, such as copper, gold, and iron (see Chapter 5), make up more than three-quarters of the total number of elements; *nonmetals*, such as, for example, chlorine, sulfur and carbon, make up much of the rest. Other elements, however, known as the *metalloids* or *semimetals*, have properties intermediary between the metals and the nonmetals (see Appendix I). Only a few elements, such as the metals gold and copper and the nonmetal sulfur, which are known as the *native elements*, occur in nature uncombined. Most elements occur naturally combined with others, forming *compounds*. It is from these compounds, which occur in the crust of the earth as minerals, rocks, or sediments, that humans extract most of the elements that they require (Klein 2000).

TABLE 1 Chemical Elements in the Earth's Crust

Element	Abundance (wt%)
Oxygen	47.0
Silicon	28.0
Aluminum	7.5
Iron	5.0
Calcium	3.5
Sodium	2.8
Magnesium	2.6
Potassium	2.1
84 others including, in descending order of abundance, titanium, hydrogen, phosphorus, barium, and strontium.	1.5

TEXTBOX**1****MATTER AND MATERIALS; ELEMENTS AND SUBSTANCES**

Everything on earth, as in the whole of the universe, is made up of matter, that is, anything solid, liquid, or gaseous that has mass and occupies space. Depending on their composition and internal structure, *materials*, as specific types of matter are known, can be of one of two fundamentally different types: either *homogeneous* or *heterogeneous*. *Homogeneous materials*, for example, water, sand, salt, and glass, have uniform, unvarying composition and properties throughout, while the composition and properties of *heterogeneous materials*, for example, granite and pottery, vary from one part to another. Heterogeneous materials are mixtures of two or more homogeneous substances (Henderson 2000).

Homogeneous Materials; Substances and Solutions

The homogeneous materials can also be classified into two distinct groups: *substances* and *solutions*. The *substances*, for example, gold, graphite, common salt, and limestone, have a definite and characteristic chemical composition and physical properties. *Solutions*, for example, the water of the seas and oceans, are mixtures, in any weight proportion, of two or more substances dispersed within each other and forming a single blend of unvarying constitution, although of no definite composition. Also the substances may be of one of two types: either *elements* or *compounds*.

Elements The chemical *elements*, or simply elements, such as gold, oxygen, and the 110 others listed in Appendix I, cannot be separated into other, simpler substances by any means. There are 112 known chemical elements

(see Appendix I), only 92 of which occur on the earth and are the constituents of all the planet's matter. The other 26, which are unstable and undergo radioactive decay (see Textbox 13), have long ago disappeared. Some of the 92 elements, such as copper, silver, and carbon, are familiar to everybody, while others, such as cerium and dysprosium, are so rare that few people are likely to hear of them, let alone encounter them. Many of the lesser-known elements are, however, important in archaeological studies. The relative amounts in which they occur in nature vary from one location to another, and this variation can be of use to characterize many natural materials and to determine their provenance, that is, their place of origin (see text below).

Compounds *Compounds* consist of two or more elements combined in singular and characteristic weight proportions; the properties of compounds differ from those of their component elements and from other elements or compounds (see Textbox 4). Their composition is independent of their origin or how they were formed, and their properties are unique and characteristic of that compound. All compounds can be decomposed, by chemical means, to yield their elemental constituents. This means that any particular compound, regardless of its origin or location, is always composed of the same elements combined in a unique weight proportion. For example, *common salt* (whose chemical name is *sodium chloride*) is a compound made up of two elements: (1) sodium, which makes up 39.39% of its total weight, and (2) chlorine, which makes up the remaining 60.61%. Additional examples of compounds are *quartz*, a constituent of common sand and limestone. *Quartz* consists of silicon dioxide, a compound formed by the combination of two elements, silicon and oxygen; silicon makes up 46.66% of the total weight of any sample of silicon dioxide, and oxygen makes up the remaining 53.33%. *Limestone* is composed of calcium carbonate, a compound made up of three elements – calcium, carbon, and oxygen; in the compound, calcium makes up 40% of the total weight; carbon, 12%; and oxygen, the remaining 48%.

Compounds are customarily classified as *inorganic* and *organic compounds*. The term *inorganic* refers (with only very few exceptions) to compounds whose composition does not include the element carbon; they are made up of combinations of two or more of any of the 92 stable elements that constitute all matter, but excluding carbon. The *inorganic compounds* are, by far, the main components of most of the matter in the universe. Compounds that include carbon in their composition are, with few exceptions, known as *organic compounds*. In the organic compounds, carbon is combined mainly with one or more of the elements hydrogen, oxygen, and nitrogen and sometimes also with a few others, such as sulfur and a few metals (see Textbox 51). The organic compounds are the main constituents of all living matter. The division between inorganic and organic

compounds, which has become blurred in recent years, arose from an old misconception, held since the early days of chemical studies, when it was believed that a vital organic force was necessary for the creation of organic compounds.

Solutions *Solutions* are homogeneous forms of matter that may be composed of a solid dissolved in a liquid – such as common salt dissolved in water; a gas dissolved in a liquid – for example, oxygen dissolved in water; or a solid dissolved in another – for example, carbon dissolved in iron in some alloys of this metal. The composition and properties of each solution are determined by the nature of the components and the relative amount of each component in the solution (see Table 2).

Heterogeneous Materials

Heterogeneous materials are made up of more or less coarse mixtures of the grains of two or more homogeneous substances. Many rocks, for example, are mixtures of fragments of two or more different minerals (see discussion below). *Pottery*, another heterogeneous material, consists of a burnt mixture of clay and one or more type of particles of such varied materials as homogeneous sand and limestone or heterogeneous dung and

TABLE 2 Homogeneous and Heterogeneous Matter

Homogeneous matter	Heterogeneous matter
<p>Elements</p> <p>92 chemical elements, including metals such as copper, gold, iron, lead, silver, and nonmetals such as, carbon, sulfur, and phosphorus</p> <p>Compounds</p> <p>Inorganic compounds (water, salt, soda)</p> <p>Minerals (cassiterite (tin oxide), galena (lead sulfide)</p> <p>Monomineral rocks [(calcite (calcium carbonate), silica sand (silicon dioxide)]</p> <p>Organic compounds (sugars, oils, fats.</p> <p>Solutions</p> <p>Seawater (salts in water)</p> <p>Gold–copper alloys (gold in copper)</p> <p>Solder (alloy of lead and tin)</p> <p>Vinegar (acetic acid in water)</p> <p>Wine (ethyl alcohol in water)</p>	<p>Most rocks (two or more mixed minerals)</p> <p>Bloomery iron (a mixture of iron, carbon and slag)</p> <p>Cast iron (a mixture of iron and carbon)</p> <p>Lime cement (lime and sand)</p> <p>Pottery (fired clay and mineral or organic grains)</p> <p>Soil (clay, sand, and organic matter)</p> <p>Wood (cellulose, hemicellulose, and lignin)</p> <p>Bone (organic and bioinorganic matter)</p> <p>Milk (fat droplets in a water solution)</p>

grass (see Chapter 7). Other heterogeneous materials are *wood* and *bone*, both examples of living forms of heterogeneous matter. *Wood* is a mixture of three organic substances – namely, cellulose, hemicellulose, and lignin (see Chapter 9); *bone* is an interspersed mixture of *collagen*, an organic substance, and *carbonated hydroxyapatite*, a bioinorganic substance (see Chapter 15). Heterogeneous materials can be separated into their homogeneous components using physical techniques (see Fig. 1).

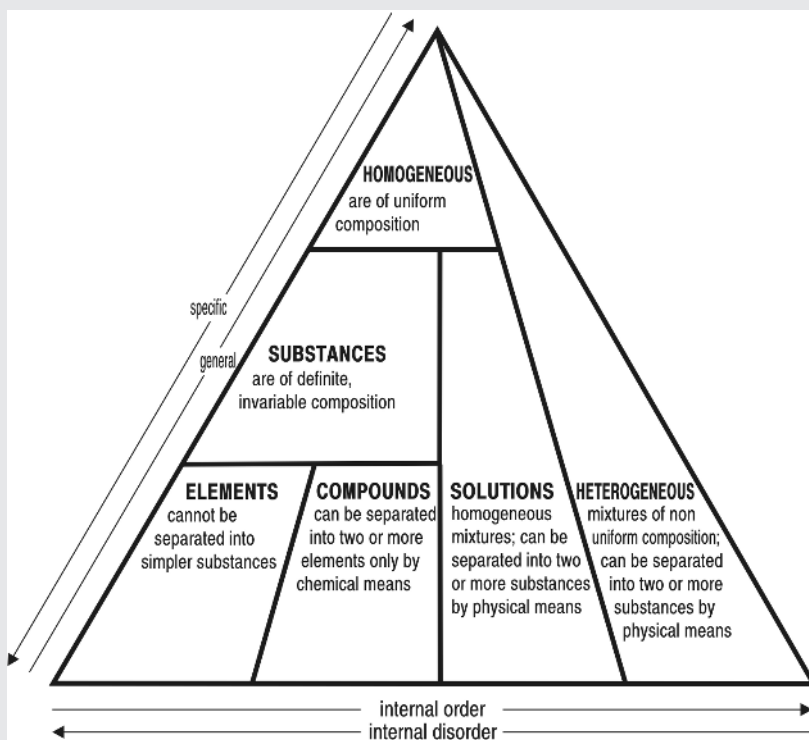


FIGURE 1 Classification of matter. Matter, everything that has mass and takes up space, is made up of very small particles known as “atoms.” Particular kinds of matter that have uniform composition and properties throughout are known as “substances.” Substances may occur alone (separate from) or mixed with other substances. Gold and lime, for example, often occur separate from others in nature: gold as gold nuggets and lime as limestone rocks. Mixtures of two or more substances may be homogeneous or heterogeneous; seawater, wine, fruitjuice, and some alloys are homogeneous mixtures, with no visible separation between their components. Seawater, for example, is a solution (a homogeneous mixture) of various salts in water. Granite, brick, pottery, cement, and wood are heterogeneous mixtures of various substances.

1.2. MINERALS AND MINERALOIDS

Minerals are the most abundant type of solid matter on the crust of the earth; they are homogeneous materials that have a definite composition and an orderly internal structure. Minerals make up most of the bulk of rocks, the comminuted particles of sediments, and the greater part of most soils. Over 3000 minerals have been identified, and new ones are discovered each year. Only a few hundred, however, are common; most of the others, such as, for example, the *precious stones*, are difficult to find (Ernst 1969). Table 3 lists common minerals and mineraloids. Many schemes have been devised for classifying the minerals. In the scheme presented in Table 4, minerals are arranged in classes according to their increasing compositional chemical complexity.

TEXTBOX 2

THE STRUCTURE OF MATTER: ATOMS AND MOLECULES

Atoms All matter is made up of very small units called *atoms*, the smallest material units having recognizable, characteristic properties, identical to those of the bulk. Atoms, which are the building blocks of the universe, can exist either alone or in combination with others. The *chemical elements*, for example, are forms of matter made up of identical atoms, each atom of an element exhibiting the same characteristic properties. When extremely strong forces are applied to matter, however, atoms may break up into smaller parts; this shows that the atoms are not single physical units, but composites having a complex inner structure of their own. Studying the processes by which atoms break up made it possible, during the early twentieth century, to understand the inner structure of atoms (Asimov 2002; Pullman 2001).

Atoms are made up of varying numbers of extremely small particles, generally referred to as *subatomic particles*, whose size is too small to see or measure even under large magnification. *Protons*, *neutrons*, and *electrons* are examples of atomic particles. The *protons*, which bear a positive electric charge, and the *neutrons*, which are electrically neutral, are concentrated in the atomic *nucleus*, located in the center of the atom, as shown in Figure 2. Since the protons have a positive electric charge, the atomic nuclei also bear a positive electric charge. *Electrons*, which are much smaller than the protons and neutrons, have a negative electric charge and move rapidly in pairs around the atomic nucleus. All the atoms of any one *element* have the same number of protons and electrons and are,

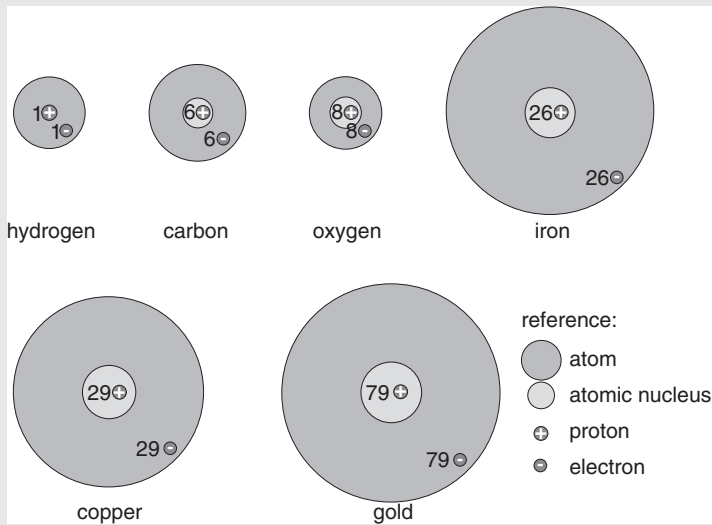


FIGURE 2 Elements and atoms. Matter that is made up of only one type of atom, and cannot be separated into simpler substances, is called an “element.” Hydrogen, carbon, oxygen, iron, copper, and gold, for example, are elements. All matter on earth is composed of relatively few (only 92) different elements. The atoms that constitute any element are identical to each other but different from those of other elements. The atoms of all the elements, however, are built from basic particles known as “subatomic” or “elementary” particles, namely, protons, neutrons, and electrons. Most of the mass of each atom resides in the neutrons and protons, which occupy the central region of the atom known as the “atomic nucleus.” The neutrons have no electrical charge and are, therefore, electrically neutral; the protons have positive electrical charges and the electrons, which surround the nucleus, have a negative electric charge equivalent to the positive charge of the proton. The figure shows diagrammatic representations of the atoms of several elements, including their nuclei and the number of protons and electrons in each atom. Atoms may combine with other atoms to form “molecules,” and any form of matter made up of only one type of molecule is known as a “compound.”

therefore, electrically balanced. Atoms of different elements, however, have different numbers of protons and electrons (Romer 1982; Asimov 1974).

Molecules Atoms of the same element or of different elements combine with each other into more complicated systems called *molecules*; *molecules* are the smallest units of chemical compounds, the basic components of the countless inorganic and organic compounds. A few molecules, such as, those of the chemical elements hydrogen, oxygen, and nitrogen, are com-

TABLE 3 Composition, Properties, and Ancients Uses of Common Minerals and Mineraloids

Common name	Physical properties					Main uses
	Composition	Color	Density (g/cm ³)	Hardness (Mohs scale)	Structure	
<i>Minerals</i>						
Alabaster	Calcium sulfate	Various colors	2.3	1.8	Crystalline	Lapidary
Alabaster (oriental)	Calcium carbonate	Various colors	2.5	2.8	Crystalline	Lapidary
Azurite	Hydrous copper carbonate	Blue	3.8	3.8	Crystalline	Ornamental stone, gemstone, blue pigment, building stone, making lime
Calcite (limestone, marble)	Calcium carbonate	White	2.7	3.0	Crystalline	Making glass
Corundum	Aluminum oxide	White	4.0	9	Crystalline	Abrasive
Diamond	Carbon	Colorless	3.5	10	Crystalline	Gemstone, abrasive, flux, and lapidary
Fluorite	Calcium fluoride	White	3.2	4	Crystalline	
Galena	Lead sulfide	Gray	7.5	2.5	Crystalline	Lead ore
Granite	Mixture of mica, quartz and feldspar	Various	2.7	6–7	Crystalline mixture	Lapidary, paving, building

Gypsum	Hydrated calcium sulfate	White	0.3	2	Crystalline	Building stone, making plaster of Paris
Common salt	Sodium chloride	White	2.2	2.5	Crystalline	Food products
Haematite	Iron oxide	Red	5.2	6	Crystalline	Iron ore, abrasive, red pigment, gemstone copper ore, green pigment
Malachite	Basic carbonate of copper	Green	3.6	3.6	Crystalline	Gemstone
Pyrite	Iron sulfide	Gold	5	6.5	Crystalline	Iron ore gemstone, making lithic artifacts
Quartz (flint, sand, etc.)	Silica	Colorless	2.7	7	Crystalline	Building material, making glass, gemstone
Turquoise	Hydrated copper aluminum phosphate	Blue	2.7	5.5	Crystalline	Gemstone
<i>Mineraloids</i>						
Amber	Fossil resin	Yellow to red	1.1	5	None	Gemstone, ornamentation
Opal	Hydrated silica	Varies	2	6	None	Gemstone
Obsidian	Natural glass	Black, brown	2.5	5.3	None	Making lithic artifacts

posed of two identical atoms bonded to each other. Most molecules however, such as those that make up all the inorganic and organic compounds, are composed of two or more different elements. The smallest molecules such as those of *common salt*, are made up of only two different elements (sodium and chlorine, in the case of salt); the largest, such as the molecules of the biological compounds *cellulose* and *DNA*, are made up of millions of atoms (Fine 1980; Fano and Fano 1973). Cohesive forces, known as *chemical bonds*, which arise from the sharing of electrons between atoms, hold the atoms together in the molecules (see Fig. 3).

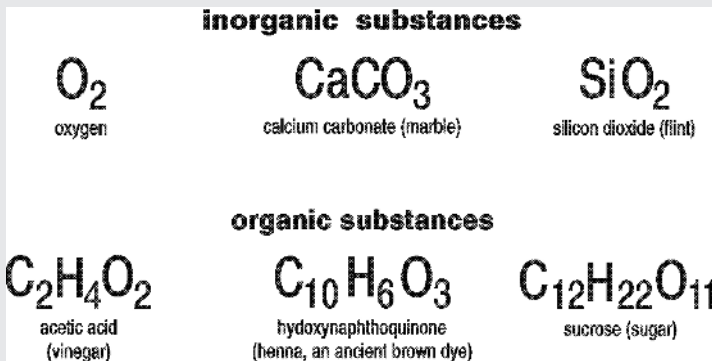


FIGURE 3 Molecules, compounds, and formulas. The atoms of the elements may combine with each other in an infinite number of ways to form molecules, and matter made up of only one type of molecules is known as a *compound*. The molecules are more or less complicated atomic structures that make up compounds, the main constituents of most matter on earth. Calcium carbonate, silicon dioxide, and sucrose, for example, are the compounds that make up marble, flint, and sugar, respectively. The molecules of calcium carbonate (lime), for example, are composed of atoms carbon, oxygen, and calcium; those of silicon dioxide (flint) are composed of silicon and oxygen, and the molecules of sucrose (a sugar) are composed of carbon, hydrogen, and oxygen. Within each molecule the atoms are linked to each other by electrical forces usually called “chemical bonds.” The exact composition of the molecules and therefore of substances is expressed by “chemical formulas,” a form of notation that conveys information on the types of atoms and their relative weight proportions in any specific substance. In the formulas, the chemical symbols of the elements indicate the types of atoms in the molecule and numerical subscripts show the relative number of each type of atom in the molecule. The chemical name and the formulas of well-known substances are illustrated.

TABLE 4 Chemical Classification of Minerals

Class	Compositional characteristic	Examples
Native elements	Single element	Native metals, native nonmetals
Oxides	Metal ion(s) + oxygen ion	Haematite (composed of iron oxide), a red pigment and an iron ore Corundum (composed of aluminum oxide), an abrasive silica (composed of silicon dioxide), common sand
Sulfides	Metal ion(s) + sulfur ion	Galena (composed of lead sulfide), a metal ore, from which lead and also silver (which occurs in galena as an impurity, are extracted Pyrite (composed of iron sulfide), an iron ore
Halides	Metal ion(s) + halogen ion	Common salt (sodium chloride), a component of animal diets Fluorite (calcium fluoride), a lapidary material and flux
Carbonates	Metal ion(s) + carbonate ion	Calcite (calcium carbonate), used for making lime, a building material Marble (calcium carbonate), building and lapidary stone
Sulfates	Metal ion(s) + sulfate ion(s)	Gypsum (calcium sulfate), raw material for making plaster of Paris Alabaster (calcium sulfate or calcium carbonate), a lapidary material
Silicates	Metal ion(s) + silicate ion	Granite (a metal silicate), used mostly for building

The (compositionally) simplest mineral class comprises the native elements, that is, those elements, either metals or nonmetals that occur naturally in the *native state*, uncombined with others. Native gold, silver, and copper, for example, are metals that naturally occur in a ductile and malleable condition, while carbon – in the form of either graphite or diamond – and sulfur are examples of nonmetallic native elements. Next in compositional complexity are the *binary minerals* composed of two elements: a metal or nonmetallic element combined with oxygen in the *oxides*, with a halogen – either fluorine, chlorine bromine, or iodine – in the *halides*, or sulfur, in the *sulfides*. The oxide minerals, for example, are solids that occur either in a somewhat hard, dense, and compact form in mineral ores and in rocks, or as relatively soft, unconsolidated sediments that melt at moderate to

high temperatures. Most of the sulfide minerals are opaque, or nearly opaque, and have distinctive colors and colored streaks. More *complex minerals* are composed of three or more elements, such as the *carbonates* and *silicates*. The *carbonates* are easily identified because, when an acid is dropped on them, they effervesce, releasing carbon dioxide. The *silicates*, which have the most complex chemical composition among the minerals, are by far the most common minerals, making up about 25% of the known minerals and almost 40% of the most common ones in the outer crust of the earth.

TEXTBOX 3

THE STATES OF MATTER

All matter exists in three states familiar to everybody: the *solid*, *liquid*, and *gaseous* states. The actual state in which any particular type of matter occurs is determined by the amount of energy of the constituent atoms or molecules. The atoms or molecules of solid matter, such as, for example, minerals, rocks, ceramic materials, or metals, have little energy, so little that they cannot flow. Moreover, the atoms or molecules that make up solids are held tightly together in fixed positions by strong interatomic and/or intermolecular forces. Solid matter occupies, therefore, a fixed volume and retains its shape wherever it is located. When supplied with enough energy, however, most solids melt and become *liquids*. The atoms or molecules in *liquid* matter, such as water or oil, have sufficient energy to flow, but insufficient to rise out of a container. Liquids have, therefore, a fixed volume but not a fixed shape; they acquire the shape of the container in which they are placed. If supplied with enough energy, liquids boil and become *gases*. The forces that hold together the atoms or molecules of *gases*, such as air, carbon dioxide, or water vapor, are very weak; gases are therefore very fluid, much more fluid than liquids; they retain neither a shape nor a volume and may rise out of a container.

Changes of State The amount of energy in a material, which determines whether it is in the solid, liquid, or gaseous state (see Figs. 4 and 5), depends on its composition, temperature, and surrounding pressure. Different materials change from one state to another at widely different temperatures, although each substance (element or compound) does so at a

specific and characteristic temperature and pressure. When iron, a solid at ambient temperature and pressure, is heated to a high temperature – namely 1538°C – it melts, turning into a liquid; and at 2861°C it boils, changing from a liquid to a gas. *Water*, on the other hand, the most abundant substance on the surface of the earth, is solid only at very low temperatures: ice (solid water) melts at 0°C and boils at 100°C. Because the temperature range of the liquid state is very narrow (only 100 degrees), water exists naturally on the surface of the planet in all three states, as ice, liquid water, and a gas (water vapor).

