19

Raw Materials

CHAPTER PREVIEW

In this chapter we look at several important raw materials used in the ceramics industry. Obtaining the necessary raw materials is the first step in the fabrication of ceramic components. This topic used to be addressed by many Departments of Mining and Mineral Engineering. It is no less important today, but few such departments still exist. There are two basic sources for these raw materials:

- Naturally occurring minerals
- Synthetic minerals

For naturally occurring minerals we will describe, in general terms, their origin, the locations in which they can be found, and their relative abundance. Naturally occurring minerals require extraction, which is often a regional industry located close to abundant quantities of the natural deposit. Most minerals need to go through some form of physical or chemical processing before use. The collective term for these processes is *beneficiation*. When you understand how oxides are manufactured, it will be clear why they are often impure and why Si, Na, Ca are the major impurities.

Materials that do not occur in nature or are rare must be synthesized (so calling them minerals is a misnomer) and we describe the processes used for their synthesis. Carbides, nitrides, and borides are becoming more common, but are generally expensive and require special processing environments. For many nonoxides the main impurities are often components of the starting material that have not reacted, e.g., Al in AlN or Si in Si_3N_4.

There are many other raw materials that play important roles in specific ceramics, but rather than providing a comprehensive discussion about every raw material, we focus on representative examples of naturally occurring minerals and synthetic ones. There are two ways of looking at this topic: the mineral we start from and the material we want to form. Here, we mix the two approaches.

19.1 GEOLOGY, MINERALS, AND ORES

Figure 19.1 shows a schematic cross section of the earth. The earth has a mean radius of about 6370 km and consists of three distinct concentric layers. The outermost layer is known as the crust and is relatively thin. The continental crust ranges in thickness from about 20 to 60 km, averaging approximately 30 km. It is the minerals that occur here that are important to us as raw materials for ceramics.

The continental crust is composed primarily of the silicates of Mg, Fe, Al, and Ca, and the alkali metals plus Al and free SiO_2. Table 19.1 lists the abundance of the major elements in the continental crust. From this you can see that O, Si, and Al together account for almost 90 wt% of the elements in the crust.

Beneath the earth's crust is the mantle. This thick layer is thought to be composed of Mg silicates and Fe silicates, free Fe, and minor Fe sulfides. Minerals in the mantle (and the core) are presently not accessible; for this reason we will not discuss them further. However, geologists can identify rocks that have moved from the mantle to the crust by natural processes. An ore is defined as a mineral from which a constituent can be profitably mined or extracted. Examples include hematite (Fe_2O_3), which is the major ore of Fe, and ilmenite ($FeTiO_3$), which is the major ore of Ti, but is also an Fe-containing mineral. Pyrophanite ($MnTiO_3$) is neither a Ti nor Mn ore, but is actually a rare mineral.

MINES

The deepest mine is ~5 km deep.

19.2 MINERAL FORMATION

Minerals are the constituents of rocks, which make up the entire inorganic,

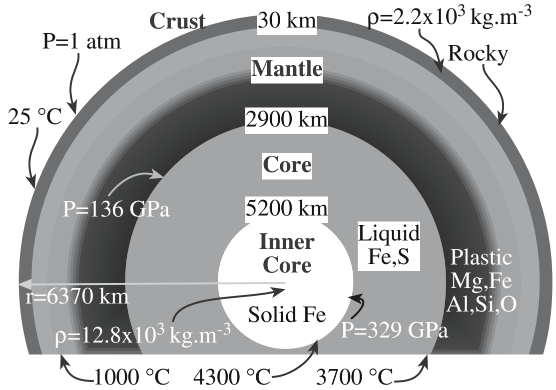

FIGURE 19.1 Schematic cross section of the earth.

TABLE 19.2 Major Oxides in Igneous Rocks and Their Ranges of Composition	
Constituent (oxide)	*Concentration (wt%)*
SiO_2	30–78
Al_2O_3	3–34
Fe_2O_3	0–5
FeO	0–15
MgO	0–40
CaO	0–20
Na_2O	0–10
K_2O	0–15

solid portion of the earth. Rocks are usually not composed of a single mineral; rather they are an aggregate of two or more minerals. Broadly speaking, geologists divide rocks into three types: igneous, metamorphic, and sedimentary.

IGNEOUS ROCK

Granite: magma cooled near the earth's surface
Rhyolite: fine grain granite
Obsidian, pumice and scoria: volcanic origin
Basalt: very small grains of usually rapidly cooled lava
Gabbro: like basalt, but has larger grains
Mafic: dark igneous (e.g., basalt)
Intermediate: e.g., diorite; Mg and Fe rich
Felsic: light igneous (e.g., granite); quartz rich

Igneous rocks form when magma cools and solidifies. Magma is a complex molten material that originates deep within the earth. The word igneous comes from the Latin word *ignis*, which means "fire"; igneous rocks then are "formed from fire." Magma is rich in the elements Si, O, Al, Na, K, Ca, Fe, and Mg. Table 19.2 shows the composition ranges for the major elements (expressed as oxides) in igneous rocks. These are the elements that when combined with SiO_2 form the silicate minerals. A limited number of silicate minerals accounts for over 90% of all igneous rocks.