The melting points of mixtures and solutions depend on the nature and the relative amount of each component of the solution. They are, however, lower than those of the separate components. *Solder*, for example, an alloy of tin and lead, melts at 183°C, a much lower temperature than either of its components: tin melts at 231°C and lead, at 328°C.

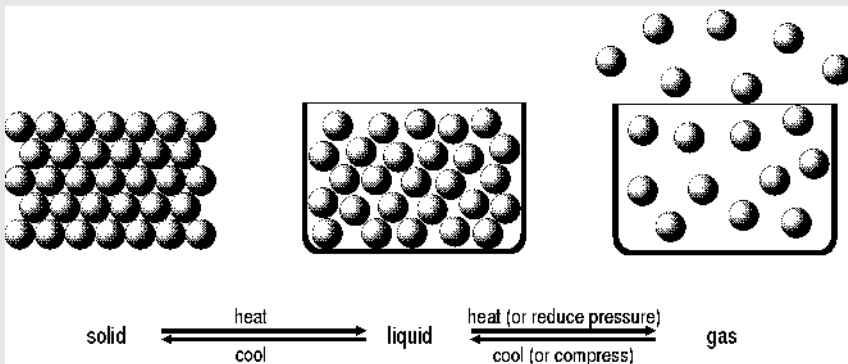
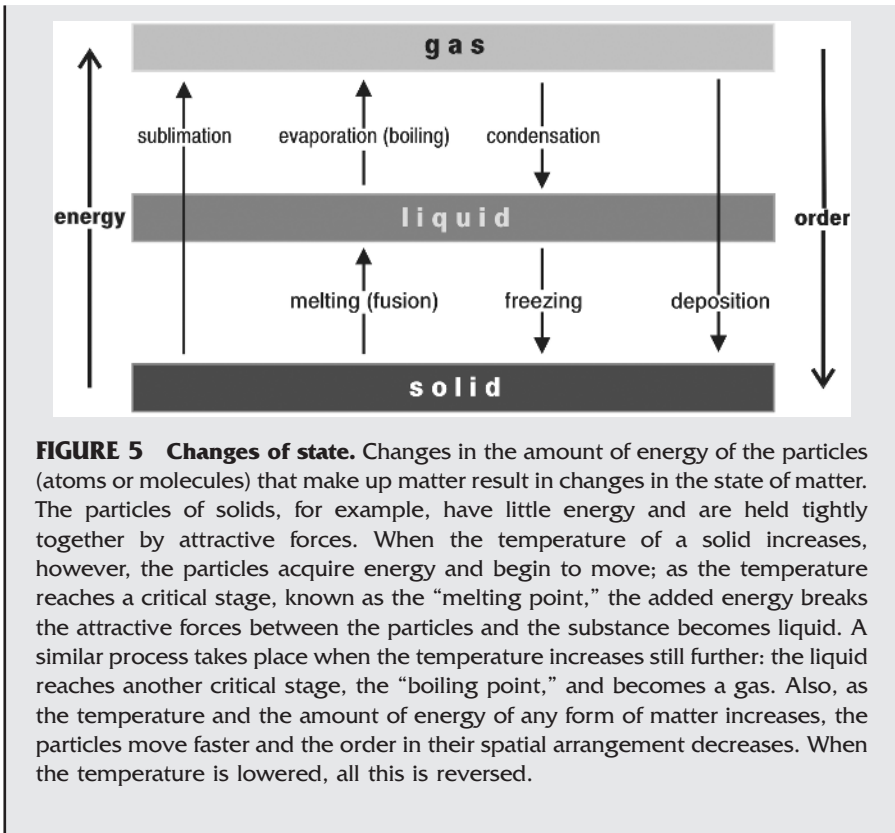


FIGURE 4 The states of matter. All matter – whether solid, liquid, or gaseous – is made up of atoms or molecules. The amount of energy of the atoms or molecules differs in each one the three states. In solids they have little energy; are tightly packed (usually in a regular pattern) and retain definite shapes. In liquids they have more energy than in solids, are closely packed together, but are not regularly arranged, sliding past each other; consequently, liquids keep no regular shape and acquire the shape of their container. The atoms or molecules of gases have much energy, move rapidly, are well separated from each other, and retain neither a regular arrangement nor a definite shape.



Any two samples of a particular mineral, whatever their source or place of origin, have the same basic composition and characteristic crystal structure; moreover, no two different minerals have identical chemical composition and crystal structure (see Textboxes 8 and 21). *Quartz*, for example, is a common and abundant mineral composed of *silicon dioxide*, a compound that occurs naturally not only as quartz but also in other crystal structures, known as *polymorphs* (polymorphs are minerals that have the same chemical composition but different crystal structure), some of which, listed in Table 23, have been used for a variety of purposes. The *crystal structure*, which is essential for the characterization of solid materials, is just one of a wide range of *physical properties*, that is, properties not involving chemical differences, which provide convenient criteria for characterizing and identifying solids.

TEXTBOX 4**THE PROPERTIES OF MATTER**

All substances – elements as well as compounds – have characteristic and distinctive *chemical* and *physical properties* (see Table 5). The *chemical properties* are related to the changes in composition that substances undergo when interacting with one another. A chemical property of solid iron, a metal, for example, is that it interacts at ambient temperature with atmospheric oxygen, forming iron oxide, a dark brown material commonly known as *rust*. Copper, another metal, interacts at ambient temperature not only with oxygen but also with atmospheric moisture and carbon dioxide, forming copper carbonate, a green substance; copper carbonate, which covers copper surfaces exposed to the environment, often forms, on its outer surface, a layer of green “patina” on antique copper objects. Whether a substance reacts (interacts) or does not react with others is also a chemical property. A chemical property of gold, for example, is that it does not react with the components of the atmosphere or the soil or, for that matter, with practically any element or compound. Because of its low chemical reactivity, gold is known as a *noble metal*. Another noble metal is platinum.

TABLE 5 Properties of Substances

Physical properties	Color, refractive index, ductility, hardness, malleability, melting point, boiling point, density, thermal conductivity
Chemical properties	Composition; reactivity with other substances; stability to heat, radiation, and electricity

The *physical properties* of substances do not involve chemical changes. *Color* (see Textbox 17) and *crystal structure* (see Textbox 21), for example, are physical properties that are characteristic of a substance that serve to identify most substances. Other physical properties, such as *density*, *hardness* (see Table 3), *refractive index* (see Table 19), and *heat capacity* (see Table 101), are also useful for characterizing and identifying substances as well as distinguishing between different substances.

In addition to the minerals, there are also some rock-forming homogeneous materials that have neither the definite chemical composition nor the distinctive crystal structure characteristic of minerals. Such materials cannot, therefore, be considered as minerals and are known as *mineraloids*. *Obsidian*, for example, a natural material that has been widely used since prehistoric times for making lithic tools and decorative objects, is a mineraloid. Obsidian has neither a definite chemical composition nor a characteristic crystal structure and is not, therefore, a mineral. *Copal* and *amber* are other mineraloids that since antiquity have been treasured as semiprecious *gemstones*.

TEXTBOX 5

ELECTROMAGNETIC RADIATION; WAVES

Electromagnetic radiation (EMR) is the generic term used to refer to all forms of energy that, in the form of waves, travel through space and matter at very high velocity. *Visible light*, to which the eyes of humans and animals are sensitive, and *radio and television waves*, which provide much of the electronic information available today, are the most familiar forms of electromagnetic radiation. Less familiar, but no less important, forms of electromagnetic radiation include *infrared* radiation (also known as *heat waves*), *ultraviolet light*, *X-rays*, and *gamma rays* (see Textbox 13).

Waves

A *wave* is a form of movement, an oscillatory disturbance characterized by repetitive patterns in fixed time intervals, that propagates through space or matter without displacing mass, but energy (see Fig. 6). Ocean waves, sound waves, and electromagnetic waves are common examples of waves. There are two main types of waves: *longitudinal* and *transversal* waves. When the oscillation takes place along their axis of propagation, the waves are known as *longitudinal waves*; when the oscillation occurs across their axis of propagation, the waves are known as *transverse waves*. Sound waves are longitudinal. Water waves, in the seas and oceans, and the waves sometimes seen on the strings of musical instruments are transverse waves. Electromagnetic waves are also transverse waves.

All types of waves, whether longitudinal or transverse, can be accurately described by their *wavelength* and *frequency* values (see Fig. 6), which are mathematically related to each other by the expression $v\lambda = c$, where the Greek letter λ (lambda) is the wavelength, the Greek letter ν (nu) is the *frequency* of the wave, and c is the *velocity* of the wave.

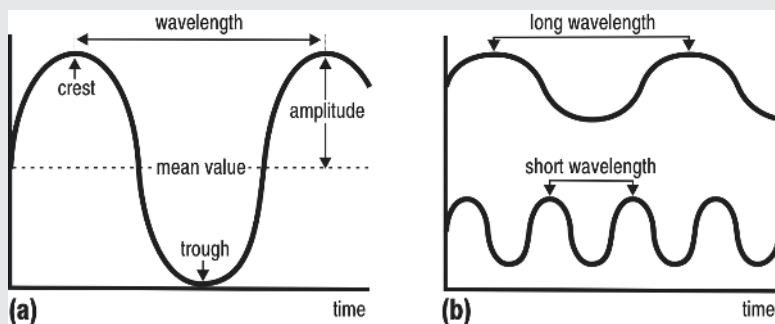


FIGURE 6 Waves. All types of waves are characterized by two features: amplitude and wavelength (or frequency). The amplitude, defined as half the linear distance between a crest and a trough (a), is a measure of the maximum displacement of a wave. The wavelength is the distance on a straight line along a wave, from one crest (or trough) to the next (a). The frequency is the number of times that a repeated event occurs per unit time; the shorter the wavelength of a wave, the higher is its frequency (b).

Electromagnetic Waves *Electromagnetic waves* are created by moving electric charges. When an electric charge moves, it creates a *magnetic field*. If an electric charge *oscillates* (moves back and forth or up and down), its electric and magnetic fields change together, creating an electromagnetic wave. Different forms of electromagnetic radiation can be differentiated by their wavelengths, as listed in Table 6 and illustrated in Figure 7 (Bekefi and Barrett 1987). After inception, electromagnetic waves propagate through empty space (vacuum) or through matter, without displacing mass but displacing energy.

In a *vacuum* (empty space), all forms of electromagnetic radiation propagate at a velocity of 300,000km per second, when propagating through air, water, or any kind of matter, they interact with the matter and their velocity is reduced. Differences in the manner of interaction between different forms of radiation and different types of matter generally reveal information on the nature and the constituents of matter.

The field of science that studies the interaction of electromagnetic radiation with matter is known as *spectroscopy*. Spectroscopic studies on the wavelength, the intensity of the radiation absorbed, emitted, or scattered by a sample, or how the intensity of the radiation changes as a function of its energy and wavelength, provide accurate tools for studying the composition and structure of many materials (Davies and Creaser 1991; Creaser and Davies 1988).

TABLE 6 Spectrum of Electromagnetic Radiation

Radiation	Typical sources	Wavelength (cm)	Frequency (Hz) ^a	Energy (eV) ^b
Gamma rays	Radioactive nuclei	below 10^{-9}	above 3×10^{16}	above 10^5
X-rays	Atoms	10^{-7} – 10^{-9}	3×10^{17} – 3×10^{19}	10^3 – 10^5
Ultraviolet	Atoms	4×10^{-5} – 10^{-7}	7.5×10^{14} – 3×10^{17}	3 – 10^3
Visible	Hot bodies	7×10^{-5} – 4×10^{-5}	4.3×10^{14} – 7.5×10^{14}	2 – 3
Infrared	Hot molecules	10^{-2} – 7×10^{-5}	3×10^{12} – 4.3×10^{14}	0.01 – 2
Microwaves	Electronic devices	10 – 10^{-2}	3×10^9 – 3×10^{12}	10 – 0.01
Radio	Communication	above 10	below 3×10^9	below 0.001

^a Hz = Hertz, unit of frequency – the number of times a wave oscillates per unit time – measured in cycles per second.

^b eV = electron volt, unit of energy equal to the work done by an electron accelerated through a potential difference of 1 volt.

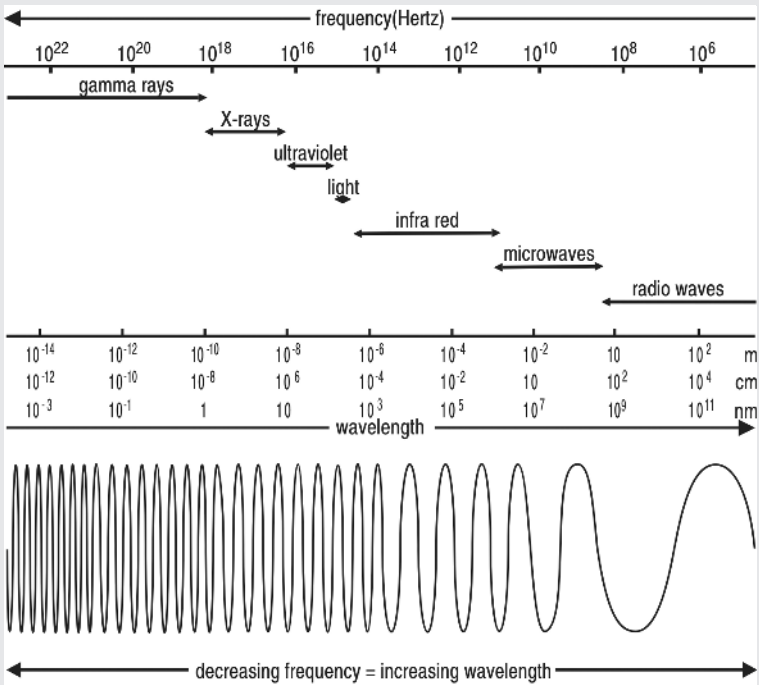


FIGURE 7 Electromagnetic radiation and the electromagnetic spectrum. The full range of electromagnetic radiation, extending from extremely long to very short wavelengths, is known as the “electromagnetic spectrum”; it includes the following well-defined regions: gamma rays, emitted by some radioactive isotopes or generated during nuclear reactions; X-rays, used for medical (radiography and the destruction of deceased cells), technological and scientific applications; ultraviolet radiation, which, from the part of the spectrum known as “ultraviolet A (UV-A),” enhances plant life and from another other part of the spectrum (UV-B) causes premature skin aging and skin diseases; visible light, which the human eye can perceive as colors ranging from violet (shorter wavelengths) to red (longer wavelengths); infrared radiation, associated with heat energy; microwaves, used in most forms of electronic communication; and long and extremely long wavelength radio radiation, also used in communication. Electromagnetic radiation with wavelengths shorter than ultraviolet rays has enough energy to cause atoms to lose electrons and become ions and is therefore known as “ionizing radiation;” long wavelength radiation, longer than those of ultraviolet rays, is “nonionizing.”

Minerals, mineraloids, and metals are advantageous for specific applications because of one or more of their physical properties. The *softness* of soapstone, for example, makes this mineral useful for shaping and carving objects. The very opposite, the extremely high *hardness* of diamond and emerald, makes them resistant to wear and scratching and, therefore, valued as gemstones. It is also because of its extreme hardness that powdered diamond is the best abrasive material for rubbing, grinding, and polishing solids. Other extremely useful physical properties of materials are color and the refractive index (see Textbox 22). The *color* of many materials, such as the characteristic red of *minium* (a lead-containing mineral) and the green of *malachite* (a copper-containing mineral) makes them useful as pigment, while the high *refractive index* of diamond and emerald makes these two rare minerals glitter and sparkle and, therefore, desirable and highly valued as gemstones often set into jewelry.

TEXTBOX 6

ATOMS AND MOLECULES; CHEMICAL NOMENCLATURE AND FORMULAS

Elements and Atoms

The *chemical elements*, the building blocks of all matter, are made up of identical atoms (see Textbox 2). Very few elements, however, occur on earth singly, uncombined with others. Most are chemically combined with other atoms, either identical or different. Examples of elements that may occur singly are the metals copper and gold and the nonmetal sulfur, which are often found in their *native* form in the crust of the earth. The gaseous elements *oxygen* and *nitrogen*, the main components of the earth's atmosphere, occur as molecules composed of two identical, combined atoms; each atom in a molecule of oxygen or nitrogen is combined to another atom of the same element.

Most elements, however, are naturally combined with one or more other elements, forming compounds. Water and calcium carbonate (also known as *calcite*, *limestone*, or *marble*) are examples of common compounds formed by the combination of two or more elements; in water, one atom of oxygen is combined with two of hydrogen; and in calcium carbonate, one atom of carbon is combined with three of oxygen and one of calcium.

Molecules

Molecules, the smallest units of matter that have the properties of a substance, are made up of two or more atoms. The molecules of some chemical elements, such as oxygen and nitrogen, mentioned above, for example, are made up of two identical atoms. The molecules of compounds, that consist of two or more combined elements are made up two or more atoms of different elements bonded together (see Textbox 2).

The chemical and physical properties of single, uncombined atoms and those of the same atoms bonded (chemically linked) to other atoms in the molecules are basically different: single atoms are usually electrically uncharged, whereas when they are part of molecules, they bear a positive or negative electric charge of some measure. Atoms bearing an electric charge are known as *ions*. Positively charged ions, formed when atoms lose electrons, are known as *cations*. Negatively charged ions, formed when atoms gain electrons, are known as *anions*. Most atoms of such metals as copper and iron easily lose electrons when reacting chemically, and form cations. When the atoms of nonmetallic elements react, on the other hand, they generally gain electrons, and form *negative* anions. The anions formed by chlorine, known as *chloride*, and by sulfur, known as *sulfide*, are examples of common anions. Some nonmetallic elements – for example, nitrogen, carbon, phosphorus, silicon, and sulfur – form *complex anions*, which are made up of atomic groups of two, three, or more atoms. The *nitrate* anion, which is made up of one atom of nitrogen and three atoms of oxygen; the *carbonate* anion, made up of one atom of carbon and three of oxygen, and the *sulfate* ion, made up of one atom of sulfur and four of oxygen, are common examples of complex anions.

A few general rules are helpful for understanding the electric charges acquired by single as well as complex ions:

- Metals and hydrogen (a nonmetal) form positively charged cations.
- Nonmetals generally form negatively charged anions.
- Some nonmetals form complex (polyatomic) anions, which consist of a group of three or more atoms bearing a negative charge.
- Cations combine with anions to form compounds known as *salts*; when dissolved in water, the salts form solutions that conduct electricity.
- Solutions of nonionic compounds in water do not conduct electricity.
- Nonmetals can also combine with other nonmetals to form nonionic compounds (most biological substances are nonionic).

Chemical Notation and Nomenclature

An internationally accepted *chemical notation* makes use of *symbols* to represent elements and compounds, and advises on naming chemical compounds. In this notation, the elements are represented by one or two letters, many of which are drawn from the elements' Latin or Greek names. The number of atoms of an element in a molecule is represented by a subscript written after the symbol; thus Au (the first two letters of *aurum*, the Latin name for gold) represents an atom of gold; Cu (the first two letters of *cuprum*, the Latin name for copper), an atom of copper; and C (the first letter of carbon), an atom of carbon; O represents an atom of oxygen and O₂, a molecule of oxygen. The symbols listed below provide examples of the presently accepted form of chemical notation:

Ag:	silver (<i>argentum</i>)
Au:	gold (<i>aurum</i>)
C:	carbon
Cu:	copper (<i>cuprum</i>)
Fe:	iron (<i>ferrum</i>)
Hg:	mercury (<i>hydrargyrium</i>)
K:	potassium (<i>kalium</i>)
N:	nitrogen
O:	oxygen
P:	phosphorus
Pb:	lead (<i>plumbum</i>)
S:	sulfur
Sb:	antimony (<i>stibium</i>)
Sn:	tin (<i>stannum</i>)
Zn:	zinc

The internationally accepted notation also establishes the method of expressing, with symbols, the composition of chemical compounds. These are expressed by chemical formulas consisting of the symbols of the component elements and numbers representing the relative amount of each elemental component in a molecule of a compound (Fox and Powell 2001). For any particular compound, the number of atoms of each element in a molecule of the compound is indicated by a subscript written after the symbol of the element; no subscript appears when there is only one atom of the element. Thus the formula of water, whose molecule consists of two atoms of hydrogen and one of oxygen, is H₂O, and that of carbon dioxide, whose molecule includes one atom of carbon and two of oxygen, is CO₂. The formula of glucose, C₆H₁₂O₆, means, therefore, that its molecule is composed of 6 atoms of carbon, 12 of hydrogen, and 6 of oxygen [since glucose belongs to the type of organic compounds known as the

carbohydrates, which are, by definition, composed of a carbon and water; the formula for glucose is sometimes also written as $C_6(H_2O)_6$].

The chemical name of compounds composed of only two elements usually ends with the suffix *ide*. The chemical name for water, for example, which is composed of two atoms of hydrogen and one of oxygen, and whose chemical formula is H_2O , is, therefore, *hydrogen oxide*. The chemical name for common table salt, composed of one atom of sodium and one of chlorine, and has the formula is $NaCl$, is *sodium chloride*. Pyrite, an iron ore composed of one atom of iron (*ferrum* in Latin) and one of sulfur, has the formula FeS , and its chemical name is *ferrous sulfide*.

The name of compounds whose molecules contain three or more elements, usually including oxygen, ends in the suffix *ate*. Thus the chemical name for *limestone*, whose chemical formula is $CaCO_3$, is *calcium carbonate*. That of green vitriol, also known as *copperas*, whose formula is $FeSO_4$, is iron sulfate. The names and formulas of some chemical compounds related to archaeological studies are listed in Table 7.

TABLE 7 Common Substances and Their Chemical Formulas

Elements		Compounds	
Name	Symbol	Name	Formula
		<i>Gas</i>	
Oxygen	O_2	Carbon dioxide	CO_2
Nitrogen	N_2	Sulfur dioxide (an air pollutant)	SO_2
		<i>Liquid</i>	
Mercury	Hg	Water	H_2O
		<i>Solid</i>	
Copper	Cu	Iron oxide (rust)	Fe_2O_3
Iron	Fe	Lead sulfide (a lead ore)	PbS
Gold	Au	Benzenamine (magenta, a dye)	$C_{20}H_{19}N_3$
Sulfur	S	Sodium chloride (common salt)	NaCl
Phosphorus	P	Sucrose (sugar)	$C_{12}H_{22}O_{11}$

Early humans learned to recognize and appreciate some specific properties of minerals and mineraloids and, accordingly, put them to use. The hardness and the *conchoidal fracture* of flint and obsidian, for example, were recognized already during paleolithic times, and it is because of these properties that these two materials were found useful for making lithic tools. *Hematite*, a red-brown-colored mineral (composed of iron oxide), has also been appreciated since ancient times. Hematite occurs in the crust of the earth in two different forms: one consolidated and relatively hard and another powdery and loose. The consolidated, hard, and brilliant variety has been valued as a semiprecious gemstone, while powdery hematite has long been and still is widely used as a pigment for the preparation of paints, as well as a mild abrasive, for smoothing and polishing the surface of solid objects. Moreover, since the discovery of the smelting of iron, hematite, in all its varieties, has been used as a source from which the metal iron is extracted (see Chapter 5). Hematite is also just one example of a wide range of minerals that have been and are still used as mineral ores, raw materials from which metals are extracted (see Chapter 5). Other minerals, such as *clays* and *sand*, have been and still are used for making artificial (synthetic), human-made materials: *clays* for making pottery and *sand* for making glass. Table 4 lists minerals and mineraloids that, because of some specific property, have been used for many millennia for some specific applications.

1.3. ROCK AND STONE

Rock is any consolidated, compact, hard or soft natural material consisting of one or more conglomerated minerals. The rocks that make up the crust of the earth consist of either single minerals or natural cohesive aggregations of grains of minerals held more or less firmly together into a solid mass. Many rocks are mixtures of two or more different minerals and are, therefore, heterogeneous materials, while some, composed of only one mineral, and therefore known as *monomineral rocks*, are homogeneous materials. Examples of the latter are *marble*, which consists entirely of calcite (composed of calcium carbonate), and *alabaster*, which consists of consolidated plaster of Paris (composed of calcium sulfate).

TEXTBOX 7**MINERAL- AND ROCK-FORMING PROCESSES – CRYSTALLIZATION AND PRECIPITATION**

Most natural solids, including minerals, are formed by one of two very different processes: *crystallization*, which takes place when a hot melt cools down slowly, or *precipitation*, which occurs mainly when a solid separates from a water solution.

Crystallization

When a hot melt cools down, the particles that make up the melt (that is to day, atoms, ions, or molecules) become rearranged, during the transition from the liquid to the solid state, into a regular, symmetric spatial arrangement, known as a *crystal structure*, which is regularly repeated throughout the bulk of the solid (see Textbox 21). Molten *magma*, for example, is a very hot, fluid mixture of liquid and gas formed deep below the crust of the earth. When magma emerges to the surface during volcanic eruptions (then known as *lava*), it cools down gradually. Depending on the chemical composition of the lava and the prevailing environmental conditions, and providing it cools down slowly, the atoms that make up lava become naturally grouped in orderly and symmetric patterns. As the melt finally solidifies, it is said to *crystallize*, the solid preserves the orderly and symmetric arrangement, known as the *crystal structure*, acquired while solidifying. The *crystal structure* of each substance is unique and characteristic, and provides a relatively easy way for characterizing minerals; the internal structure of several crystalline substances is shown in Figure 17.

When molten lava cools down rapidly, however, the orderly arrangement of the component particles into symmetric structures is curbed and the melt solidifies into an amorphous mass that lacks internal order. Such a substance is known as a *mineraloid*. Although mineraloids have a mineral appearance, they lack an internal orderly arrangement and are said to be *natural glasses* (see Textbox 27). *Obsidian*, widely used since prehistoric times for making tools and decorative objects, is a type of mineraloid. Another well-known mineraloid is *opal*, certain varieties of which have long been appreciated as gemstones (Middlemost 1985).

Precipitation

Precipitation, the other process by which minerals and rocks are formed, takes place from a solution. When solid particles separate out from a solution as the water evaporates, or as a consequence of cooling or of the

biological activity of aquatic plants and animals, they are said to *precipitate*. The extremely small particles that precipitate bond with one another, forming larger particles that sink and create unconsolidated accumulations known as *sediments*. In time, as more particles precipitate, layers of sediments are formed. If this process continues over periods of time lasting millions of years, more layers accumulate; the higher-lying layers press down and compact the lower ones, a process that ultimately results in the formation of *sedimentary rocks*. Limestone (composed of calcium carbonate) and gypsum (composed of calcium sulfate) are examples of sedimentary rocks formed as a result of precipitation processes (Collinson and Thompson 1989; Ehlers and Blatt 1982).

Recrystallization

Extremely high pressures, shearing stresses, and/or high temperatures, although not sufficiently high to cause melting, may affect the internal structure of minerals and rocks and transform them into *metamorphic rocks*. The transformation (into metamorphic rock), known as *recrystallization*, a process that is seldom accompanied by changes in composition, but takes place merely through the formation of new crystalline structures and new textures (Herz and Garrison 1998; Raymond 1995).

Mineral or rock that has been naturally or artificially broken, cut, or otherwise shaped to serve some human purpose is known as *stone*. For millions of years, long before the discovery of the metals, humans used stone for making tools; erecting houses and monuments; building roads, floors, and roofs; sculpting statuary; and carving ornaments. It is not surprising, therefore, that stone is one of the most frequently encountered materials in archaeological excavations and one of the most often studied (Waelkens et al. 1992; Shadmon 1996).

1.4. STUDY OF ARCHAEOLOGICAL STONE

The study of archaeological stone is based mainly on chemical, physical, geologic, and mineralogic investigation; this entails identifying the composition of the stone, characterizing its structure and other physical properties, and elucidating the changes that it may have undergone since it was created or last used (Jeffery and Hutchison 1981). Additional, more specific studies of stone, however, are often also conducted in the framework of *petrology*, the

science that deals with the origin, composition, and structure of rocks; and *petrography*, the classification and systematic description of rocks (Kempe and Harvey 1983). The main objective of analyzing archaeological stone, as well as most other archaeological materials, is usually to identify the rock unequivocally. This is not, however, the only objective, since the results of chemical analyses often also provide insights into any weathering processes that the stone may have undergone (see Textbox 45), as well as its provenance and chronology.

The Components of Materials. The composition of most materials – whether of natural origin, such as minerals, rocks, wood, and skin, or made by humans, as for example, pottery, glass and alloys – includes several kinds of components: *major*, *minor*, and *trace* elements (see Textbox 8).

TEXTBOX 8

COMPOSITION OF MATERIALS: MAJOR, MINOR, AND TRACE COMPONENTS

Substances prepared under carefully controlled conditions and using very pure chemicals, in a modern laboratory, for example, contain only the basic component elements, those that determine the actual composition and nature of the substances. Natural substances, whether of mineral or biological origin, and also most synthetic (human-made) substances contain, in addition to their main components, *impurities* foreign to their basic composition. Most impurities usually enter substances such as minerals, for example, in relatively small amounts, when the substances are created. Others, such as those in some rocks and the wood of trees, do so in the course of their existence. Once within a substance, impurities become an integral part of the host substance and impair the purity of the substance. Although they alter the actual composition of substances, impurities do not affect their basic properties.

Thus, three types of components can be distinguished in most substances, whether of natural origin or made by humans: *major*, *minor*, and *trace components* (see Table 8). The *major components*, also known as the *main* or *matrix components*, are those that determine the chemical nature and properties of a substance. The major components occur in the substance in high concentration, generally exceeding 1% of the total weight. In minerals and biological substances, for example, the major components are those that appear in the chemical formula that expresses their composition.

TABLE 8 Components of Most Natural Materials

Component	Relative concentration (%)
Major (matrix)	above 1
Minor	1.0 – 0.1
Trace	below 0.1 ^a

^aParts per million (ppm) or parts per billion (ppb).

In practically all natural and in most synthetic substances there are, mixed with the major components, impurities in minor and trace amounts. *Minor components* occur in concentrations below 1% and down to about 0.1% of the total weight of a sample of the substance. Many additional impurities, usually referred to as *trace components* or *trace elements*, occur in host substances at extremely low concentration, generally below 0.1%; their concentration is generally expressed either as parts per million (ppm) or parts per billion (ppb) (1 ppm is equivalent to a one gram in one ton; 1 ppb, to one gram in one million tons). Minor and trace impurities do not alter the basic composition, nor do they affect most of the properties of substances, but they may change, even drastically, some of their physical properties. Trace impurities in otherwise colorless minerals, for example, often make the minerals highly colored.

A colorless mineral known as *corundum* (composed of aluminum oxide) is colorless. A red variety of corundum known as *ruby*, a precious stone, owes its color to impurities of *chromium* within the crystal structure of corundum. Blue and violet varieties of corundum are classified as *sapphires*, the blue being the result of iron and titanium impurities, and the violet of vanadium impurities within the corundum crystal structure. Another colorless mineral is *beryl* (composed of beryllium aluminum silicate); but blue *aquamarine*, green *emerald*, and pink *morganite*, are precious varieties of beryl including different impurities: aquamarine includes iron, emerald chromium and vanadium, and morganite manganese.

Impurities and Provenance

The nature and the relative amounts of the impurities in many natural and in some synthetic materials, are often characteristic of the geographic area where the materials occur or were made. This is of particular interest in archaeological studies, since determining the nature and the relative amounts of impurities in many materials allows one to determine their *provenance* (Maniatis 2004; Guerra and Calligaro 2003).

In any specific material, the *major* or *matrix* components (those that define and characterize the material) are always the same, regardless of how and where the material was created or where it is located. The matrix components of most sand, for example, are the same everywhere on earth, since sand consists of *silicon dioxide*, a compound in which silicon is bonded to oxygen in a well-known weight ratio: one part of silicon to two parts of oxygen. Pure silicon dioxide, however, is a colorless substance, while most sand on the surface of the earth or on the bottom of seas and oceans is colored. Its color is due to *impurities*, elements foreign to silicon dioxide, the main component of sand, that penetrated the silicon dioxide matrix in relatively small amounts, as minor or trace elements, when the sand was created. Much sand, for example, is yellow or red, colors that are due to small amounts of iron oxide within the silicon dioxide matrix; the color of black sand, on the other hand, is caused by minor or trace amounts of manganese dioxide within the silicon dioxide. It should be mentioned here that iron and manganese oxides occur as impurities not only in sand but also in many other natural materials such as clays and soils and also endow these materials with their characteristic (mostly dark brown) color. Moreover, iron impurities in clay and sand cause the characteristic color of human-made pottery and glass: red-brown in pottery and green in glass. Like sand, most rocks contain impurities, which may vary in number, from only a few to several dozens, and in concentration, from as little as a few parts per billion to as much as 1%. It is through the investigation of the nature, relative abundance, and properties of many minor and particularly trace elements that the *provenance* and *chronology* of archaeological rock and stone, as well as of other archaeological materials, can be studied.

1.5. CHEMICAL ANALYSIS OF ARCHAEOLOGICAL MATERIALS

Sampling archaeological materials for analytical purposes may sometimes be the most difficult stage in an analytical procedure (Bellhouse 1980; Cochran 1977). Since rock, ceramics, and cement are heterogeneous materials, obtaining a representative sample of them may be the most difficult step in a whole analytical procedure.

TEXTBOX 9**ANALYTICAL CHEMISTRY**

Analytical chemistry is the branch of chemistry that deals with the composition of materials: whether they are single substances or mixtures, what their components are, and how much of each component they contain. Since it provides basic information on the nature and the composition of materials, analytical chemistry is of extreme importance in the study of archaeological materials (Pollard et al. 2007). Analyzing metallic objects, for example, reveals whether they are made of metals or alloys and which are the elemental components of the latter (see Chapter 5). Analyzing the composition of soils discloses their nature and may reveal whether and how human inhabitation affected their composition (see Chapter 8) (Ciliberto 2000; Pernicka 1996). Since the composition of materials quite often bears a relationship to their place of origin, chemical analysis also makes it possible to differentiate between materials from different regions. Moreover, as it discloses information on the components of materials from which objects are made, the analysis of archaeological materials provides clues for establishing their *provenance* and, at times, for differentiating between genuine objects and suspected (and even unsuspected) fakes or forgeries.

The nature and the relative amounts in which the components of materials have to be detected in different analytical studies varies greatly: from the identification and determination of the few major elements that make up a material, to the wide range, often in almost vanishing concentrations, of impurities. From a practical point of view and regardless of the objective of, or the type of information required from an analysis, most analytical procedures entail a sequence of three main operations:

1. *Sampling* a material
2. *Analyzing* and determining the nature of the constituents of the sample and their relative amounts
3. *Interpreting* the analytical results

Sampling

Sampling is the process of obtaining a small and representative portion from the relatively large amount of material that makes up an object or a feature in an object (Stoeppler 1997; Cochran 1977). Sampling homogeneous materials generally presents no particular problems. It merely entails separating a small portion from the whole. Sampling heterogeneous materials is, however, a complex task, at times the most difficult stage of an analytical procedure. Two simple guidelines need to be observed

to ascertain that a sample from a heterogeneous material is unquestionably representative of the whole:

1. The sample should be as large as possible.
2. If the material sampled is made up of particles of different sizes, the large and small particles should be sampled separately and in the respective proportions in which they are present in the bulk. Moreover, each sample should contain as many particles as possible.

Sample Preparation A sample submitted for chemical examination is often in a form unsuitable for analysis. Generally it requires a process of preparation so as to bring it into such a condition that its characteristic chemical and physical properties and those of its constituents can be easily identified and evaluated. During the preparatory stage a solid sample may, for example, be dissolved or converted into a liquid or gas. Moreover, some of its components, which may be irrelevant for the purpose of the analysis and might interfere with an analytical procedure, are generally removed during this stage.

Analysis

A wide range of analytical techniques are today available for identifying and characterizing materials (Hancock 2000). Some, known as *qualitative techniques*, are designed to provide information only on the nature of the components of materials, that is, which components, elements, and/or compounds, make up a material (Masterton and Slowinski 1986). Most often, however, it is also essential to disclose precisely how much of each particular component there is in a material, and thus to reveal its exact composition. Such information is derived using *quantitative techniques* (Harris 2002; Jeffery et al. 1989).

The actual procedures by which the nature or the constituents of a material are qualitatively identified, quantitatively appraised, or both, constitutes the heart of the analysis; these are based, essentially, on identifying and measuring the magnitude of some property or properties of an element or compound in the material analyzed that makes possible their unequivocal identification. Fortunately, almost every element and compound has some characteristic chemical and/or physical properties that, under particular conditions, allow it to be distinguished from all others. This property may be a unique chemical reaction, a change in weight, volume, color, or wavelength of radiation absorbed or emitted, or any one of many others. What is important is that the property selected should be related, in a clear and unique way, to only one of the elements or compounds being analyzed, so as to make it positively identifiable. For

TABLE 9 Methods of Chemical Analysis and Their Uses

Analytical method	Components or characteristics determined					
	Single element	Multiple elements	Molecules	Surface composition	Crystal structure	Other
Gravimetry	✓	✓	-	-	-	-
Volumetry	✓	✓	-	-	-	-
Chromatography	-	-	✓	-	-	Separation
Electrochemistry	✓	✓	✓	-	-	✓
Electron probe microanalysis	✓	✓	-	✓	-	-
Mass spectrometry (MS)	✓	✓	✓	-	-	-
Nuclear activation analysis	✓	✓	-	-	-	-
Spectroscopy						
Emission spectroscopy	✓	✓	-	-	-	-
Absorption spectroscopy						
Infrared	-	-	+	+	✓	-
Fourier transform infrared	-	-	✓	-	-	-
Raman	-	-	✓	-	-	-
Ultraviolet	✓	✓	-	-	-	-
Visible	✓	✓	-	-	-	-
Auger spectroscopy	✓	✓	-	✓	-	-
Thermal methods	-	-	✓	✓	-	-
X-ray technology						
X-ray diffraction	-	-	✓	-	✓	-

historical reasons, the methods and techniques used in analytical chemistry are classified into two main groups: *chemical* (or *classical*) analysis and *physical* (or *instrumental*) analysis.

Chemical Methods of Analysis The *chemical methods* of analysis are those in which, in order to identify and/or measure the relative amounts of the constituents of a sample, use is made of characteristic and unique chemical reactions that alter the sample in a specific and unique way. Changes in the weight of the sample, for example, are studied using *gravimetric techniques*, while changes in the volume of solutions in which the sample is dissolved are studied using *volumetric techniques* (Harris 2002). When using *gravimetry*, samples are converted, by precipitation or combustion, to pure elements or compounds that, when weighed, provide an exact measure of the relative amount of each component in the sample. *Volumetry*, on the other hand, requires that samples be first dissolved in a suitable solvent so as to form solutions of known volume in which their components are dissolved in unknown concentrations. The concentration and, therefore, the relative amounts of these components in the sample are then determined by adding and accurately measuring the volume of solutions of specific reagents in precisely known concentrations until the reaction is complete. The relative amount of a component of a sample can then be calculated from the measured volume of solution added.

Physical Methods of Analysis The *physical methods* of analysis are based on measuring some specific physical property of a component of a sample that serves to ascertain its nature and/or its the relative amount in the sample. Such methods, most of which have been made possible only by modern developments in physics and electronics, make up the main source of analytical information on all substances at the present time (see Table 9 and Textbox 10) (Settle 1997).

The choice of the most appropriate technique for a particular analysis is determined by a number of considerations, the most important of which is the nature of the material to be analyzed. The size of the sample available, the accuracy required, the number of samples involved, and the speed with which results are required, however, also warrant attention. Sometimes, priorities may have to be established before deciding on the most appropriate method for the analysis of a particular sample.

TEXTBOX 10**PHYSICAL METHODS OF ANALYSIS FREQUENTLY USED IN ARCHAEOLOGICAL STUDIES**

Most of the essential information on archaeological materials is derived, at the present time, using *physical methods* of analysis. This may include the qualitative or quantitative assessment of their composition, their provenance, the techniques used for their production, and their age. Some of the most widely used methods of chemical analysis based on physical principles are succinctly reviewed in the following paragraphs.

Spectroscopic Analytical Methods

Spectroscopy, the study of the interaction between matter and electromagnetic radiation, provides a wide range of analytical methods. The energy of all atoms and molecules is discrete (is said to be *quantized*); when atoms or molecules interact with (absorb or emit) radiation, a type of energy, they do so in a distinct manner characteristic of a given composition. This means that when they absorb or emit electromagnetic radiation, each type of atom and molecule does so at well-defined wavelengths. Detecting and measuring the spectroscopic characteristic of material provides, therefore, a powerful tool for the study of their composition and structure. Since the form of interaction of different types (infrared, visible, ultraviolet, X rays) of electromagnetic radiation with materials is different, spectroscopic studies also yield information on a variety of other characteristics of the materials (Davies and Creaser 1991; Creaser and Davies 1988).

Infrared spectroscopy, for example, studies the interaction of materials with infrared radiation and reveals information on their nature: detecting the wavelength at which a material absorbs infrared radiation and measuring the relative drop in the intensity of each wavelength absorbed provides information about their composition, the nature of the component molecules, and the concentration of particular molecules in a material or solution (Stuart et al. 1996). Another spectroscopic technique, known as *Raman spectroscopy*, is based on the scattering, by some substances of monochromatic light, mostly in the infrared, but also in the visible or near-ultraviolet ranges of the electromagnetic spectrum. Raman spectroscopy reveals information on the composition and structure of molecules in materials (Ferraro and Nakamoto 1994).

Atomic absorption spectroscopy and *atomic emission spectroscopy* are analytical techniques in which the wavelength of radiation absorbed

or emitted by substances reveals information on the nature of the constituent atoms, while the intensity of the radiation absorbed or emitted is indicative of the relative amounts of specific atoms in a substance. *Atomic absorption spectroscopy* is based on the detection of the specific wavelengths of light depleted by atoms in a material from a continuous source of energy. *Atomic emission spectroscopy* rests on the detection of the characteristic wavelengths of the light emitted by atoms heated to high temperature (Young and Pollard 2000; Metcalfe and Prichard 1987).

Mössbauer spectroscopy is an analytical technique that, in archaeological ceramic studies, provides information on the condition and characteristics of the compounds of iron in pottery. Using the technique makes it possible to determine the relative amounts of the different (ferrous and ferric) ions of iron and hence to ascertain the firing conditions of the pottery at the time it was made. The technique involves irradiating a sample of pottery with gamma rays and then assessing the amount of radiation absorbed by the nuclei of the ions of iron within the pottery (Feathers et al. 1998; Béarat and Pradell 1997).

Nuclear magnetic resonance spectroscopy is a technique that, based on the magnetic properties of nuclei, reveals information on the position of specific atoms within molecules. Other spectroscopic methods are based on the detection of fluorescence and phosphorescence (forms of light emission due to the selective excitation of atoms by previously absorbed electromagnetic radiation, rather than to the temperature of the emitter) to unveil information about the nature and the relative amount specific atoms in matter.

X-rays Technology

Analytical *X-rays* techniques are used to characterize solids in a number of ways. *X-rays* penetrate solids opaque (impenetrable) to visible light but are slightly attenuated by matter. Irradiating a solid object with *X-rays* in *radiographic* equipment yields, therefore, an image, known as a *radiograph* of the internal structure of the object (Lang and Middleton 1997). Other *X-rays*-based analytical techniques frequently used in archaeological research include *X-rays fluorescence* and *X-rays diffraction* instruments. *X-rays fluorescence* (XRF) identifies the elemental constituents of a solid by the wavelength of electromagnetic radiation emitted by the atoms in the substance when excited by *X-rays*, while *X-rays diffraction* reveals the internal morphology as well as the atomic and molecular structure of substances (Jenkins 1999; Cullity 2001).

Spectroscopic analysis, in all its forms, is being strongly affected by the development of *lasers*, *microtechnology*, and *computers*. The high radiation intensities emitted by small lasers and the reduction in the size of samples made possible by microtechnological developments are being combined with the working proficiency of computers; such a combination provides new, small, portable, and extremely powerful instruments that can be taken to the field, and there yield highly sensitive analytical results, sometimes down to the level of detecting even single atoms and molecules.

Neutron Activation Analysis

Neutron activation analysis (NAA) is a technique for the qualitative and/or quantitative determination of atoms possessing certain types of nuclei. Bombarding a sample with neutrons transforms some stable isotopes into radioactive isotopes; measuring the energy and/or intensity of the gamma rays emitted from the radioactive isotopes created as a result of the irradiation reveals information on the nature of the elements in the sample. NAA is widely used to characterize such archaeological materials as pottery, obsidian, chert, basalt, and limestone (Keisch 2003).

Mass Spectrometry (MS)

In *mass spectroscopy*, sample molecules are ionized and the different masses of the ions formed are selected by use of an electric or magnetic field. In its simplest form, a *mass spectrometer* is an instrument that measures the mass-to-electric charge ratios of ions formed when a sample is ionized. If some of the sample molecules are singly ionized and reach the ion detector without fragmenting, then the mass-to-electric charge ratio of the ions gives a direct measurement of the weight of the molecule (de Hoffmann and Stroobant 2001).

Microscopy

The microscope is arguably the most widely used scientific instrument. Microscopes are used routinely in analytical chemistry and materials science, mineral exploration, and environmental science. The three most common types of microscopes, the *light microscope*, the *electron microscope*, and the *scanning microscope* are essential tools for the measurement of properties or for observing and measuring such qualities as the size and shape of particles, the texture and chemical composition of materials, and such physical properties as color, crystallinity, melting point, and refractive index (Eastaugh et al. 2005; Goodhew et al. 2000).