All silicate minerals contain tetrahedral silicate [SiO_4] groups. Classification of the silicate minerals is based upon the way in which these groups combine, as described in Chapter 7.

The specific mineral crystallizing from magma depends both on the composition and temperature of the magma. The order of crystallization of the main silicate minerals is given by Bowen's reaction series, which is shown in Figure 19.2. Olivine and Ca feldspar form at high temperatures and may separate early from the melt. Other minerals solidify as the temperature falls. The last minerals to crystallize are K feldspar, muscovite mica, and quartz, the major constituents of granite. Finally, water in the magma carries metals and S in solution through cracks in the surrounding rock and deposits them as sulfides in veins.

Metamorphic rocks have undergone structural and/or chemical transitions (metamorphism or metamorphosis)

TABLE 19.1 Abundances of the Major Elements in the Continental Crust

Element	*wt%*	*at%*	*vol% of ion*
Oxygen	47.2	61.7	93.8
Silicon	28.2	21.0	0.9
Aluminum	8.2	6.4	0.5
Total Iron	5.1	1.9	0.4
Calcium	3.7	1.9	1.0
Sodium	2.9	2.6	1.3
Potassium	2.6	1.4	1.8
Magnesium	2.1	1.8	0.3
Hydrogen	trace	1.3	0.0

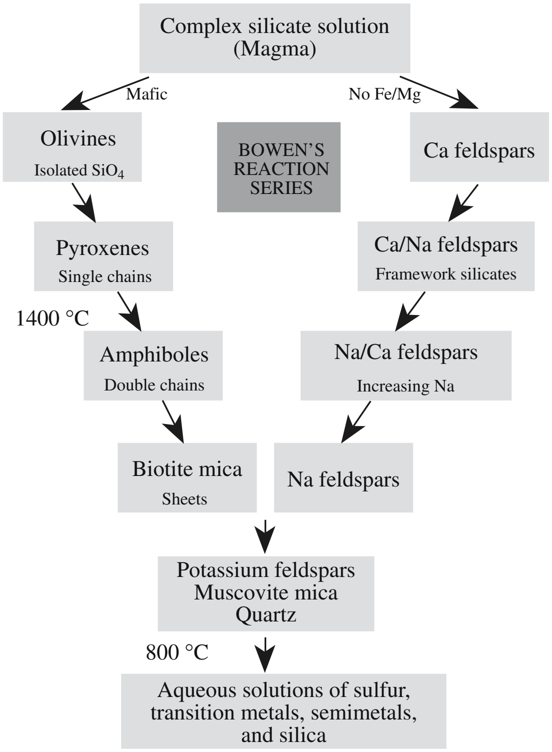

FIGURE 19.2 Bowen's reaction series.

from their original form as a result of high temperatures and pressures deep beneath the earth's surface. These transitions occur in the solid state without melting and result in the formation of new minerals, such as kyanite, staurolite, sillimanite, andalusite, and some garnets. Other minerals, such as some of the igneous minerals, may be present in metamorphic rocks, although they are not necessarily the result of metamorphism.

The word "metamorphic" has a Greek origin coming from *meta* meaning "change" and *morphe* meaning "shape."

Sedimentary rocks are formed when small particles or precipitated crystals become cemented together. Sedimentary rocks are classified as either clastic or chemical.

Clastic sedimentary rocks form when rock particles produced by mechanical and chemical weathering are transported by water, ice, and wind to new locations where they become cemented together.

Chemical sedimentary rocks form when highly soluble ions, such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, F^-, $(SO_4)^{2-}$, $(CO_3)^{2-}$, and $(PO_4)^{3-}$, from existing rocks are dissolved in water and subsequently precipitate forming layers in oceans and lakes where they become cemented together. The composition of sedimentary rocks depends on the

- Composition of the original source rocks
- Chemical and mechanical resistance of each mineral component
- Distance traveled

Resistant minerals such as quartz are common constituents of sedimentary rocks, and some more rare minerals (e.g., garnet, rutile, and zircon) have similar properties. Feldspar is less resistant, but is so common that it is a major constituent of many sedimentary rocks. Precipitated minerals include the carbonates (e.g., calcite and dolomite), sulfates (e.g., gypsum and anhydrite), chlorides, and chalcedonic silica (e.g., chert and flint).

The three rock types are compared below; Figure 19.3 shows what is called the rock cycle.

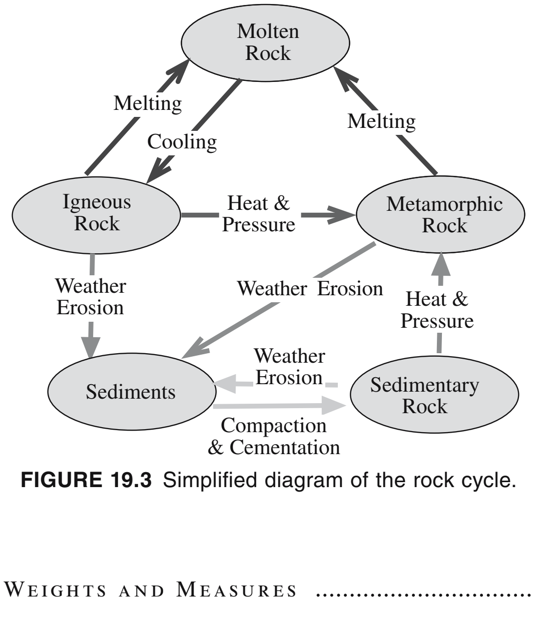

FIGURE 19.3 Simplified diagram of the rock cycle.