Separation Techniques

Complex mixtures, such as those that occur in ancient human remains or as residues in ancient vessels and tools, may need to be separated into their components before they can be analyzed. *Separation techniques* are analytical techniques used for separating and sometimes even identifying the components of chemical mixtures (Setford 1994). Two widely used separation techniques are *chromatography* and *electrophoresis*. *Chromatography* is based on allowing a gaseous or liquid mixture or solution, usually known as the *analyte*, to seep through a *stationary*, usually *solid medium* that separates between the components; the separation depends on the rates at which the different components of the analyte move through or along the stationary medium. If the moving mixture consists of gases, the technique is known as *gas chromatography* (GC); if it consists of liquids or is a liquid solution, it is known as *liquid chromatography* (LC) or *high-performance liquid chromatography* (HPLC) (Setford 1994; Miller 1988).

Hyphenated Analytical Techniques

Two or more combined analytical techniques, generally called *hyphenated* or *tandem techniques*, provide more information than that obtained from single traditional physical techniques, thus yielding more reliable results (Rouessac and Rouessac 2000). Many challenging analytical problems, for example, involve more or less complex mixtures that require, as an important first step, separation of their components. Some hyphenated techniques, therefore, couple a separation technique with an analyzing technique so as to separate and analyze complex mixtures. Such is the case with gas chromatography (GC), which is coupled with another separation and analyzing technique, mass spectroscopy (MS), to yield the *gas chromatography – mass spectrometry* (GC-MS) analytical technique. The combination of the two techniques allows a much finer degree of substance identification than does either technique used separately (Kitson et al. 1996; Scott 1997).

In many instances when analyzing archaeological objects, removing a sample may be aesthetically deleterious to the object, therefore rendering the removal of samples totally inadequate, or allowing the removal of extremely small samples so as not to affect the appearance of the objects. In such cases it is often necessary to turn to specialized techniques, such as nondestructive techniques, which do not require the removal of samples altogether, or to micro analytical techniques, for which extremely small samples are needed (see Textbox 11).

TEXTBOX 11

NONDESTRUCTIVE TESTING AND MICROANALYSIS

The terms *nondestructive testing* and *microanalysis* refer to techniques for examining the internal structure and analyzing the composition of objects that, because of aesthetic or other considerations, cannot be studied by conventional techniques.

Nondestructive Testing

Techniques of *nondestructive testing* (NDT) are material appraisal techniques that neither require sampling nor physically damage or impair the integrity of objects studied. Such techniques are invaluable for studying the constitution or the internal structure of unique archaeological objects. Most modern nondestructive techniques are based on the application of forms of *penetrating energy*, such as *acoustic waves* (sound and ultrasound waves) and *electromagnetic radiation*, as, for example, X-rays and gamma rays, as listed in Table 10 (Biro 2005; Shull 2002; Mix 1987).

TABLE 10 Techniques of Nondestructive Testing (NDT)

Technique	Characteristics detected
Optical (visual)	Cracks, color, finish, scratches
Electrical	Cracks, inclusions, voids
Magnetic	Inclusions, shape of internal parts
Radiographic	Inclusions, voids, materials variations, placement of internal components
Ultrasonic	Cracks, inclusions, voids, interfaces

Microanalysis

Microanalysis is the common name used to refer to a variety of techniques for identifying, characterizing, and evaluating minute amounts of materials. Some microanalytical techniques are scaled-down versions of well-known conventional or physical analytical techniques; others are specialized techniques that can be implemented only on extremely small samples. Table 11 lists the minimum size of samples required for microanalysis and the minimum amount of substance detectable by microanalytical techniques (Janssens and Van Grieken 2004).

TABLE 11 Analytical Techniques and Size of Sample Required

Analytical method	Minimum detectable (mg)	Sample size (mg)
Macro	10	over 100
Semimicro	1	about 10
Micro	0.01	about 1
Semimicro	0.001 (10^{-3})	0.01–0.1
Ultramicro	0.00001 (10^{-5})	0.0001–0.001 (10^{-4} – 10^{-3})
Submicro	0.0000001 (10^{-7})	0.000001–0.00001 (10^{-6} – 10^{-5})

Isotopes in Archaeology

The *isotopes* of many elements (see Textbox 12) provide important tools for obtaining information on many archaeological investigations; their use may enable researchers, for example, to determine the provenance (see Textbox 30) or the age of materials (see Textboxes 15 and 16), calculating ancient temperatures (see Textbox 47), or elucidating the nature of the ancient diets of human beings as well as of animals (see Textbox 59).

TEXTBOX 12

ISOTOPES

The basic material units of each chemical element are the almost identical atoms. Each atom of an element includes equal numbers of positive and negative electrically charged particles: positively charged *protons* in the nucleus and, surrounding the nucleus, negatively charged *electrons*. The nuclei of most atoms also include a variable number of *neutrons*, elementary particles that have a definite mass but are not electrically charged. Since the neutrons have mass, the nuclei and accordingly also the atoms of an element having different numbers of neutrons, have different masses. Any two atoms of any one element (which include in their nuclei an equal number of protons) may, therefore, have a different number of neutrons. The *atomic weight* of the two atoms is consequently different. Atoms of one element that have an equal number of protons but a different number of neutrons are known as *isotopes* of the element (see Fig. 8) (Putnam 1960).

All the *isotopes* of an element have the same number of protons in their nuclei and, therefore, they also have the same *atomic number*; consequently, they are chemically identical and indistinguishable from each other (the *atomic number* of an atom is the number of protons in its nucleus and determines the chemical properties of an element). Because they have different numbers of neutrons, however, each isotope of an element has a different atomic weight and, therefore, also slightly different physical properties.

The structure of some isotopes, generally referred to as *stable isotopes*, is immutable (see Textbox 13). Others, known as *radioactive isotopes* or *radioisotopes*, are unstable: in time they undergo what is known as

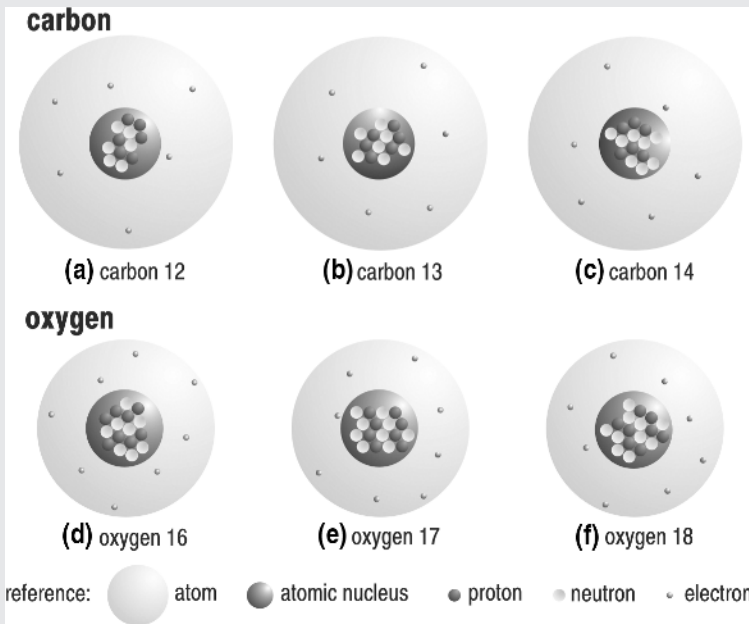


FIGURE 8 Isotopes; the isotopes of carbon and oxygen. Atoms of the same element can have different numbers of neutrons in their nuclei, and the different possible versions of each element are known as “isotopes.” Carbon, for example, has three isotopes: carbon 12, carbon 13, and carbon 14. Carbon 12 (a), the most abundant, has six neutrons; carbon 13 (b) has seven, and carbon 14 (c), also known as “radiocarbon,” has eight neutrons; carbon 14 is unstable and radioactive and is of use for dating archaeological finds. Oxygen has also three isotopes: oxygen 16, oxygen 17, and oxygen 18; the most common, oxygen 16 (d), has eight neutrons, oxygen 17 (e) has nine and oxygen 18 (f) has ten neutrons. The weight ratio between the isotopes of oxygen in seawater, ice, and seashells, for example, provides a reliable indicator of past temperatures and climatic conditions.

radioactive decay processes, when they break down into smaller atoms. Moreover, the breakdown process is accompanied by the emission of various forms of *ionizing radiation* (see Textbox 13 and Fig. 9). Ionizing radiation can easily be detected and quantitatively measured with specialized instruments known as *radiation detectors*. Detecting and characterizing the radiation emitted by unstable isotopes makes it possible to qualitatively identify the isotopes, while measuring the intensity of the radiation makes it possible to quantitatively assess their amount.

Most naturally occurring elements are mixtures of two or more isotopes in which just one predominates. Isotopes can also be prepared

TABLE 12 Isotopes Used in Archaeological Studies

Isotope	Applications
<i>Stable Isotopes</i>	
Argon-40	Potassium–argon dating
Carbon-13	Provenance studies, study of ancient diets
Lead-206	Provenance studies
Lead-207	Provenance studies
Lead-208	Provenance studies
Neodymium-143	Provenance studies
Neodymium-144	Provenance studies
Nitrogen-15	Study of ancient diets
Oxygen-18	Paleotemperatures Provenance studies
Strontium-86	Provenance studies
Strontium-87	Study of ancient diets Provenance studies
Sulfur-32	Study of ancient diets
Sulfur-34	Study of ancient diets
<i>Radioactive Isotopes</i>	
Carbon-14	Radiocarbon dating
Cesium-137	Gamma-ray radiography
Cobalt-60	Gamma-ray radiography
Potassium-40	Potassium–argon dating
Thorium-232	Alpha recoil tracks dating
Thulium-170	Gamma-ray radiography
Uranium-234	Uranium series dating
Uranium-235	Uranium series dating
Uranium-237	Alpha recoil tracks and uranium series dating
Uranium-238	Alpha recoil tracks and uranium series dating

artificially. When some stable isotopes are irradiated with neutrons or with other energetic particles, they are converted into unstable, radioactive isotopes, some of which do not occur naturally on earth. The newly formed isotopes can then be identified and characterized using radioactivity detection methods. This has given rise to a significant branch of analytical chemistry known as *neutron activation analysis*, which is often used for the study of such materials as obsidian, glass, and pottery (see Textbox 10) (Neff 2000).

Many stable and unstable isotopes are used for studying processes relevant in archaeology (Katzenberg 2000). Carbon-14, also known as *radiocarbon*, an unstable isotope of carbon, for example, is of prime importance for dating archaeological finds (see Textbox 55). Carbon-13, a stable isotope of carbon, provides a tool for studying ancient diets (see Textbox 57). The heavy isotopes of oxygen, oxygen-17, and particularly oxygen-18 are of use for estimating past temperatures (see Textbox 47) (Wagner 2000). Isotopes frequently used in archaeological studies are listed in Table 12.

1.6. PROVENANCE OF ARCHAEOLOGICAL MATERIALS

The term *provenance*, or *provenience*, as the word is often also spelled, is used to refer to the geographic location, that is, the area or place from which a material or artifact originates. The main interest in the study of the provenance of archaeological materials and objects is twofold: determining the geographic source of archaeological materials, and studying the eventual distribution of such material to other areas and the routes through which they were traded (Hughes 1991). The study of provenance is based on the assumption that most materials have some detectable compositional characteristics that are uniquely related to their place of origin and particularly to the nature and the relative amount of the minor and trace elements at the place, which generally vary from place to place. To ascertain whether the composition of a material may provide relevant information on its provenance, it is necessary to ascertain three basic conditions:

1. Different samples of the material from a single source are of uniform composition.
2. There are compositional differences between samples of the same material from different sources.
3. Such differences can be unequivocally recognized and distinguished.

To be of value for reliable differentiation, such compositional differences should be greater between samples from different sources than between different samples from a single source. Most archaeological provenance studies have so far been related to stone, ceramics, glass, and metals. Compositional evidence on stone was used, for example, to prove that in neolithic times, large stones from Pembroke in Wales, in the British Isles, were transported a distance of about 200 miles to Wiltshire in England, where they were used to build a megalithic ring at Stonehenge (Newall 1959).

Some studies on the provenance of stone have been based on determining the weight ratios between different minor or trace elements or on the relative abundance and weight ratios of the stable isotopes of such elements as carbon and oxygen. Thus have been studied the provenance of some types of rock (Giauque et al. 1993; Waelkens et al. 1992), marble (Craig and Craig 1972), and pottery (Perlman and Yellin 1980; Millett and Cattling 1967). Establishing the provenance of metals presents a most difficult problem. With the exception of the native metals, that is, gold and silver, limited amounts of copper, and very little iron, most metals do not occur naturally as free metals but are combined with others, mainly as metal ores from which they have to be extracted by *metal smelting* procedures. Unlike stone, which is used "as is," metal ores undergo, during *metallurgical operations*, drastic chemical changes. As a consequence of these changes, there is usually little or no compositional correlation between the minor or trace element in mineral ores and in the metals derived from them. On occasion, however, the relative amount of the minor or trace elements in the ore and in the metal smelted from it bear some relationship and make it possible to elucidate the provenance of the metal (Cherry and Knapp 1991; La Niece 1983).

1.7. CHRONOLOGY OF ARCHAEOLOGICAL MATERIALS

Human evolution can be understood properly only if the time element is considered; establishing the chronology of past events and of ancient objects has been a preoccupation of historians since history was first recorded. In archaeology, in particular, dating ancient artifacts and structures is of fundamental importance, and an endless search continues for methods to accurately date material remains: to establish the time of occurrence as well as the chronological succession of past events. It has been only over the period of the last 5000 years (however, this date varies for different geographic regions on the surface of the planet) that written chronological data have become available. The nonliterate past of humans (*Homo sapiens*)

left no records of the time of occurrence of events or the manufacture of objects during prehistoric times. The lack of chronological information led to the development of a number of methods for ascertaining, independently of written records, the age of materials and ancient objects and for establishing their chronological sequence (Hedges 2001; Taylor and Aitken 1997).

Chronology may be expressed in two forms: *absolute* and *relative chronology*. *Absolute chronology* depends on knowing the precise date of events or age of materials or objects. To sequence events or objects in absolute chronology implies organizing them in a certain order, for example, from oldest to most recent. *Relative chronology* is not expressed in specific dates but rather in a sequential relationship of events. *Relative dates* are therefore expressed in relation to those of other objects or events; they do not specify the precise age of objects or the time of occurrence of events. *Absolute dates* provide the precise age of objects and the time of occurrence of events, and are derived independently of those of other objects or events.

One method most widely used in archaeology for determining relative dates and elucidating chronology is *stratigraphy*, the study of stratified sediments and ancient remains. In any stratified sequence, higher strata were deposited later than lower ones. Provided there has been no disturbance of a stratigraphic sequence, therefore, remains in the higher strata are younger than those in the lower ones. This also determines the chronological sequence of objects buried in the different strata and therefore their relative chronology (Harris 1997). Another method for determining the relative date of tools is *seriation typology*, in which specific types of objects are classified according to the way in which some specific characteristic (e.g., their shape) undergoes successive gradual changes during the passing of time. Typological resemblance between objects may indicate that they are contemporary, although differences do not necessarily imply that they are not. Up to the mid-twentieth century serial types were usually constructed using a combination of empirical observation and intuition. Since then a mathematical approach and, since the mid-1990s, phylogenetic methods, borrowed from evolutionary biology, have been applied for the study of typology-based chronology (O'Brien and Lyman 1999; Dunnell 1996, 1971).

Already during the late nineteenth century a search began for techniques of dating involving the chemical and/or physical properties of materials (Carnot 1893; Middleton 1845). Some techniques, such as the *fluoridation of bone* (see Textbox 69), *geomorphology*, and *palaeomagnetism*, have been used for quite some time. Today, most dating methods are *radiometric*, based on the *half-lives* of *radioactive isotopes*, or the rate of cumulative changes to matter caused by *radioactive decay* processes. The possibility of determining *absolute dates* became possible only after the discovery of *radioactivity* and the process

of *radioactive decay*, particularly since the 1950s, following the development of *nuclear* techniques. Since then, a wide and still increasing number of scientific dating methods have been and still are being developed (see Fig. 8) (Schwarcz 2002; Taylor and Aitken 1997).

TEXTBOX 13

RADIOACTIVITY

The *stability* of atoms – their property of being steadfast and remaining unchanged – is determined by the nature of their nuclei (see Textbox 12). Nuclei in which the number of neutrons is smaller than or equal to the number of protons are stable, while those in which the number of neutrons is larger than the number of protons are unstable. *Unstable nuclei* have a tendency to adjust the disparity between the number of neutrons and protons and become stable; they may do so by one of two processes, by *radioactive decay* or *nuclear fission*.

Radioisotopes and Radioactive Decay

Radioisotopes may occur in the earth naturally as *primordial radioisotopes*, formed when the planet was created, or be produced by natural or artificial processes. Most fast decaying primordial radioisotopes have long disappeared from the planet; since the earth originated about 4.5 billion years ago, such isotopes have decayed and reached a final, stable form. The relatively few primordial radioisotopes still extant in the earth today, therefore, decay very slowly. Among these are *potassium-40* and some isotopes of uranium, such as *uranium-235* and *uranium-238*, which are of use for dating archaeologically related minerals and rocks (see Textboxes 15 and 16).

Some radioisotopes are continuously being produced by the bombardment of atoms on the surface of the earth or in its atmosphere with extraterrestrial particles or radiation. One of these is *carbon-14*, also known as *radiocarbon*, which is widely used for dating archaeological materials (see Textbox 55). Many radioisotopes that are not primordial or are not created by natural processes are now produced artificially using specialized equipment; many of the “artificial” isotopes are of use for probing and analyzing materials.

The process of *radioactive decay* (also known as *radioactivity*) involves the ejection from a nucleus of one or more nuclear particles and ionizing radiation. *Nuclear fission* is a reaction in which the nucleus splits into smaller nuclei, with the simultaneous release of energy. Most radioisotopes undergo radioactive decay processes and are converted into different smaller atoms.

Radioactive Radiation

The *radiation* emitted when radioisotopes decay may be of one or more of three different types: alpha and beta radiation, which are streams of energetic particles, and gamma rays. *Alpha radiation* is a stream of bundled, positively charged particles known collectively as *alpha particles*; each alpha particle has a mass and charge equal in magnitude to two protons together with two neutrons. Alpha radiation travels very short distances (only a few centimeters) in air, as the particles lose their energy as soon as they collide with anything; they are therefore easily shielded by a sheet of paper or by human skin (see Fig. 9).

Beta radiation is a stream of negatively charged particles, known as *beta particles*, which have the same mass and electric charge as the electrons. Beta radiation travels in the air longer distances than alpha

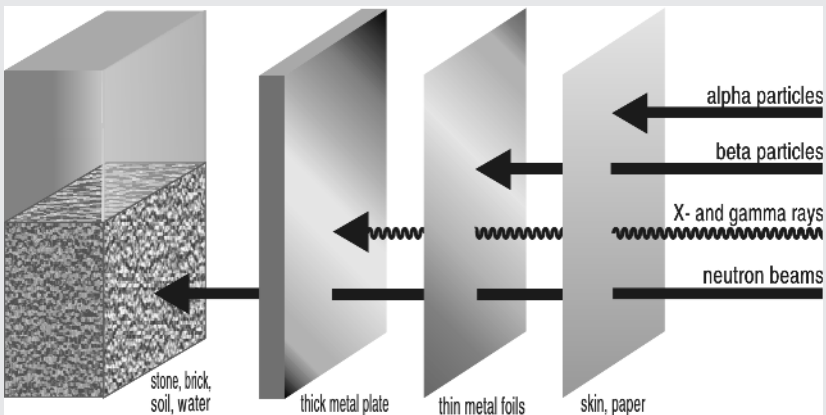


FIGURE 9 Penetrating radiation. Ionizing radiation (see Fig. 8) has sufficient energy to penetrate and interact with some types of matter and is therefore also known as “penetrating radiation.” Gamma and X-rays, for example, travel many meters in air and readily penetrate thick layers of many materials, such as rock and metal. By extension, the term “penetrating radiation” is also used to refer to streams of energetic particles that penetrate and interact with matter. Streams of alpha particles emitted from some atomic nuclei undergoing radioactive decay, for example, known as “alpha radiation,” have a very short range of penetration; alpha radiation travels only a few centimeters in air, but does not penetrate human skin or clothing. Streams of beta particles, which may travel several meters in air, are known as “beta radiation;” beta radiation penetrates human skin, other animal and vegetable tissues, and thin metal sheets, but not thick metal plates. Neutron beams, streams of uncharged nuclear particles, are the most penetrating form of particles. Neutrons (which can be generated with special equipment) penetrate very thick layers of most materials.

radiation (about one meter), passes through a sheet of paper, but is blocked by thin metal foils. Beta radiation is sometimes used to study archaeological problems as for example, to measure the thickness of gilding layers, to determine the relative amount of lead in lead glass, and to differentiate between different types of glass.

Gamma rays have no mass and no electric charge. They are highly energetic forms of electromagnetic radiation, similar to visible light or X-rays, but having very short wavelengths, the shortest wavelengths in the whole spectrum of electromagnetic radiation (see Textbox 5). Because of their high energy, gamma rays penetrate any type of matter, whether gaseous, liquid, or solid.

The wavelength of the gamma rays emitted by a radioisotope is unique and characteristic of the radioisotope; this makes gamma rays extremely useful for identifying radioisotopes. In *neutron activation analysis*, for example, gamma rays are used to characterize and determine the relative amounts of different elements in a sample (see Textbox 10). The attribute to penetrate solid matter makes gamma rays also a suitable complement to X-rays for radiographic purposes. Gamma rays emitted from a small sample of a radioisotope, for example, can be used for radiographing objects that would be difficult and often impossible to radiograph with X-rays (Hinsley 1959).

Radioactive isotopes that decay by the emission of alpha or beta radiation undergo a change in the nature of their nuclei and are converted into isotopes of other elements. The emission of gamma rays, on the other hand, does not change the nature of the nuclei of the radioisotopes from which the rays are emitted. Gamma rays are a form of dissipation of nuclear energy.

Some radioisotopes decay emitting only gamma rays, but many do so by the concurrent emission of beta and gamma radiation. The rate at which radiation is emitted from the nuclei of different radioisotopes varies considerably. Each radioisotope has a unique form of decay that is characterized by its *half-life* ($t_{1/2}$), the time it takes for the radioactivity of the radioisotope to decrease by one-half of its original value (see Textbox 14).

Radioactive decay is a stochastic process that occurs at random in a large number of atoms of an isotope (see Textbox 13). The exact time when any particular atom decayed or will decay can be neither established nor predicted. The average rate of decay of any radioactive isotope is, however, constant and predictable. It is usually expressed in terms of a *half-life*, the amount of time it takes for half of the atoms in a sample of a radioactive isotope to decay to a stable form.

TEXTBOX 14

HALF-LIFE

The concept of *half-life* applies to processes involving changes in which the rate of change of some quantity in a system depends on this quantity. The half-life is the time required, under specific conditions, for a quantity to decrease by one-half. After one half-life has elapsed, only 50% of the original quantity remains. During the second half-life, one-half of the remaining quantity vanishes, leaving one-quarter (25%) of the original. One-eighth (12.5%) is left after the third half-life, and so on. The decrease in the quantity follows a geometric regression, being continuously reduced by one-half, as illustrated in Figure 10. The half-life of specific materials is of use for dating the materials.

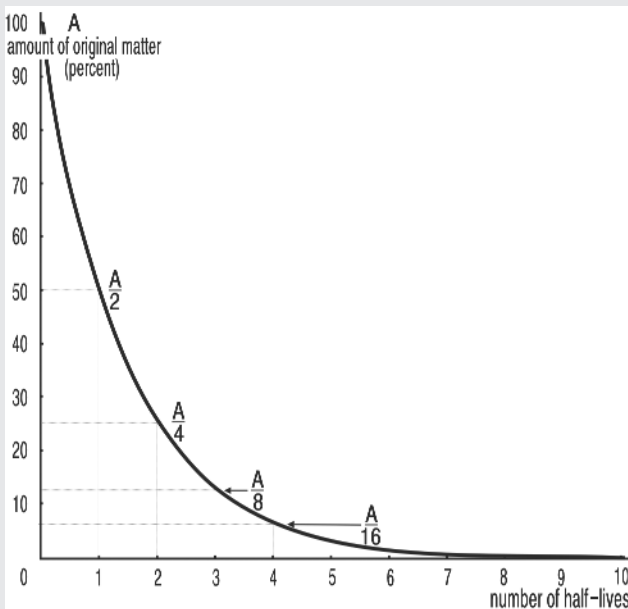


FIGURE 10 The half-life. It is impossible to predict when a radioisotope or an unstable substance (molecule) will decay or be decomposed. On an average, however, only half of any type of radioisotope or unstable substance (molecule) remains after one half-life ($A/2$); one-quarter will remain after two half-lives ($A/4$), one-eighth after three half-lives ($A/8$), and so on. The half-life is characteristic of every radioisotope and unstable molecule; that of radioisotopes is not affected in any way by the physical or chemical conditions to which the radioisotope may be subjected. Not so the half-life of chemically unstable molecules, which is altered by changes in temperature and by other physical and chemical conditions.

Isotopic Half-life

The half-life ($t_{1/2}$) of a radioisotope is the amount of time it takes for that isotope to undergo radioactive decay and be converted into another. It is also a measure of the stability of the isotope: the shorter its half-life, the less stable the isotope. The half-life of radioisotopes ranges from fractions of a second for the most unstable to billions of years for isotopes that are only weakly radioactive. In the case of radiocarbon (carbon-14), for example, the half-life is 5730 years (see Fig. 61).

Chemical Half-life

The concept of half-life also applies to chemical reactions. The half-life of a chemical reaction is the time it takes for the amount of one of the reactants to be reduced by half. In some reactions the reaction rate is determined by the concentration of one particular reactant; as the reaction proceeds and the concentration of this reactant decreases, so does the rate of the reaction. This is the case for example, with amino acids, the components of proteins. *Amino acids* may occur in one of two different forms, the *l* and *d* forms (see Textbox 24). In living organisms, however, the amino acids occur only in the *l* form. After organisms die, the amino acids in the dead remains racemize and are gradually converted into the *d* form. Ultimately, the remaining amino acid, which is then known as a *racemic mixture*, consists of a mixture of 50% of the *l* form and 50% of the *d* form.

If the environmental temperature is constant, the racemization process takes place at a uniform rate, which is determined, at any time during the process, by the relative amounts of *l* and *d* forms of the amino acid can be measured. As the racemization proceeds and the concentration of the *l* form amino acid decreases, the rate of racemization gradually slows down. When there is a mixture of 50% of each of the *d* and *l* forms, the racemization process stops altogether. The half-life of the racemization of *aspartic acid*, for example, a common amino acid in proteins, at 20°C is about 20,000 years. This half-life makes it possible to date proteins as old as about 100,000 years. So far, however, the dates obtained with the technique have proved somewhat inconsistent, probably because of the difficulty in verifying whether the temperature of the amino acids has been constant.

TABLE 13 Radiometric Methods of Dating Used in Archaeology

Method	Measurement	Applicability	Reference
<i>Methods Based on Measurement of Radioactive Radiation or Amount of Radioactive Isotope or Daughter Isotope in Materials</i>			
Radiocarbon	Counting of beta radiation or amount of carbon-14	Organic matter	Textbox 52
Potassium argon	Relative amounts of parent- and daughter-isotope	Volcanic rocks	Textbox 15
Uranium series	Relative amounts of parent- and daughter-isotope	Calcareous rocks, shell	Textbox 16
<i>Methods Based on Measurement of Cumulative Changes Caused by Radiation on Materials</i>			
Fission track	Number of fission tracks in a solid	Obsidian, glass, slag	Textbox 26
Thermoluminescence	Amount of light emitted at high temperature	Pottery, burned flint	Textbox 24
Optically stimulated luminescence	Amount of light emitted when sample is illuminated with laser light	Sediments and soil	Textbox 24

Comparing the relative amount of a particular radioactive isotope of known half-life remaining in a sample of material with that of its decay products, or measuring the effects of the radiation of such an isotope on surrounding matter, for example, enables one to estimate the time that the material has existed. The most convenient isotopes for archaeological dating are those that are relatively common in nature and whose half-lives are compatible with archaeological dates. Table 13 lists radiometric methods of dating that are widely used in archaeological studies.

Potassium–Argon Dating

Potassium–argon dating is the only feasible technique for dating very old rocks that include potassium in their composition. It is based on the fact that one of the radioactive isotopes of potassium, potassium-40 (K-40), decays to an isotope of the gas argon, argon-40 (Ar-40). Since the half-life of potassium-40 is known, by comparing the relative amount of potassium-40 to that of argon-40 in a sample of rock, the date the rock was formed can be determined (see Textbox 15). Unlike the case in other radiometric dating techniques used in archaeology, the materials dated with the potassium–argon

method, rocks, are directly related not to human activities but to geologic events. It is important, therefore, when using the potassium–argon method, that the association between the rocks dated and the human evidence to which the rock is related be carefully established. Bearing in mind this limitation, potassium–argon is the only viable method for dating very old, archaeologically related rocks such as hornblende, certain kinds of feldspar, lava, some natural glass, and types of clay (Walther 1997). A useful application of the technique in archaeological studies is, for example, to date volcanic tuff or lava flows overlying layers bearing evidence of early hominids and/or their activity; such dates provide evidence that the layers bearing archaeological evidence are older than the overlaying lava or tuff.

TEXTBOX 15

POTASSIUM–ARGON AND ARGON–ARGON DATING

Potassium–Argon Dating

Potassium (K) is one of the most abundant elements (2.4% by mass) in the earth's crust, where it occurs in three isotopic forms: *potassium-39*, *potassium-40*, and *potassium-41*. *Potassium-40*, which is radioactive, is the least abundant of the three isotopes, making up a very small fraction, just over 0.01%, of the total amount of potassium; one out of every 10,000 potassium atoms is radioactive potassium-40. The isotope decays by two different pathways: (1) 88% of the potassium-40 decays to *calcium-40*, and (2) the remaining 12% decays to *argon-40*, a stable isotope of argon also known as *radiogenic argon* (see Fig. 11). The decay of potassium-40 to argon-40 is the relevant decay pathway in the potassium–argon (K–Ar) dating method.

Potassium-40 decays, and as a consequence, in any mineral or rock containing potassium, the concentration of potassium-40 is gradually reduced, while, provided the rock is impervious to argon, the amount of argon-40 increases. Since the half-life of potassium-40 has been precisely determined (1.28×10^9 years), measuring the concentration of potassium-40 and argon-40 in minerals, rock, or volcanic ash enables one to determine their age (Faure 1986). Thus, if argon remains trapped within the minerals that make up rock or volcanic ash, *potassium–argon dating*, as the method is known, provides an invaluable tool for studying early evidence on human evolution. It should be noted, however, that potassium–argon ages are not directly related to human activity. They provide maximum time limits, indicating whether dated minerals, rocks or ashes are younger, or older, than the remains of the activity of humans. If human remains lie between two layers of volcanic deposits, for example, the potassium–argon dates of the

layers provide a minimum and maximum age for the activity of humans. The method, which is particularly useful for dating mineral, rock, or ash rich in potassium, can be applied to mineral matter as old as the earth (4.5 billion years ago) and as recent as under 100,000 years ago (Walter 1997; Guillot and Cornette 1986).

Methodology

The determination of the potassium–argon age of rock involves the following experimental stages:

1. Sampling the rock
2. Isolating the potassium-40 and argon-40 in the sample from the rest of the mineral matter
3. Determining the relative amounts of these elements in the sample
4. Calculating the potassium–argon date of the mineral or rock

Experience shows that samples weighing 0.2–20 g are usually sufficient for dating by this method. The determination of potassium-40 is, at present,

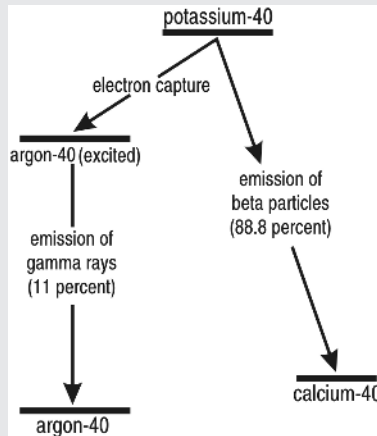


FIGURE 11 The decay of potassium-40. Potassium-40 may decay by one of two different radioactive decay modes: either by the emission of beta particles or by electron capture. The emission of beta particles is, however, its main mode of decay: almost 90% of radioactive potassium-40 decays by this mode to calcium-40; the other nearly 10% decays by electron capture, to excited argon-40. The diagram illustrates the two different decay modes. Only the decay by electron capture to excited argon-40, which is followed by the emission of gamma rays to argon-40, is the decay path used in the potassium–argon method of dating.

generally done using instrumental techniques, particularly absorption spectroscopy.

As for the determination of argon, since argon is a gas, it is extracted from rock by fusing the sample at a very high temperature (over 1600°C) and then, using a mass spectrometer, measuring the amount of gas released (Layer et al. 1987).

Knowing the total amounts of potassium-40 and of radiogenic argon-40 in a sample enables one to calculate first, their relative weight amounts and then, from these values, the age of the sample. The reliability of a potassium–argon date is generally expressed as a plus or minus value after the calculated date.

Relevance of the Technique

Not all potassium-bearing minerals are suitable for K–Ar dating. Some minerals are porous or permeable to gases and lose radiogenic argon; using the potassium–argon method for determining the age of such minerals therefore invariably yields inaccurate, young ages of no significance. Common minerals that can generally be dated using the potassium–argon method are listed in Table 14. There is practically no upper limit to the range of dates to which the method can be applied. Since samples of archaeological interest are relatively young, however, the lower limit of applicability of the method requires that samples suitable for dating be rich in potassium.

TABLE 14 Minerals and Rocks Suitable for Dating Using Potassium–Argon Technique

Minerals:

Adularia^a

Anorthoclase^b

Biotite^b

Glaucinite

Hornblende^b

Lepidolite^b

Leucite^a

Plagioclase^a

Rocks: basalt^b

^aYields occasionally unreliable dates.

^bYields consistently reliable dates.

Errors

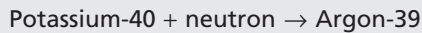
When a rock is formed from a lava melt, different grains of the same mineral within the rock solidify at slightly different times. The distribution of potassium-40 and consequently also of radiogenic argon is not

homogeneous throughout any given rock; for the determination of reliable dates, therefore, the relative amounts of potassium-40 and argon-40 should be determined in the same sample. For practical reasons, however, the amounts of the two elements are generally measured in different samples of the same rock. It is important, therefore, to ascertain that every sample analyzed for dating should be truly representative of the composition of the whole rock.

One of the basic assumptions in the potassium–argon dating method is that the rock dated constitutes a *closed system*; this implies that it contains all the argon-40 generated in it, with nothing having escaped, and that it does not contain radiogenic argon other than that resulting from the decay of potassium-40. The largest errors in the method, however, are related to the occurrence of either an excess or a deficiency of argon-40 caused by geologic or weathering factors.

Argon–40/39 Dating

Relatively recent studies have led to the development of an additional dating method based on the use of argon-40, known as the *argon–argon* or, more specifically, the *argon-40–argon-39* dating method. Like the potassium–argon method, the argon–argon dating method is based on determining the relative amounts of the potassium and argon in a sample, but it uses a different methodology: the sample to be dated is irradiated with neutrons so as to convert potassium-40 to argon-39:



After the sample has been irradiated, heating the sample until it melts releases all the argon in the sample, including the isotopes argon-40, created by the decay of potassium-40, and argon-39, formed when the potassium-40 in the rock was irradiated with neutrons. Separating the two isotopes (argon-40 and argon-39) and finally determining the weight ratio between them provides values from which the age of the sample can be calculated (McDougall and Harrison 1999; Walter 1997).

The argon-40–argon-39 method thus provides a variation of the potassium–argon method; both methods yield the age of a sample by ascertaining the relative amounts of potassium-40 and argon-40. However, whereas in the potassium–argon method, the amount of potassium is determined directly in the sample, in the argon–argon method the potassium is instead converted to argon-39, and only then is the amount of the latter measured. It is claimed that the argon–argon method provides some advantages over the conventional potassium–argon method, such as the need for smaller samples and greater precision of the results, particularly when dating weathered rock.

Some of the most important applications of the potassium–argon dating method in archaeology have probably been for dating Pleistocene deposits whose age is reckoned in hundreds of thousands of years; the method may yield valuable information on extinct species, for example, by providing dates for the geologic beds in which their remains are found. Other valuable applications are for establishing a Cenozoic chronology and, most important, for providing a timescale for the evolution of humankind, from the earliest known hominids onward. Since it was first used, the potassium-argon dating method has made possible comparative studies on early humans over a timespan of several million years. The method have been used to date early hominids, including Java's *Meganthropus* and Olduvai Gorge's *Zinjanthropus* in East Africa (Evernden and Curtis, 1965).

Argon–Argon Dating

Another dating method based on the use of the decay of potassium-40 to argon-40 is the *argon–argon* dating technique (see Textbox 15). This technique is, however, applicable only to rocks containing substantial amounts of potassium, but makes it possible to date very young samples with relatively low accuracy (about 10%). Using the argon–argon method for dating pumice rock ejected from the Vesuvius volcano (during the eruption that destroyed Pompeii and Herculaneum during the year 79 C.E.), for example, made it possible to precisely date the eruption to 1929 ± 94 years ago, only seven years off from the true date (Renne et al. 1997).

Archaeologically Related Rock and Stone

Early in the development of humans, a variety of stones, such as flint, obsidian, basalt, marble, and turquoise, were put to multifarious uses; many of these stones were used for manufacturing implements, constructing buildings and roads, decoration and adornment or, after comminution into fine powders, as *pigments* and *abrasives* (see Table 15). *Flint* and *obsidian*, which were widely used for making implements, weapons, and decorative objects, are discussed in Chapter 2. Some others are described in the following pages. Their description and uses are followed by a discussion of studies addressed to characterize them and to elucidate the time of their use, their provenance, and the changes they have undergone since they were last used (Waelkens et al. 1992).

Limestone. *Limestone* usually occurs as a white or light-shaded sedimentary monomineral formed by the consolidation of calcite (composed of calcium carbonate) sediments. It is a soft rock that can easily be cut and shaped into any size and form, so it has been used, since early antiquity, for

TABLE 15 Archaeologically Related Stone

Stone	Common use	Compositional characteristics	Remarks
<i>Igneous</i>			
Andesite	Making tools	Complex metal silicates (about 60% silica)	Compact and tough; chips easily
Basalt	Building	Complex metal silicates (about 50% silica)	Dark-colored, fine-grained
Diamond	Precious-stone grinding and polishing	Pure carbon	High refractive index; hardest material on earth
Emerald	Gemstone	A variety of beryl	Very hard
Jade	Making jewelry and decorative objects	Metal silicates	Two varieties: jadeite and nephrite
Obsidian	Making tools and decorative objects	Natural glass	Extremely dense; sharp edges; conchoidal fracture
<i>Sedimentary</i>			
Alabaster	Making decorative objects	Calcium sulfate	Easily shaped and polished
Alabaster, oriental	Making decorative objects	Calcium carbonate	Easily shaped and polished
Flint	Making tools	Mainly silica	Very compact; sharp edges, conchoidal fracture
Gypsum	Building; making plaster of Paris	Calcium sulfate	Easily shaped and polished; decomposed by heat
Limestone	Building; making lime	Calcium carbonate	Easily shaped; decomposed by heat
Sandstone	Building	Mainly silica	Conglomerate of rounded silica fragments consolidated within calcium carbonate
Turquoise	Semiprecious gemstone	Hydrated phosphate of aluminum and copper	Carved with relative ease
<i>Metamorphic</i>			
Marble	Building; making statuary	Calcium carbonate	Easily shaped and polished
Quartzite	Making statuary	Mainly silica	Easily shaped and polished
Soapstone	Carving decorative objects	Complex silicate of magnesium	Greasy feel; easily carved

building and statuary. It is also the raw material from which lime cement is made (see Textbox 34), and an essential component in the process for recovering some metals from their ores and in the manufacture of glass. When added to iron ores during the iron-smelting operations, limestone reacts with the nonmetallic component of the ore forming a slag that can be easily separated from the molten iron. Limestone is also an important component of the most common type of glass, sodalime glass, in which it serves as a stabilizer that makes the glass resistant to dissolution by water and to decay.

TEXTBOX 16

URANIUM SERIES DATING

Uranium series dating is based on the decay characteristics of isotopes of uranium. The method takes advantage of the tendency of uranium dissolved in groundwater and seawater to precipitate together within calcium carbonate. The latter constitutes such minerals as calcite and aragonite and is a main constituent of bone, shell, coral, and speleothems (*speleothems* are mineral deposit formed in caves as stalactites and stalagmites by the evaporation of mineral-rich water). Ancient bone acquires most uranium after burial in the ground; shell, coral, and speleothems acquire it during their formation stages. All these can be dated by the uranium series dating method. The applicability of the method ranges from a few hundred to well over 500,000 years; Uranium series dating is particularly useful, therefore, for dating materials from the period beyond the useful time range of radiocarbon dating, that is, earlier than 50,000 years ago (Latham 2001; Schwarcz 1997).

Uranium, the heaviest element in the earth, is probably the best known of the radioactive elements. The use of compounds of uranium – for example, its natural oxide – dates back to at least the first century C.E., when uranium oxide was used to color ceramic glazes. But its use for dating is quite recent, beginning only in the last decades of the twentieth century. The atomic number of uranium is 92, which is also the number of protons in its nucleus. The number of neutrons in the nuclei of different uranium isotopes varies; therefore, uranium has several isotopes, three of which occur naturally: uranium-238 (which makes up 99.3% of the total amount of uranium), uranium-235 (0.7%), and uranium-234 (0.005%). Only the most abundant isotope, uranium-238, and the lightest, uranium-234, are used for dating. The two isotopes decay to form, ultimately, stable isotopes of lead; uranium-238 yields lead-206, while uranium-235 yields lead-207. The two do not, however, decay directly into stable lead isotopes; they do so through a rather long series of intermediate steps during which

transient, radioactive daughter isotopes are formed. Uranium-238, for example, initially yields uranium-234, which then decays to thorium-230; only many more steps afterward is stable lead-206 finally formed. The half-lives of the transient daughter isotopes range from fractions of a second to hundreds of thousands of years. The longest-lived isotopes, including uranium-234, whose half-life is 250,000 years, and thorium-230, with a half-life of 75,000 years, are used to date prehistorical materials (see Fig. 12).

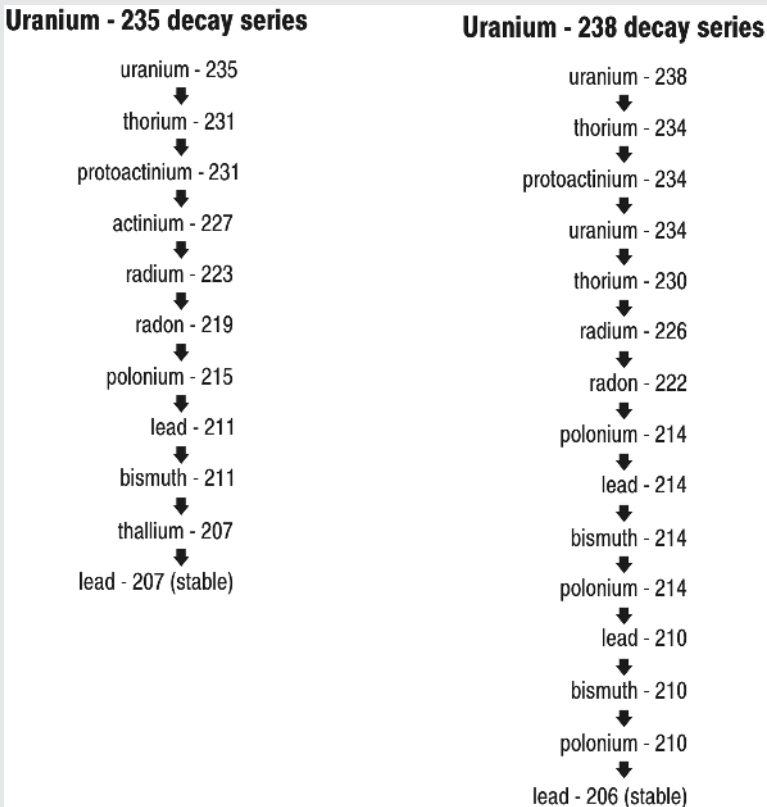


FIGURE 12 The decay series of the uranium isotopes. Most radioactive isotopes decay into stable ones. Some, however, decay into intermediate, unstable isotopes, over and over (repeatedly) in long “decay series,” which terminates only when a stable isotope is formed; the stable isotope formed at the end of all the decay series is always an isotope of lead. Three decay series occur naturally in the crust of the earth: one beginning with the isotope thorium-232 and two others that begin with isotopes of uranium, namely, uranium-235 and uranium-238. The last two, which are of use for dating archaeological materials, are illustrated. Determining the length of burial time of objects that absorb uranium, such as bone, teeth, and eggshell, are typical applications of the uranium series method of dating.

The half-life implies that in any material where there is a certain amount of a decaying *parent isotope* there will be only half of the original amount after one half-life, the other half having decayed into a *daughter isotope*. In another half-life, half of the remaining parent isotope will decay, and the material will now consist of only one-fourth of the parent to three-fourths of the daughter isotope (see Textbox 14). Conversely, calculating the weight ratio of daughter to parent isotope in any given material makes it possible to calculate the length of time that has passed since the parent isotope started decaying, that is, since the material was created, as, in speleothems, or since the parent isotope was deposited within the material, as in buried bone.

Once uranium is incorporated into buried bone, shell, coral, or speleothems, the isotope uranium-235 decays, initially into the short-lived isotope (thorium-231) and then into long-lived protoactinium-231. Uranium-238, on the other hand, decays first into two successive short-lived isotopes (thorium-234 and protoactinium-234) and only then into a long-lived isotope, uranium-234 (see Fig. 12). The decay of uranium-235 to long-lived protoactinium-231 is used to date events up to 150,000 years in age; that of uranium-234 (derived from uranium-238) to thorium-230 is of use for dating events within the time range 1000–500,000 years.

Measuring the relative abundance of the successively formed isotopes is generally done using the mass spectroscopy technique, but it is also possible using nondestructive analytical techniques based on counting the alpha or gamma rays emitted during the decay of the isotopes. Dates obtained using the mass spectrometric technique have errors of $\pm 0.5\text{--}1\%$, while with alpha ray counting the errors are much larger, $\pm 5\text{--}10\%$. Comparing the relative amounts of isotopes from the decay of uranium-235 and uranium-238 makes it possible to verify the accuracy of the age estimated using the half-life of one of them.

Marble. The word *marble* is used as the common name for two types of *monomineral rocks*: one derived from *limestone* and therefore composed of calcium carbonate, the other derived from *dolomite* and composed of calcium magnesium carbonate. Extremely high pressures and heat during past geological times modified the structure of both limestone and dolomite, compacting them into a characteristic crystal structure. Most marble is white; however, minor and trace amounts of metallic impurities cause the formation of stains in a variety of colors, hues, and patterns, or of colored marble.

Marble occurs in many locations on the crust of the earth, so that many types of marble were known to the ancients. White Pentelic marble, from

Mount Pentelikus in Attica, Greece, and Carrara marble from Carrara in Italy, were probably the best known in classical antiquity. Red-mottled Siena marble, from Tuscany in Italy, and Tecali marble from Mexico are other well-known examples of widely used types of marble. Because it is easily shaped and polished, marble has been widely used since early antiquity for building and statuary. It is hardly surprising, therefore, that the characterization of archaeological marble, the determination of its provenance, and the study of ancient marble trading patterns have attracted and continue to attract much attention (Getty Museum 1990). A wide range of analytical techniques have been used to study, for example, the provenance of marble (Maniatis 2004). Some of these techniques include analysis of trace elements (Mathews 1997), thermoluminescence and electron spin resonance (Armiento et al. 1997), and determination of the ratios of stable isotopes of oxygen and carbon (see Fig. 13) (Walker and Matthews 1988; Craig and Craig 1972).

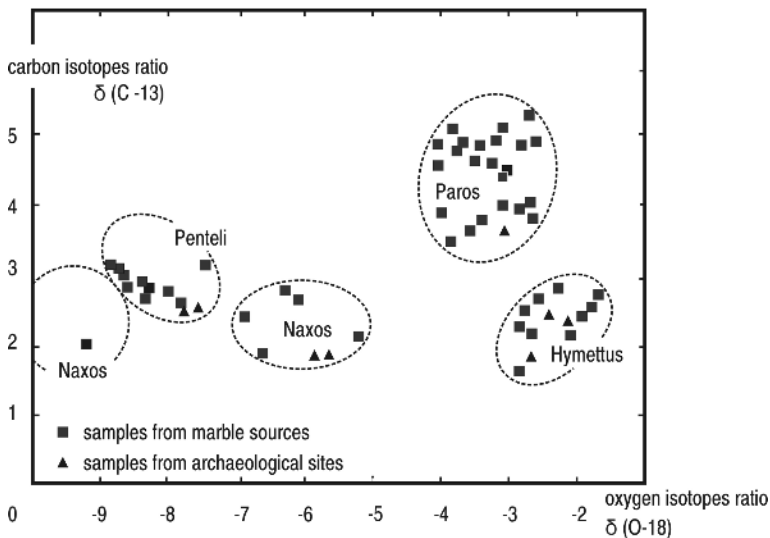


FIGURE 13 Carbon and oxygen isotopes in marble. Measuring the weight ratios between the stable isotopes of carbon and oxygen (i.e., of carbon-13 to carbon-12 and of oxygen-18 to oxygen-16) in marble often enables one to differentiate between different sources of the rock. Having determined such ratios (represented by δ in the graph) in samples from well-known ancient marble sources from the Greek Aegean Islands and from archaeological marble made it possible to identify the sources of the marble. With only one exception, that of marble from the Naxos quarries, these ratios are specific for each source and different from isotopic ratios in other sources (Craig and Craig 1972).

Quartzite. *Quartzite* is a very compact, exceptionally hard and tough metamorphic rock derived from sandstone. It consists mainly of rather large crystals of *quartz* (composed of silicon dioxide) naturally cemented by secondary quartz. Most varieties of quartzite contain over 90% quartz, and in some cases the quartz content exceeds 95% of the total weight of the stone. The color of most quartzite is white or light yellow, but if it contains iron oxide impurities it is red, while other metal oxide impurities may cause the rock to display patchy color variations. Quartzite is very hard, which makes it difficult to quarry. Nevertheless, because of its strength and resistance to weathering, it has occasionally been used for construction, sculpting statuary, and ornamentation.

During the fourteenth century B.C.E., for example, the ancient Egyptians used quartzite for making statuary, stelae, and other constructions. Among these is a famous group of monumental statues known by the plural name *Colossi of Memnon*, near Thebes (see Fig. 14). It is known that one of the Colossi was damaged in antiquity and repaired during Roman times by order of the emperor Septimus Severus. The *provenance* of the quartzite from which the Colossi of Memnon were made was studied using neutron activation analysis to analyze samples removed from the sculptures as well as from a number of quartzite sources from different geographic sites. Comparing the analytical results revealed that the quartzite used to make the statues most probably originated from a quarry quite a distance away from the location of the sculptures: almost 700 km down the Nile from Thebes. The quartzite used for the Roman repair, however, seems to have come from quarries nearer Thebes, upstream the river Nile (Bowman et al. 1984; Heizer et al. 1973).

Soapstone. *Soapstone*, also known as *steatite*, is a very soft metamorphic rock that feels greasy to the touch and can be easily carved and shaped. It consists mainly of the mineral talc (composed of hydrous magnesium silicate), often mixed with small, varying amounts of *magnetite* (composed of iron oxide), and/or *chlorite* (a complex silicate of aluminum, iron, and magnesium). Large outcrops of soapstone occur in many areas on the surface of the earth. Because of the ease with which it can be shaped, soapstone has been widely used since prehistoric times to manufacture small articles such as bowls, vessels, beads, and other decorative objects. It is for this reason that identifying the provenance and the routes of trade of ancient objects made from soapstone has been a subject of investigation since the late nineteenth century. Soapstone from different sources, and even from single sources, generally has variable composition, making it rather difficult to elucidate the provenance of soapstone. Some studies seem to indicate, however,

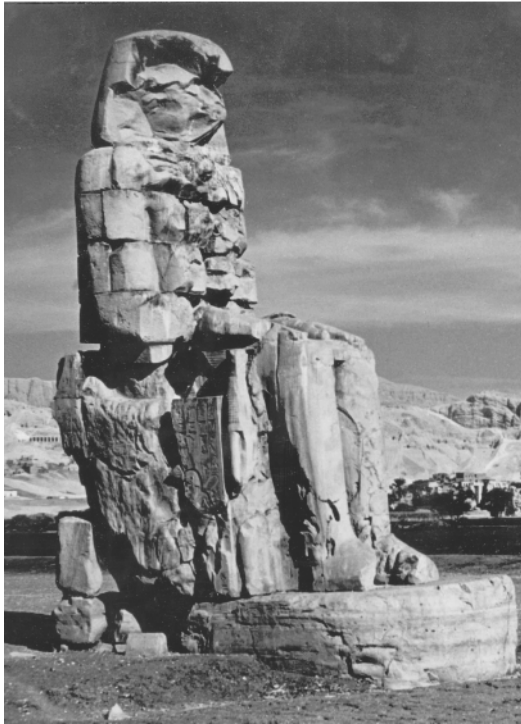


FIGURE 14 The Colossus of Memnon. The photograph shows one of two massive statues (each about 20m high) that once flanked the entrance to the mortuary temple of Amenhotep III, a pharaoh of the eighteenth dynasty of Egypt, on the west bank of the river Nile near Thebes. The statues were sculpted during the fourteenth century B.C.E., each from a single block of quartzite. One of the statues was damaged in antiquity during an earthquake and, since then, it produces at sunrise a musical sound. The ancient Greeks related this sound to the mythological king Memnon calling to his mother. The present condition of the statues is not good, mainly because quartzite is prone to weathering.

that determining the nature and relative amounts of trace elements in the rock may contribute to distinguishing between samples from different sources and to the provenance of archaeological soapstone (Truncer et al. 1998; Kohl et al. 1979).

1.8. PIGMENTS

Pigments are intensely colored and finely powdered solids used (mainly in paints) to impart color to other materials. Since early antiquity most pig-

ments have been prepared by mechanically grinding solid raw materials esteemed for their specific color; most are derived from minerals, although some are of vegetable and animal origin, derived from the bark of trees, the shells of nuts, and the bones and horns of animals (Eastaugh et al. 2004). A few artificial, human-made (synthetic) pigments, known by the generic names *frits* and *lakes*, have also been manufactured since antiquity (Barnett et al. 2006; Koenig and Metz 2003) (see Textbox 20).

TEXTBOX**17****COLOR AND COLORANTS – PIGMENTS AND DYES**

The meaning of the word *color* varies in diverse fields of interest. In the behavioral sciences, for example, color refers to the psychophysiological perception of the appearance of objects or light sources; in chemistry, to substances that have certain optical properties (to exhibit color), and in physics, color refers to a specific property of visible light (Orna 1976). Different colors (i.e., different psychophysiological sensations) are perceived when light from, say, a blue sky, a red rose, or a green leaf falls on the retina of human eyes. Color may be perceived directly from a light source, where it originates, as, with a burning substance that emits colored light, or reflected from colored objects, as with the blue sky or the red rose.

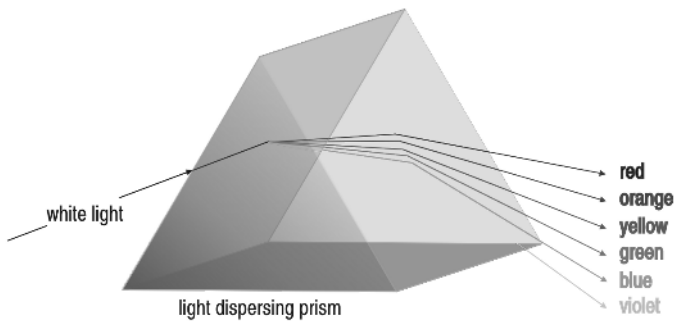
In chemistry, color is generally associated mainly with *colorants*, intensely colored substances that may be either inorganic or organic, of natural origin or artificially made (Billmeyer and Saltzman 1981). Colorants that are insoluble in most liquids, particularly water, and that generally (not exclusively) are of inorganic origin, are known as *pigments* (see below, this chapter) (Lewis 1988). Organic colorants soluble in water and other solvents are known as *dyes* (see Chapter 15) (Hallas and Waring 1994). The color of pigments as well as of dyes is determined by the characteristic range of light wavelengths that they reflect. It is this property to reflect light of specific wavelengths (colors), that makes the pigments and dyes suitable for coloring other materials (McLaren 1986).

In physics, color is an optical property of electromagnetic radiation that is visible to the human eye and has wavelengths ranging between about 410 and 770 nanometers (see Textbox 22). White, colorless light is a mixture of light of all wavelengths within this range. If a beam of white light falls on a transparent glass prism, it is dispersed into a sequence of colored bands, each band characterized by a narrow range of wavelengths, as illustrated in Figure 15.

An object that reflects only part of white light (between, say, 540 and 600nm) appears yellow. Yellow light can also be generated by the

combination of orange–red and green, the two colors adjacent to yellow in the spectrum of white light, or by the combination of all colors except blue, the *complementary* color of yellow (*complementary colors* are pairs of colors that, when mixed with each other, produce another color; all colors have complementary colors).

(a) The dispersion of light by a prism



(b) The spectrum of visible light

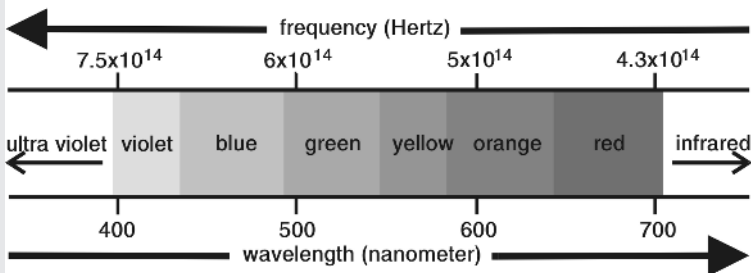


FIGURE 15 The spectrum of visible light. Visible light is the only form of electromagnetic radiation that humans can see. When all the wavelengths of the visible light spectrum in a beam of radiation strike the human eye at the same time, white light is perceived. White is not an actual color, but a combination of all the colors of the visible light spectrum. This can be seen when a beam of white light passes through a prism. Each one of the different colors that make up the beam has a different wavelength and interacts differently with the material from which the prism is made. As it passes through the prism, each color bends differently and the original white beam is spread out into a range of colors as in a rainbow **(a)**; violet has the shortest wavelength (and highest frequency) and red, the longest (and lowest frequency) **(b)**.

Two main properties render a material valuable for producing a pigment: that it reflects light of a particular color and that it covers and hides underlying surface imperfections, a property known as *hiding power*. It is also these two properties that make pigments ideal materials for making *paints*, preparations used to decorate and protect surfaces and obliterate their imperfections (see Textbox 18). Paints have been made and used since very early antiquity (Colombo 1995; Ashok 1993).

TEXTBOX 18

PAINT AND PAINTING

Paint

Paints are colored fluid preparations that are applied as thin coatings to the surface of solid materials where they *set*, serving decorative and/or protective purposes. After a paint is applied and *sets* (it is usually said that it “dries”), it forms a solid, stable, and generally durable coating that imparts its color and often also protects the underlying surface. Humans have been using paints for decorative purposes for well over 20,000 years. It was apparently only during the Middle Ages that it was recognized that the coating formed after paints set also shields the underlying surface from the surrounding environment; since then, paint has been applied specifically also for protective purposes (Gottsegen 1987; Doerner 1984).

Generally, although not exclusively, paints are mixtures of at least three basic components: a *pigment*, a *medium*, and a *binder*. The *pigments* are extensively discussed elsewhere in this chapter. The *medium*, as its name suggests, provides the material agent in which the other components of the paint (the pigment and the binder) are either dissolved or suspended. The medium also determines the *fluidity* (the flowing characteristics) of the paint and it is therefore instrumental in the manner that the paint is applied and the way it sets. The *binder*, also known as the *film former*, is the component that, as the paint sets, forms a solid film that binds the particles of pigment to each other and to the painted surface. Most binders are fluids that solidify to form more or less transparent films. Binders used in antiquity included mainly carbohydrates (such as vegetable *gums*) and proteins (such as animal *glues*) (see Textbox 55). The use of drying oils (and particularly of linseed oil) as binders (see Chapter 10), which became increasingly widespread after the fifteenth century, can be traced no further back than the sixth century c.e. (Wehlte 2001; Masschelein-Kleiner 1985).

Painting

The most common technique of painting, used since antiquity, entails the application – usually with a brush but also with a swab, a stick, or the fingers – of a coating of fluid paint to a surface. *Watercolor* painting, for example, entails the use of transparent paints made up of a mixture of pigments, water, and a gum, such as gum arabic. In *tempera* painting, the pigment is mixed with egg yolk (egg tempera) and often, also with water; in *oil* painting the paint is made by mixing the pigment with a drying oil, usually linseed oil in Europe and tung oil in eastern Asia in the past. Oil paint takes several days to set (“dry”) into a compact and shiny paint coating (the oil does not really dry but sets by polymerizing into a solid layer that holds the pigment and adheres to the substrate). Less common painting techniques used in the past include *fresco* and *wax* (or *encaustic*) painting (Shirano and Hayakawa 2006).

Fresco *Fresco* (the Italian word for “fresh”) painting entails mixing dry pigments with fresh, wet plaster of Paris or lime plaster, which serve as both medium and binder. After the mixture is applied as a coating to a surface (mainly walls, ceilings, and sometimes floors), the plaster dries and sets (hardens), binding the pigment to the surface, which remains permanently colored. The fresco technique employing plaster of Paris was used in India during prehistoric times. In Europe, where fresco painters seem to have preferred mainly lime plaster, the technique was used in Crete, as early as the fifteenth century B.C., to decorate extant Minoan buildings. Later, the Greeks and then the Romans widely expanded the use of fresco painting (Danti et al. 1990; Procacci and Guarnieri 1975).

Encaustic *Encaustic* or *wax painting* is a painting technique in which *beeswax* serves as both the paint’s medium and the binder. *Beeswax*, the wax made by the common bee, is a solid at ambient temperatures that melts at about 65°C. For encaustic painting, pigments are mixed with previously heated, molten wax and the mixture is then applied to the surface to be painted, usually by one of two different techniques: *cestrum* (stump, in Latin) *encaustic*, in which the tool used to apply the paint is a short piece of wood, and *cauterium* (spatula in Latin) *encaustic*, in which a hot spatula serves to apply the paint mixture to the surface being painted, on which it hardens and becomes fixed on cooling. Encaustic painting was practiced by the ancient Egyptians in Fayum, for example, where the *cauterium* technique, in particular, was used for painting ancient portraits (Doxiadis 1995). After the sixth century C.E., the encaustic technique seems to have been almost forgotten in most areas of Western civilization (Mattera 2000; Laurie 1978).

TABLE 16 Natural Pigments

Color	Name	Composition
<i>Inorganic Pigments</i>		
Black	Pyrolusite	Manganese dioxide
	Graphite	Carbon
White	Chalk (also known as whiting)	Calcium carbonate
	Gypsum	Calcium sulfate
	Kaolin	Aluminum silicate
Yellow	Orpiment	Arsenic trioxide
	Ochers and siennas	Natural earths, mixtures of silica and iron oxides
Red	Red ocher	Mixture of silica and iron trioxide
	Vermillion, or cinnabar	Mercury sulfide
Green	Malachite	Basic copper carbonate
	Chrysocolla	Copper silicate
	Green earth	Mixture of aluminum silicates
Blue	Mountain blue or azurite	Basic copper carbonate
	Ultramarine or lapis lazuli	Mainly a mixture of silicate and sulfide of sodium and aluminum
	Glaucophanes	Sodium magnesium aluminum hydrosilicate
<i>Organic Pigments</i>		
Black	Charred bone, charred wood	Mixture of charcoal, calcium phosphate, and calcium carbonate
	Soot	Mixture of charcoal and ash charcoal
White	Burned bone	Mixture of calcium phosphate and calcium carbonate
Brown	Tree bark	Mostly a mixture of cellulose and lignin
	Nut shells	Mostly a mixture of cellulose and lignin

The pigments can be classified according to a variety of criteria, such as their color (blue, red, green, etc.), composition (inorganic or organic), origin (natural or human-made), or other characteristics (Lewis 1988; Feller 1986). Common pigments used since antiquity are listed and classified, according to their color, in Table 16; some of those most commonly found in archaeological sites are discussed in the pages that follow.

White Pigments

The Latin term *terra alba* (white earth) is often used indiscriminately to refer to such white minerals as *chalk*, *gypsum*, and *kaolin*. *Chalk*, also known as

whiting (composed mainly of calcium carbonate), and *gypsum* (composed of calcium sulfate) were the most commonly used white pigments of antiquity. *Kaolin* was used only in limited geographic regions where this primary clay was abundant or easily available. Chalk and gypsum rocks are widely distributed on the surface of the earth. Before being used as pigments, they are crushed and ground into fine powders. *Kaolin*, also known as *China clay*, generally occurs naturally mixed with unwanted contaminants, from which it is separated before use (see Chapter 4).

Probably one of the first artificially made pigments was *bone white*. Preparing bone white is usually done by first burning bones, generally in open fires, until all the organic material in the bones is burned away, and then crushing the product into a white-grayish, slightly gritty powder. Almost any sort of bone would suffice for making bone white, although many ancient recipes particularly recommended the use of specific types of bone such as from the wings of birds or the legs of domestic animals. White bone is composed mainly (85–90%) of calcium phosphate mixed with calcium carbonate (13–9%), minor constituents making up the rest.

Lead white (composed of highly poisonous basic lead carbonate) is another white pigment known since ancient times; its use seems to have started during Greek or Roman times. Lead white has excellent hiding power, that is, it effectively obliterates underlying imperfections on the painted surface; it also weathers well, remaining in a very good condition for long periods of time. These properties are unequaled by either chalk or gypsum. Although it occurs naturally, artificially made lead white seems often to have been preferred. Artificial lead white was made by exposing lead to the corrosive effect of vapors of vinegar (a natural solution of acetic acid) and carbon dioxide. The places where it was manufactured were reported in many catalogs and lists of pigments written since ancient times and on into the nineteenth century. Despite its toxicity, of which they may have been unaware, the ancient Romans used lead white not only as a white pigment but also as a cosmetic face powder (Gettens et al. 1967).

Black Pigments

The black pigments of antiquity fall into one of two categories: *mineral blacks* and human-made *vegetable* and *animal blacks*. The most common mineral blacks are *pyrolusite* and *graphite*. *Pyrolusite*, also known as *manganese black* (composed of the dioxide of manganese) has been widely used not only as a black pigment but also as a glass decolorizer (see Chapter 3). *Graphite*, also known as *plumbago*, can be either black or dark gray. It is composed of elemental carbon, as it is one of the two naturally occurring mineral allotropes

of this element (see Textbox 19). Artificial, human-made black pigments have been derived mostly from either vegetable or animal matter. *Animal blacks* are made by charring (partly burning) either bone or ivory. To prepare *bone black*, bones are burned in an oven or closed pit in which there is a reducing atmosphere, that is, a restricted supply of air and therefore a dearth of oxygen.

TEXTBOX 19

ALLOTROPES

A number of chemical elements, mainly oxygen and carbon but also others, such as tin, phosphorus, and sulfur, occur naturally in more than one form. The various forms differ from one another in their physical properties and also, less frequently, in some of their chemical properties. The characteristic of some elements to exist in two or more modifications is known as *allotropy*, and the different modifications of each element are known as its *allotropes*. The phenomenon of allotropy is generally attributed to dissimilarities in the way the component atoms bond to each other in each allotrope: either variation in the number of atoms bonded to form a molecule, as in the allotropes oxygen and ozone, or to differences in the crystal structure of solids such as graphite and diamond, the allotropes of carbon.

Oxygen and Ozone

Oxygen has two allotropes, ordinary *oxygen* and *ozone*. Its allotropy is due to variations in the number of atoms bonded to each other in a molecule. The molecules of the most abundant allotrope, common *oxygen*, the gas that makes up over 20% by volume of the atmosphere of the earth, consist of two atoms of oxygen bonded together (O_2); those of *ozone*, also a gas, are made up of three bonded atoms of oxygen (O_3) as illustrated in Figure 16. The formation of ozone on earth is initiated mostly by ultraviolet radiation from the sun, which, on entering the stratosphere, splits oxygen molecules into separate atoms. Following the split, the separate atoms of oxygen recombine back into molecules, mainly of oxygen, but also of ozone. It is for this reason that most of the earth's ozone occurs naturally in the stratosphere, in the ozone layer, at a height between 15 and 30 km above the surface of the earth (see Fig. 82).

In the lower layers of the atmosphere, ozone occurs only in trace quantities. Some ozone, however, is also created in the lower atmosphere by lightning, during electric storms, accounting for the "smell of rain" that

often arises when lightning strikes. Usually, a short while after lightning strikes, most of the ozone thus created begins to gradually revert back to ordinary oxygen. The small amounts of ozone that remain in the atmosphere constitute an active air pollutant and an aggressive oxidizing agent that greatly contributes to the decay of much organic matter. Archaeological materials that are attacked by ozone include skin and leather, textile fibers, dyes, and the remains of dead organisms.

Carbon: Graphite and Diamond

The allotropy of carbon is due to variations in the crystal structure of the element. There are three allotropes of carbon: graphite, *diamond*, and

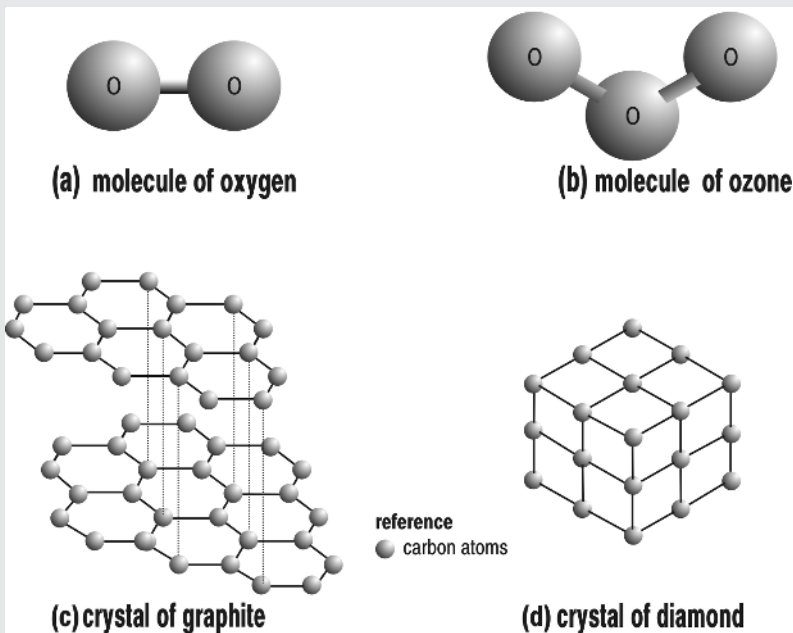


FIGURE 16 Allotropes. Allotropes are structurally different forms of the an element. Oxygen, for example, occurs naturally in two allotropic forms: oxygen and ozone. The molecule of oxygen (a) consists of two bonded atoms of oxygen, while that of ozone (b), which is extremely active in the decay of ancient organic materials and particularly of dyes and textiles, is made up of three bonded oxygen atoms. Carbon also occurs naturally in two allotropic forms: graphite and diamond. In graphite (c) the carbon atoms are arranged in planar sheets, stacked parallel and loosely bonded to each other, which easily flake apart. In diamond (d) the atoms of carbon are arranged in a three-dimensional cubic pattern, which makes it extremely strong and hard.

fullerene. Only the first two, graphite and diamond, occur in nature; *fullerene*, which is artificially made by humans, was discovered quite recently, at the end of the twentieth century. *Graphite* occurs naturally as a dark gray, greasy-feeling mineral, which has been used, since antiquity, as a black pigment. Its greasy feel is due to the crystal structure of graphite: each carbon atom in the graphite structure is attached to another three, forming large, flat sheets of hexagonally bonded carbon atoms. The sheets have smooth surfaces that can easily slide and move relative to one another and also provide the greasy feeling. *Charcoal*, often found in archaeological excavations, consists of a porous mixture of graphite and partially carbonized organic compounds. It is formed when organic matter, particularly wood, burns in an atmosphere lacking or devoid of oxygen. In *diamond*, a gemstone, each carbon atom is attached to others within the ordered crystalline, tetrahedral structure. Since the carbon atoms are relatively small and the bonds between them are very strong, diamond is very hard, the hardest material known. It is because of its hardness, for example, that diamond powder has long been used as an abrasive for drilling holes and polishing surfaces. The crystals of diamond are also very tough and resistant to pressure; if tapped in just exactly the right place, however, they cleave along crystal faces.

Tin and Tin Pest

Another element that exhibits allotropy because of variations in the crystal structure is tin. The common allotrope is *tin metal*, also known as α (*alpha*) *tin*, which is stable at ambient temperatures. The other allotrope, which generally occurs as a gray powder and is known as β (*beta*) *tin*, but also as *tin pest*, is formed only at very low temperatures: when tin cools down to temperatures below -18°C , the ordinary allotrope, α tin, is converted to β tin, and the transformation is irreversible under ordinary temperatures. Tin objects exposed to temperatures below -18°C in very cold regions of the world, for example, are generally severely damaged when part of the tin converts to tin pest. In extreme cases, when exposure to low temperatures extends for long periods of time, the allotropic conversion may result in the transformation of tin objects into heaps of gray β -tin powder.

Black pigments of vegetable origin have generally been made from various kinds of charred plant matter, mostly wood, but also leaves or seeds; the *charcoal* formed during the charring process is then washed, to remove soluble matter, and finally ground to powder. Over 95% of well-burned char-

coal black consists of elemental carbon; the remainder is ash, composed of salts and minerals in the original vegetable matter.

Red Pigments

The best-known and most widely used ancient red pigments were *red ocher* and the mineral *vermilion*. The *ochers* and *siennas*, also known by their more general name, *natural earths*, are a group of mixtures of clay, silica, and iron oxides. Their color, which may vary from yellow or light brown to dark brown and even to orange and red (see discussion on red ocher, below), is due mainly to iron oxides that occur either as *hematite* (composed of ferric oxide), or as *limonite* (composed of hydrated ferric oxide). Often the natural earths also contain small amounts of black *pyrolusite*, which makes them darker, and/or calcium and barium carbonates, which make them lighter. There is no sharp compositional difference between ochers and siennas, in either iron content or color; it is customary, however, to classify natural earths of lighter color and lower iron oxide content as ochers, and those of darker color and slightly higher iron oxide content as siennas. The intense red of red ocher, for example, is due mainly to a relatively high proportion of hematite (which is red) in the mixture. Deposits of red ocher abound in many places on the surface of the earth; only a few, however, are considered red enough and suitable for use as pigments. Red ocher has excellent hiding and staining powers, and it probably was one of the preferred red pigments of antiquity.

Vermilion and *cinnabar* are two bright red, toxic minerals that share an identical composition (they are both composed of mercury sulfide) but have different crystal structures. Two kinds of vermilion are known: one of natural origin and another made artificially. Finely ground natural vermilion may vary in hue from red to liver-brown and even to black. Artificial vermilion was made from mercury and sulfur; the method of preparation seems to have been developed by the Chinese and was introduced into Europe only during the eighth century C.E. (Gettens et al. 1972).

Red lead, also known as *minium*, is a bright red pigment with excellent hiding power. It is composed of lead tetroxide and occurs naturally as a mineral. Much of the minium used in the past as a pigment, however, seems to have been artificially made by oxidizing at high temperature, about 500°C, either metallic lead or the mineral litharge (composed of lead monoxide). To prepare minium, one of these materials, either the metal or litharge, was heated in a well-aired atmosphere, to ensure an abundant supply of oxygen, until the product acquired a desired red color. Red lead has been identified

in wall paintings from China and Central Asia. It seems that in Egypt red lead was used only since Greco-Roman times; in latter times it became the favorite pigment of Persian and Byzantine illuminators (Fitzhugh 1986).

Another artificial red pigment is *madder lake*, an artificial, human-made pigment (Textbox 20). Madder lake is obtained when madder dye (see Chapter 14) is deposited on the surface of powdered kaolin or chalk grains. Preparing madder lake was, and still is, such a complicated process that even today some manufacturers are unwilling to disclose either its formulation or details on the actual method of preparation. A pink color in paintings on the plaster in tombs from the Greco-Roman period was identified as consisting of madder dye on a gypsum base.

TEXTBOX 20

MAN-MADE PIGMENTS: FRITS AND LAKES

Frits and *lakes* are two basically different types of human-made synthetic, pigments. *Frits* consist of colored glass, *lakes* of white or transparent painted powders. *Frits* are made by heating together, to high temperatures, a mixture of two or more minerals (including at least silica and lime) until they melt and form a colored glass (see Chapter 3). After cooling, the resulting solid is usually ground into a fine powder; it is only then that it becomes known as a frit, which can be used as a pigment. *Egyptian blue* is an example of a frit known since early antiquity (see Chapter 7).

Lakes are made by conferring a more or less permanent color to the surface of the grains of white or transparent powders insoluble in water. The powder is almost invariably of inorganic origin, for example, gypsum, chalk, or kaolin. To prepare a lake, any one of these materials, in powdered form, is treated with a water solution of a dye of a wanted color; the dye is either adsorbed on the surface of the powder grains, where it becomes more or less firmly held, or it reacts (chemically) with the surface of the grains. In either case, the result is a colored powder, insoluble in water that has the same coloring properties as natural pigments (Kirby 1977, 1988). Lakes were prepared in antiquity from many dyes. Some were valued for their bright colors, although most faded rapidly under sunlight. *Madder lake*, for example, derived from madder dye, and *lac*, derived from the red lac dye, have been widely used for painting since ancient times (Harrison 1936).

Yellow Pigments

Three main types of natural yellow pigments were known to the ancients: *yellow ochers* and *siennas* (see descriptions above) and *orpiment* (a highly poisonous, soft, lemon-yellow mineral composed of arsenious sulfide). Orpiment was identified in Egyptian paintings at Tell-Amarna, in Egypt, and it is mentioned in the writings of the Roman writers Vitruvius and Pliny. In the past orpiment was used not only as a pigment but also for the removal of hair from animal hides before the tanning processes (see Chapter 11). Another artificial yellow pigment, generally known by its Italian name *giallolino*, is composed mainly of basic lead antimoniate. It seems that *giallolino* was first prepared during the seventh century C.E. by heating a mixture of tartar emetic (composed of antimony potassium tartrate), common salt (sodium chloride), and lead nitrate; cooling the molten mixture resulted in the formation of a yellow solid that, when crushed into a powder, produced the pigment.

Green Pigments

A variety of mineral ores, mostly copper minerals such as *malachite* and *chrysocolla*, were probably the most used green pigments in the past. Various green minerals derived from metals other than copper, such as *green earth* (see below) were used in confined regions.

Malachite is a bright green mineral (composed of basic carbonate of copper), which is widely distributed in nature. The consolidated form of the mineral has also been appreciated since antiquity as a semiprecious gemstone. Powdered malachite was used as a pigment by the ancient Egyptians from predynastic times, later by the Romans in illuminated manuscripts, and by the Chinese in paintings from the ninth century C.E. *Chrysocolla*, also a copper mineral (composed of hydrated silicate of copper), may range in color from bright green to bright blue. It is often found naturally mixed with other minerals of copper, such as malachite and azurite.

Green earth, best known by the Italian name *terra verte*, is probably the main green pigment not derived from copper. Terra verte is a mixture of two minerals, *caledonite* and *glauconite*, both complex silicates of aluminum, calcium, iron, magnesium, and potassium silicate (Grissom 1986).

The most widely used artificial green pigment was *verdigris* (composed of basic acetate of copper). Exposing either metallic copper or copper minerals to vinegar for a few weeks, while allowing free access of air, results in the formation of a green solid composed of basic acetate of copper. Drying the solid and then crushing and powdering it produced verdigris.

Blue Pigments

Mountain blue, *ultramarine*, and *glaucothane* were the most widely used natural ancient blue pigments. *Mountain blue* is made by crushing and reducing to a powder the bright blue mineral *azurite* (composed of a basic carbonate of copper) that occurs in only a few regions of the world from where it was and still is exported in the form of massive rocks. *Ultramarine* is the name of the dark blue pigment obtained when lapis lazuli is crushed and powdered. Lapis lazuli, a rare rock of gemstone quality, is a mixture of minerals that include *calcite*, *muscovite*, and *lazurite* (composed of sodium calcium aluminum silicate sulfate). The source of most lapis lazuli used in the ancient world seems to have been mines in the Badakhshan region of Afghanistan, from where it has been continuously exported for over six millennia (von Rosen 1990). *Glaucothane*, a blue mineral (composed of sodium magnesium aluminum hydrosilicate), was used by the Greeks as a blue pigment as early as the seventeenth century B.C.E.

Egyptian blue is an artificial blue pigment that was made in the ancient Middle East, particularly in Egypt, where it is still made and used. Egyptian blue should not be confused with another, also blue or greenish-blue, *Egyptian faience*, which is made from much the same raw materials (see Chapter 7). *Egyptian blue* is made by first preparing a mixture of sand, natron, and copper filings and then heating the mixture to about 850°C. The raw materials melt at this temperature, reacting with each other to form a definite chemical compound (composed of copper calcium tetrasilicate). As the melt cools, it does not crystallize but solidifies into a *frit* (see Textbox 20), which is then powdered (Tite 1986).

Another artificial pigment, a particular light blue, is *Maya blue*, which was made by the Maya Indians in pre-Columbian Mexico. Maya blue is not a frit, however, as is Egyptian blue, but probably a lake. Although its precise components are still unknown, it may have been prepared by thoroughly mixing a clay (such as attapulgite or palygorskite) with blue indigo dye and then heat-treating the mixture before use (Reyes-Valerio 1993).

1.9. ABRASIVES

Cutting, grinding, and shaping stone, and in particular burnishing and polishing the surface of stone as well as metals, requires the use of *abrasive* materials that are harder than the solids to be cut, ground, burnished, or polished. Sapphire and ruby, two very hard gemstones, for example, can be cut or polished only with the assistance of diamond powder, an abrasive that is harder than sapphire or ruby. Diamond is the hardest material

TABLE 17 Natural Abrasives

Excellent (hardness above 7 on Mohs scale)	
Diamond	Garnet
Corundum	Emery
Average (hardness 5.5–7 on Mohs scale)	
Basalt	Quartz
Feldspar	Sandstone
Inferior (hardness below 5.5 on Mohs scale)	
Clay	Limestone
Alumina	Magnesia

known, and diamonds can be cut, ground, or polished only using diamond powder.

Abrasives are hard materials that, in powdered form, are used to cut or alter the dimensions, shape, or condition of the surface of solid bodies by abrasion, that is, by scraping away or rubbing the solid material. The abrading effectivity of any abrasive is determined mainly by its *hardness* (see Textbox 23), although it is also affected by its *toughness* (the resistance of materials to fracture under stress), as well as by the shape of its grains (Jacob 1928). All the abrasives used in antiquity were hard and tough powdered minerals such as *flint*, *corundum*, *emery*, and *garnet*. There is evidence, for example, that as early as the fifteenth century B.C.E. Egyptian crafters used abrasives when carrying out grinding and polishing operations (Peltz and Bichler 2000). A convenient way of classifying abrasives is by hardness and the type of minerals from which they are derived, as shown in Table 17.

1.10. GEMSTONES

Minerals, rocks, and a few consolidated materials of organic origin that, when cut and polished, acquire visual appeal and are also durable and relatively rare are known as *gems* or *precious stones*. *Gemstones* have been used since time immemorial for ornamentation and personal adornment, their use representing a sign of social position and wealth. The interest of human beings in gemstones can be traced so far back that the trail is lost in the dim reaches of time. Probably the earliest evidence of working gems is from Spain and southern France, where over 70,000 years ago stone, ivory, and horn were carved and polished. Since that time there has been a continuous and growing interest in gems. The transportation of gems through trade routes seems to be well over 5000 years old; lapis lazuli, probably from Afghanistan,

for example, was then being traded in western Asia and Egypt (von Rosen 1990). Emeralds seem to have been favored during the Hellenistic period, while amethyst, sapphire, and diamond became relatively popular during Roman times. Many of these gemstones, set in jewelry, have survived to the present day (Hackens and Moucharte 1987).

Most gemstones are minerals; only a few are other inorganic or organic materials. Out of an estimated 3000 minerals known on the crust of the earth, however, only about 100 are valued as precious and semiprecious gemstones. When extracted from the crust of the earth, most gemstones have a rough surface and irregular shape, and to reveal and enhance their beauty they have to be cut and polished. Minerals of gem quality are formed and found in the most varied environments. Diamonds, for example, occur mainly among igneous rocks but also in sand or gravel deposits. Sapphires and rubies are usually found within metamorphic rocks. *Jade* is, in itself, a type of metamorphic rock. Turquoise and opal are formed in sedimentary rocks as a result of groundwater seeping through and dissolving rocks; when the water evaporates, the dissolved solids finally precipitate to form the stones.

TEXTBOX 21

THE STRUCTURE OF SOLIDS: AMORPHOUS AND CRYSTALLINE MATERIALS

Solid materials can be classified, on the basis of how their constituent particles (atoms, ions, or molecules) are arranged in space, into two groups: *amorphous* and *crystalline solids*. *Amorphous solids*, literally “solids without shape,” such as obsidian and glass (see Chapters 2 and 3), are devoid of any regular internal arrangement. Their component particles are distributed at random within the bulk of the solid and lack short- or long-range geometric order. In *crystalline solids* such as table salt and quartz, the component particles occupy definite, fixed positions; they are arranged in a characteristic, symmetric, and repeating pattern that extends from one edge of the solid to the other. A crystalline solid is therefore a solid characterized by an ordered, regular, and symmetric three-dimensional arrangement of its component particles (see Fig. 17).

Crystalline Solids

Crystalline solids have a regular geometric shape bound by plane surfaces that intersect at characteristic angles. Their shape results from the arrangement of the particles (atoms, ions, or molecules) within the crystals, in an

orderly pattern and connected by bonds in a repeating layout. Essentially, all crystalline solids are made up of basic units cells containing a small number of particles, thus known as *unit cells*, repeated in a regular way, again and again, throughout the solid. The geometric, regular arrangement of the unit cells is known as the *crystal form* and the surfaces that bound a crystal are known as the *facets*.

The most characteristic and unique property of crystalline solids is however, neither the shape of their crystals nor the relative size of the crystal faces, but the angle between any pair of crystal facets. For any substance, the angle between the crystal facets is constant and invariable, regardless of the overall shape or size of the crystals. Under some circumstances a substance may form short, wide crystals, while under others, the

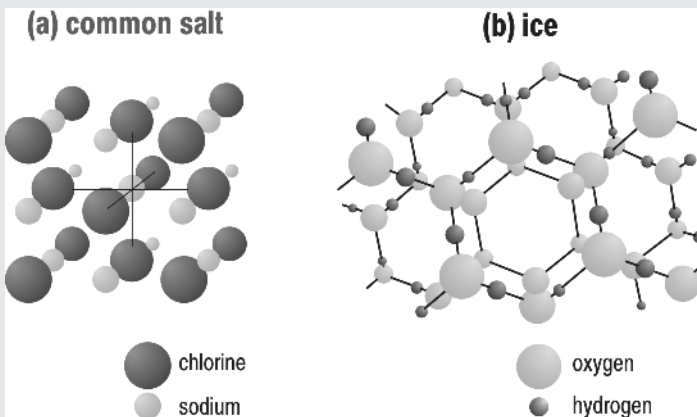


FIGURE 17 Crystalline solids. A “solid” is a relatively compact state of matter in which the component atoms are close together, forming a rigid structure that has a definite volume and shape. There are two main types of solids: crystalline and amorphous solids. In “crystalline” solids the atoms are arranged in orderly, regular and repeating patterns known as “crystals.” The arrangement of the atoms within the crystals determines many of the chemical and physical properties of the solids. The smallest repeating pattern in a crystal is a “unit cell,” a geometrically regular arrangement of atoms held together by electrical forces known as “bonds.” All minerals are crystalline solids. In the crystals of sodium chloride (common salt) (a), for example, the atoms of sodium and chlorine are interlocked in a cubic spatial arrangement in which the unit cell is made up of four atoms of sodium and four of chlorine. In ice (b), also a crystalline solid, each atom of oxygen in the unit cell is surrounded by four atoms of hydrogen. The extremely small unit cells, invisible to the naked eye, combine with each other to form visible crystals. One small grain of common salt, for example, contains about 10^{18} (1,000,000,000,000,000,000) unit cells. In amorphous solids, such as obsidian and glass, the atoms that make up the material are randomly oriented relative to each other, lacking any long-range order.

crystals of the same substance may be long and narrow. The angle between any single pair of crystal faces, whether the crystals are short and wide or long and thin, will be the same in all the crystals of any substance, regardless of their dimensions.

All minerals and many solid substances of inorganic as well as organic origin exhibit characteristic crystal structures. The crystal structure of the *primary minerals*, for example, is formed when hot magma cools down; as the temperature of the magma decreases, the component atoms of minerals become spontaneously ordered in unique, symmetric arrangements. When the mineral finally solidifies, the solid preserves this symmetric arrangement in its characteristic crystalline structure. In *secondary minerals* the crystals are formed as a result of the integration, at a specific temperature and pressure, of small crystallites that came out of solution and precipitated (Goldman 1991).

The Study of Crystals

The structure of crystalline materials is studied using *crystallographic techniques*. Based mainly on the use of penetrating radiation, such as X- and gamma rays but also on other physical techniques, *crystallographic studies* reveal the exact position of atoms within solids. Such studies thus clarify the relationship between the structure and the properties of crystalline solids. Graphite and diamond provide illuminating examples of how the extremely different properties of these two substances are determined solely by the spatial arrangement of the atoms of a single element, carbon (see Textbox 19).

Gemstones can usually be identified and characterized by a number of physical properties; if they are minerals, mainly by their crystal structure, but also by their density, hardness, color, and other physical properties. All gemstones of any one type of mineral have the same crystal structure (see Textbox 21), but the crystal structure varies from one type of gemstone to another.

Mineral gemstones that have the same basic chemical composition, that is, are composed of the same major elements and differ only in color, are considered as variations of the same mineral species. As gemstones, however, minerals that have the same composition and crystalline structure but exhibit different colors are classified as different gemstones. *Beryl*, for example, a mineral (composed of beryllium aluminum silicate), includes a pink variety, known by the gemstone name of *morganite*, and also a well-known green variety, *emerald*. Table 18 lists and classifies, by composition and color, gemstones that have been appreciated since antiquity.

TABLE 18 Gemstones

Gemstone and Varieties	Composition	Color
<i>Metal Silicates</i>		
Adularia	Potassium aluminum silicate	Varies
Beryl	Beryllium aluminum silicate	
aquamarine		Green-blue
emerald		Brilliant green
Jade		
jadeite	Sodium aluminum silicate	Mainly green, but also
nephrite	Calcium magnesium silicate	other colors
Quartz	Silica	
agate		Banded or patterned
amethyst		Purple
jasper		Varies
onyx		Black and white bands
rock crystal		Transparent
Topaz	Aluminum fluorosilicate	Pink to red
Tourmaline	Complex borosilicate	Variable
Turquoise	Hydrous copper aluminum silicate	Light blue
Zircon	Zirconium silicate	Variable
<i>Metal Oxides</i>		
Chrysoberyl	Beryllium aluminum oxide	
cat's eye		Variable
alexandrite		Red/green
Corundum	Aluminum oxide	
ruby		Red
sapphire		Any color but red
Spinel	Magnesium aluminum oxide	Variable
<i>Unrelated Composition</i>		
Diamond	Carbon	Usually colorless
Garnet	Mixture of several minerals	Variable
Opal	Variable	Flashing
<i>Organic Origin</i>		
Amber	Fossil resin	Yellow//brown/red
Coral	Calcium carbonate	Red/pink
Ivory	Mixture of calcium carbonate	Creamy white
Jet	Fossilized wood	Black
Nacre	Aragonite + organic compounds	Mainly white; iridescent
Pearl	Aragonite + organic compounds	Mainly white; iridescent

The color of most gemstones is due to either chemical impurities within their crystal structure or defects in the arrangement of the atoms that make up crystals [the word *impurity* is used here to refer to atoms, generally, although not exclusively, for metals, which occur in extremely small (trace) amounts, within the crystal structure of the gemstone (see Textbox 8)]. As a result of the impurities absorbing or reflecting light incident on them, gemstones display particular and characteristic colors. Pure *corundum*, a mineral of gem quality (composed of aluminum oxide), for example, is colorless when the only elements in its crystals are aluminum and oxygen. Even if minimal amounts of aluminum atoms in the corundum crystal are replaced by those of other metals, however, the mineral exhibits other colors. *Sapphire*, for example, is a variety of corundum in which some of the atoms of aluminum have been replaced by those of titanium or iron. If the replacing atoms are of chromium, the gemstone is deep red and is then known as *ruby* (O'Donoghue 1970; Herbert Smith and Phillips 1962).

TEXTBOX 22

LIGHT: ITS NATURE AND PROPERTIES

Light is electromagnetic radiation that is visible to the human eyes. The range of light wavelengths extends between approximately 410 and 770 nanometers, an extremely limited and narrow range when compared with the entire spectrum of electromagnetic radiation (see Textbox 5). All light originates in *excited atoms*, that is, atoms having more energy than do regular atoms. Excited atoms are formed when regular atoms gain energy from external sources, as, for example, when heated or struck by other particles. Atoms heated to high temperatures, above about 450°C, for example, acquire energy, get excited, and become *incandescent*, releasing the added energy in the form of light. The emission of light reveals the loss of previously acquired, excess energy. Light acquired from the sun is used by plants for carrying out the photosynthesis process (see Textbox 54) and by animals and humans to see. Since it originates in atoms, light is also extremely useful for a range of physical and chemical studies on matter, particularly for the identification and characterization of elements and substances.

The Nature of Light

Light has a dual character – it may be described either as a *wave motion* or as a *stream of moving particles*. Since light is a form of electromagnetic radiation, its properties, as with all forms of electromagnetic radiation, are

those of a *wave motion* (see Textbox 5). In some cases, however, light behaves as a *stream of particles* moving along a straight line. Thus, although light can be accurately described as a wave motion, it can also be described as a stream of small particles, known as *photons*. Regardless of how it is described, whether as a wave motion or as a stream of moving particles, light carries energy, and the amount of energy it carries determines its color.

Light, as do all forms of electromagnetic radiation, moves very fast. In a *vacuum* (in empty space, devoid of any matter) light travels at the highest velocity that anything can move in the universe, 300,000 kilometers per second; when it travels through any kind of matter, however, its speed is reduced. This happens because in empty space there is nothing to obstruct the path of light and its traveling velocity is maximal; when it passes through any type of matter, however, light interacts with particles that it encounters in its path and is slowed down. The interaction of light with different forms of matter gives rise to various phenomena, such as those of *reflection, refraction, absorption, dispersion, scattering, polarization, and luminescence*.

Light Reflection and Refraction

When a beam of light reaches a surface delimiting between two different materials, such as air and water, glass and water, or any other pair of materials, part of the light beam is *reflected*, that is, it is turned back from the surface. Provided the second material is transparent, the part of the beam that is not reflected passes through the surface, enters the material and changes its path. Such a beam is said to be *refracted*.

The angle between the path of an incoming beam and the *normal* (the line perpendicular) to the surface is known as the *angle of incidence*. A reflected beam makes the same angle to the normal as the incoming beam but on the other side of the normal. When a beam of light is reflected from a smooth surface, all of the light is reflected in the same direction. If it is reflected from a rough surface, however, the beam is said to be *diffracted* (split) into many reflected beams going in many directions. This is because the normal at each spot on the rough surface points many different ways (see text below).

As for the *refracted* beam, the change in its direction is due to a change in the velocity of light as it passes from one medium to another. When a beam of light passes from a fast medium (such as a vacuum or air) to a slower medium (e.g., a crystalline solid), the change in velocity causes the beam to bend toward the normal (line perpendicular) to the boundary between the two media (see Fig. 18). The *index of refraction*, also known as the *refractive index*, the numerical value of the ratio between the speed of light in a vacuum to the speed of light in a material, provides

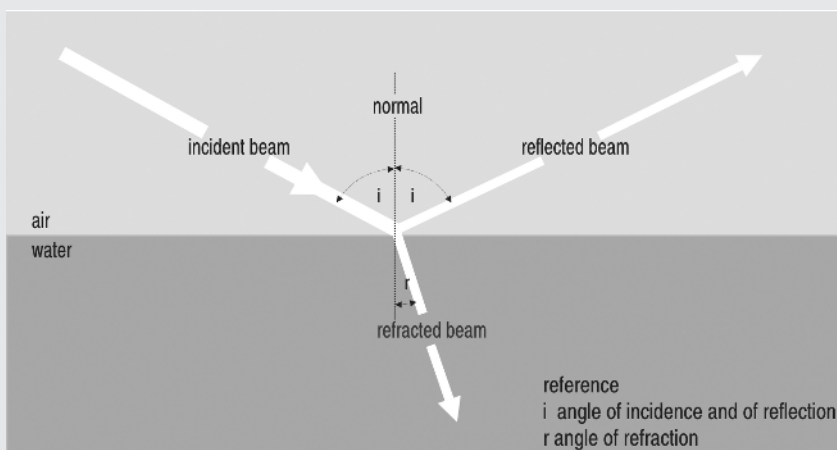


FIGURE 18 The reflection and refraction of light. Objects can be seen by the light they emit or, more often, by the light they reflect. Reflected light is light thrown back from a surface; it obeys the law of reflection, which states that the angle of reflection equals the angle of incidence (i) (the angle of incidence is the angle an incident beam makes with an imaginary line perpendicular to the reflecting surface). Light that passes with an imaginary line perpendicular to another as, for example, when traveling from air into water, is known as “refracted light.” On changing media (from air to water in the example above), the speed of the light changes and consequently, in almost every case the angle of refraction (r) is different from the angle of incidence.

a measure of the extent to which a beam of light changes direction as it passes from a vacuum to a material. The index of refraction is characteristic for each material and different from that of other materials.

Measuring the index of refraction of a material is generally done using an instrument known as a *refractometer*. Typical values of the index of refraction of gemstones and other materials are listed in Table 19. The relatively high index of refraction of diamond, for example, accounts for its distinct brilliance and multicolor display; the index of refraction of rutile, a gemstone composed of titanium dioxide, is even higher than that of diamond, and rutile is indeed more brilliant than diamond.

Light Dispersion

White, ordinary light consists of a mixture of wavelengths. When a beam of white light refracts at a surface, the paths of the beams of different wavelengths *refract* to slightly different angles. After *refraction*, a beam of white light is, therefore, spread into many beams of diverse colors. The greater the index of refraction of the substance, the higher the dispersion

TABLE 19 Refractive Index of Common Archaeological Solids

Material	Refractive index (ρ)
Amber	1.55
Beryl	1.57–1.60
Calcite	1.48–1.66
Diamond	2.41
Ivory	1.51–1.55
Glass	
Soda-lime glass	1.50–1.55
Crystal (lead glass, flint glass)	1.60–1.85
Ice	1.33
Ivory	1.54
Obsidian	1.48–1.51
Opal	1.41–1.45
Pyrite	above 1.81
Quartz	1.54–1.55
Ruby	1.76
Rutile	2.65–2.69
Sapphire	1.76–1.78
Topaz	1.60–1.65
Turquoise	1.62–1.65
Water	1.31

of the light and the wider the spread of the different-colored beams (see Fig. 15a). The spreading of a beam of white light into beams of different wavelengths and of different colors is known as the *dispersion of light*. When a beam of white light passes through a transparent prism, for example, the white light is dispersed into different colors ranging in wavelength from about 400 nanometers (violet) to 770 nanometers (red), known collectively as the *visible light spectrum*, shown in Figure 15b.

Most materials exhibit specific colors because they absorb certain wavelengths (colors) from white, ordinary light. A red object exposed to white light, for example, appears red because atoms on its surface absorb all the other colors in the beam and reflect only red. If transparent materials contain coloring materials, such as dyes or pigments, they absorb the characteristic color of the coloring material.

Light Scattering

When a beam of light strikes small particles in its path, the light is said to be *scattered*: the particles send off the light incident on them in many directions. Part of a beam incident on a translucent material, for example,

is scattered by particles or air bubbles within the material and only the remainder of the beam passes through. It is the scattering of light that makes it impossible to see through translucent materials. Opaque materials scatter and absorb all the light incident on them, blocking its passage.

Light Interference

When the paths of two light beams cross at a given spot, they are said to *interfere* with each other; they either add light to or subtract light from each other. If the two beams add together to form a stronger, more intense beam, providing brighter light than either beam separately, the phenomenon is known as *constructive interference*. If the beams subtract from each other, they give rise to a weaker, dim beam, or even to a region of darkness. This latter phenomenon is known as *destructive interference*. The interference of white light, for example, results in spectral colored fringes. It is the interference of light that causes the iridescent colors often seen in decayed archaeological glass.

Light Polarization

The electric field that creates the waves of a beam of ordinary light *oscillates* (varies in strength) in many directions perpendicular to that of the path of the beam (see Textbox 5), and ordinary light is said to be *unpolarized*. The phenomenon known as *light polarization* is caused by oscillations (variations in the strength) of the electric fields that make up a wave of light. If the direction of the oscillations points in just one direction the light is said to be polarized. Polarized light is used to characterize amino acids and also to date animal remains (see Textbox 66).

Luminescence

Materials gain energy either when heated or when irradiated with some form of energetic radiation, such as ultraviolet light or gamma rays. The higher the temperature or the amount of radiation, the higher the energy gained. When heated to high temperature most materials lose part of the energy gained by emitting light; at about 450°C rocks, minerals, and metals, for example, become *incandescent*, spontaneously losing part of the energy gained and shining brightly.

Many forms of nonmetallic matter can also lose energy they gained by processes other than becoming incandescent. Some materials previously heated or irradiated with some form of energetic radiation may even lose energy long before becoming incandescent and do so by a process known as *luminescence*. Two forms of *luminescence* are generally distinguished, *fluorescence* and *phosphorescence*. If the luminescence is emitted at the time of irradiation but ceases to be so immediately after the

irradiation is discontinued, the luminescence is known as fluorescence. The fluorescence phenomenon is often used in archaeological studies to distinguish between genuine and fake materials (see Chapter 18). If the luminescence persists and continues after irradiation, it is known as *phosphorescence* [phosphorescence can sometimes be seen at night, at sites where bones have been exposed to intense solar (ultraviolet) radiation]. A particular form of luminescence, known as *thermoluminescence*, is emitted when some insulating materials, such as minerals and pottery, are heated below the temperature required for *incandescence*. Thermoluminescence is used to date archaeological pottery and other materials (see Textbox 24).

Other optical properties of gemstones, which also determine their beauty and other characteristics that make some of them unique, include the way they *disperse light* incident on them (see Textbox 22), their *refractive index*, which is unique to, and characteristic of every type of gemstone and is often used for their identification (see Textbox 22), and their *luster*, *adularescence*, *asterism*, and *brilliance*.

Luster, the gleam or brilliance of a solid surface in reflected light, can be either metallic or nonmetallic. The luster of gemstones is nonmetallic, and its characteristics are determined by the translucence and clarity of the mineral. Luster can be dull, glistering, shining, or superior. Other ways of describing luster include one or more of the following terms:

- Greasy* – when it has an oil-coated look
- Pearly* – when its iridescence is that of pearls
- Resinous* – when it has a resinlike look
- Silky* – when it reflects light in a silk-fiber manner
- Vitreous* – when it has a glassy appearance

Adularescence refers to changes in the color of the luster when an illuminated gemstone is turned, such as a change from white to pale blue and vice versa, resulting in a remarkable flash across the surface of the stone; changes of this type are particularly characteristic of *adularia* (a rare gem variety of the mineral feldspar orthoclase), although of other gemstones as well. *Asterism*, whereby light reflected from the stone appears in the form of a radiating star, is characteristic of such gemstones as ruby and sapphire. *Asterism* occurs when light reflected from the gemstone is concentrated into several rays that

intersect with one another creating six-point stars, as in some rare gemstones. *Brilliance*, the property of gemstones to appear luminous, refers only to faceted gemstones; brilliance is due to the interaction between light beams incident on and reflected from the gemstone. Nonfaceted gemstones are never brilliant, although they are lustrous.

If the color and light dispersion characteristics determine their beauty, the durability of gemstones, that is, their resistance to being broken or abraded, therefore preserving their beauty, is determined by their *hardness* (see Textbox 23). Few minerals are valued as gems unless they can last in an unimpaired condition, unbroken and lustrous for a long time. Only very hard minerals, rated 7 or more on the Mohs hardness scale (see Table 20), wear well as gems. Quartz, for example, rated 7 on the scale, cannot be scratched with sharp steel instruments or with glass. Diamond, the hardest substance known, rated 10 on the Mohs scale, can scratch any other mineral but is not itself scratched by any material (Anderson 1974).

TEXTBOX 23

HARDNESS

Hardness is the property of solid materials to withstand abrasion, wear, penetration, or deformation by external forces. Some materials, such as the mineral talc, are so soft that rubbing them with the fingers breaks the bonds that hold them together and they become powdery; others, such as soapstone and marble, are somewhat harder but can be shaped by carving or abrasion. Still others, such as topaz and diamond, are extremely hard and are virtually unaffected by external penetrating or deforming forces. The particles that make up these hard materials are very strongly bonded to each other. In diamond in particular, the atoms of carbon are so strongly bonded to each other that diamond is the hardest natural material known; it cannot be scratched by other materials.

The hardness of any solid can be assessed with testing equipment that measures the relative ease with which a surface can be either scratched or penetrated by another solid of known hardness. A long-used classification of the hardness of minerals, the *Mohs scale of hardness*, is based on the *scratch test*: ten rather common minerals are arranged in the scale in order of their increasing relative hardness and listed in a scale varying from 1 to 10 (see Table 20). Each mineral in the Mohs scale scratches those with lower hardness numbers but does not scratch higher-hardness minerals. If a

TABLE 20 Mohs Scale of Hardness

Mohs hardness	Mineral	Common test	Relative hardness
1	Talc	Easily scratched by fingernail	1
2	Gypsum	Scratched by fingernail	3
3	Calcite	Scratched by copper	9
4	Fluorite	Scratched by mild steel	21
5	Apatite	Scratched by hard steel	48
6	Feldspar	Scratched by glass	72
7	Quartz	Scratched by glass	100
8	Topaz	No simple test	200
9	Corundum	No simple test	400
10	Diamond	Scratches all materials	1500

mineral or any other solid, for that matter, can be scratched by feldspar but is not scratched by apatite, for example, its hardness is between 5 and 6.

Other methods of determining the hardness of a material include a variety of "penetration" tests that yield hardness values measured in scales known as the *Brinell*, *Rockwell* (B or C), and *scleroscope scales*. These scales provide reliable hardness values for most materials, including ceramics, glass, metals and alloys, and wood (see Table 21). Unfortunately, as can be seen in the table, the various tests provide somewhat different hardness values for the same materials.

TABLE 21 Hardness: Conversion of Numerical Values between Different Hardness Scales

Brinell	Rockwell (C)	Rockwell (B)	Scleroscope
780	70	–	106
700	66	–	102
600	58	–	81
500	51	118	68
400	42	113	55
300	32	107	43
200	14	94	29
100	–	60	–

Cutting and Polishing Gemstones

The hardness, index of refraction, and transparency of gemstones determine the way they are cut and polished. Since ancient times gemstones have been shaped in two main styles: (1) as faceted gems, with many plane polished sides called facets, or (2) as nonfaceted, rounded, and polished gems, known as cabochons.

Some Archaeological Gemstones

Diamond. *Diamond*, the most brilliant, hardest, stiffest, and least compressible natural material and the most highly valued of all gemstones, consists of crystallized carbon. Its name is derived from the Greek word *adamastos*, meaning indestructible, and diamond is indeed chemically inert to most acids and alkalis. If diamond is heated to high temperatures in an oxidizing atmosphere, however, it burns, combining with oxygen to form carbon dioxide. The transparency of diamonds extends through the whole range of wavelengths of infrared, visible, and ultraviolet radiation. Their brilliance is due to a very high refractive index and a high dispersion of light (see Textbox 22). Gem diamonds are colorless and clear if composed only of carbon. Trace impurities within the crystal structure produce, however, diamonds in all the colors of the rainbow. Boron impurities, for example, which give diamonds a bluish color, and nitrogen, which adds a yellow cast, are common trace impurities. Since antiquity, diamonds have been appreciated for their beauty; and powdered diamonds have been used as abrasives for smoothing, cutting, carving, and drilling other gemstones and hard materials.

Emerald. *Emerald* is a brilliant, rich green, rare variety of the mineral beryl, which has been widely appreciated since antiquity as a gemstone. It is a relatively hard stone, 7.5 on the Mohs scale, harder than quartz, but not as hard as sapphire. Pure beryl (composed of beryllium aluminum silicate) is colorless, and the green of emeralds is due to trace amounts of chromium in the crystals (Ward 1994; Webster 1955). The name of the gemstone is derived from the French *emeraude*, which in turn goes back via Latin (*smaragdinus*) to the Greek root *smaragdos*, meaning simply “green gemstone.” The provenance of emeralds set in a large variety of artifacts, dating from Gallo-Roman times (the first century B.C.E.) to as late as the eighteenth century, has been studied, using the weight ratio between the isotopes of oxygen in the gemstone as an indicator of its provenance (see Textbox 47). The study revealed that most of the analyzed emeralds from this long period of time

originated from deposits that supposedly had been discovered as recently as the twentieth century. It seems that emeralds from Pakistan and Egypt, for example, were being traded already in antiquity by way of the Silk Route. Moreover, emeralds from these two sources and from Austria were the only ones from which European and Asian traders obtained gem-quality emeralds. It was only during the sixteenth century that a new source appeared and a new trade route for emeralds evolved; emeralds mined in Colombia were initially traded via Spain to Europe, the Middle East, and India, and later on directly via the Philippines to India (Giuliani et al. 2000, 1998).

Jade. *Jade* is the name shared by two usually green but distinct minerals that have been appreciated for many millennia. One is *nephrite* (composed of hydrous calcium, magnesium, and iron silicate), the most abundant in nature and apparently the earliest known form of jade. The other is *jadeite* (composed of aluminum sodium silicate), the most valued form of jade; jadeite is also known as Chinese jade, although it is found naturally in Burma and not in China (see Table 22). Although nephrite and jadeite are similar in appearance, they differ not only in composition but also in their index of refraction, petrographic microstructure, and X-rays diffraction (XRD) pattern. Thus, determining any one of these properties makes it possible to differentiate between the two. Jadeite is usually green, but white and red varieties are also common. It is remarkably tough and hard to carve or polish, the polished surfaces having a “greasy feeling” to the touch (Desautels 1971; Laufer 1912).

In ancient times the Chinese buried jade with their dead in the belief that the stone would prevent decomposition of the corpse. During the Han Dynasty (third century B.C.E. – third century C.E.), for example, pieces of jade were placed in each of the body orifices to ward off decay. It is ironic, therefore, that in contact with the corpse jade decayed and its hard, polished surface became damaged by chalky blemishes (Gaines and Handy 1975).

TABLE 22 Jade Minerals

Mineral	Color	Composition	Specific gravity	Hardness (Mohs scale)
Jadeite	Mostly green, but also white and red	Silicate of aluminum and sodium	3.3–3.5	6.5–7
Nephrite	Yellow, brown, green, blue, red, lavender	Silicate of calcium, magnesium and iron	2.9–3.2	6 –6.5

Ruby and Sapphire. *Ruby* and *sapphire* are “sister stones”: both are gemstone forms of the mineral *corundum* (composed of aluminum oxide). Pure corundum is colorless, but a variety of trace elements cause corundum to exhibit different colors. Ruby is red corundum, while sapphire is corundum in all colors except red. The red in rubies is caused by trace amounts of chromium; the more intense the red color of a ruby, the more chromium it contains. The blue in *sapphires* is caused by titanium and/or iron impurities (Garland 2002; Hughes 1997).

Turquoise. *Turquoise* is an opaque, usually blue, mineral (composed of hydrated aluminum copper phosphate) that has been widely prized as a semiprecious gemstone for well over 8000 years, having been used to make beads, rings, and other decorative objects. Deposits of turquoise are formed when water flows and dissolves part of rocks rich in aluminum and then evaporates. The blue color of the stone is due to the copper; iron impurities give rise to shades of blue-green and even to green turquoise. Turquoise deposits occur in only a few and limited arid regions of the world, such as the Sinai Peninsula in the Middle East and the southwest of North America. There seems to have been a wide network of transportation and trade of turquoise from the places where turquoise was extracted to where it was worked and eventually used. Identifying the distribution routes of ancient turquoise has attracted much attention, and a number of investigations have been centered on establishing the distribution of turquoise from various mining regions. In one such study, concerned with turquoise beads in North America, differences in the nature and concentration of impurities in the gemstone were used to distinguish between turquoise from pre-Columbian sites in the midwest of the United States and some parts of Mexico. Most of the turquoise analyzed seems to have originated from mines in the southwest of North America, from where it was distributed, through well-established trade routes, to the workshops where it was worked (Harbottle and Weigard 1992; Sigleo 1975).