Igneous	Rocks are formed by cooling and solidification of magma.
Metamorphic	Rocks have undergone structural and/or chemical transitions.
Sedimentary	Rocks are formed when smaller particles become cemented.

19.3 BENEFICIATION

Beneficiation is the process through which most minerals need to go before they can be used to produce ceramics. Physical beneficiation includes crushing and grinding of coarse rocks. The particle size of the raw material may affect subsequent steps in the production process. An example that we use is producing alumina from bauxite, a process that involves a chemical reaction.

Chemical beneficiation includes processes of separating the desired mineral from unwanted waste products, for example, by dissolution in a suitable solvent followed by filtration. The Bayer process for producing alumina is also a good example of chemical beneficiation. Bauxite contains many impurities.

The purity of the raw materials will be reflected in the composition of the final product. For many ceramics careful control over purity is required. For these applications the raw materials are synthesized. Furthermore, several important ceramics do not occur naturally in mineral form and must be fabricated chemically. Synthesis of ceramic powders can have advantages not only in purity but also in allowing the generation of fine particle-sized powders having a well-defined morphology. We will show in Chapter 24 the importance of particle, size on the densification of a ceramic component by sintering.

19.4 WEIGHTS AND MEASURES

The SI unit of mass is the kilogram (kg), which is interesting for a few reasons. It is the only basic SI unit defined with a prefix (*kilo*) already in place, and it is the only one defined by reference to a physical object—a mass of platinum-iridium held at Sevrès in France. To express the large quantities of material that we encounter in the extraction and processing of ores it is usual to use the metric ton (sometimes written tonne: symbol t):

$$1\,\mathrm{t} = 1\,\mathrm{Mg} = 10^3\,\mathrm{kg}$$

Possible confusion exists because of special British and U.S. units that are still in use in these countries.

$$1\,\mathrm{t} = 0.984\ \text{UK (long) ton}$$

$$1\,\mathrm{t} = 1.103\ \text{US (short) ton}$$

The situation is even more complicated in the UK where the short ton is often used in mining metal-containing ores, but the long ton is used in coal mining. We will use the metric ton (written simply as ton) unless specifically stated otherwise. You can see that for "ballpark" estimates of mass it really does not make much difference. When we discuss single crystals in Chapter 29 we will introduce units of mass that are used to describe very small quantities of a material.

Determining the quantity of all commercial minerals produced is straightforward. The United States Geological Survey maintains updated information on their website in the form of Mineral Commodity Summaries and the Minerals Yearbook. These sources provided most of the numbers given in this chapter. Obviously, like all commodities, the production of minerals may vary from year to year based on many different factors such as supply, demand, and reserves. The problems at the end of this chapter will help you think about some of those factors for specific minerals.

19.5 SILICA

Silica (SiO_2) is an important raw material for ceramics. The major use (accounting for about 38% of U.S. production) is in glass manufacture. For example, incandescent lamp bulbs are made of a soda-lime silicate glass containing about 70 wt% SiO_2. The SiO_2 content of high-quality optical glasses can be as high as 99.8 wt%.

A major source of silica is sand. Industrial sand and silica sand are two terms used by the ceramics industry for sands that have a high percentage of SiO_2. In some of the high-quality silica sand sources mentioned below the SiO_2 content is >99.5%.

Sand is defined by the American Society for Testing and Materials (ASTM) as granular rock particles that pass through a No. 4-mesh (4.75-mm aperture) U.S. standard sieve, are retained on a No. 200-mesh (75-μm aperture) sieve, and result from the natural disintegration or comminution of rock. Sands are also produced by physical beneficiation of rocks by crushing. These sands have various chemical compositions, determined by the type of rock being mined.

The United States is the largest producer of industrial sand in the world. The states of West Virginia, California, Illinois, Pennsylvania, Ohio, and New Jersey supply about 80% of all the high-quality silica sand used domestically. In Illinois and Missouri, practically all the glass-grade silica is derived from the St. Peter sandstone formation. Other quality deposits are the Oriskany sandstone deposits in West Virginia and Pennsylvania. Deposits are usually found in dune forms or in deposits lying 20–30 m under layers of silts, clays, and shales.

The mining of industrial silica is, in general, a regional market. Unless the material possesses unique characteristics, such as a certain grain size or shape, the geographic market of a plant rarely extends beyond 200 miles. This is because of the high transportation cost relative to the price of the materials and the extensive location of mines.

SILICA PRODUCTION

Annual production of silica in the United States is approximately 30 Mt, valued at around $700 million.

TABLE 19.3 Abundance of Minerals in the Earth's Crust

Mineral groups	*vol%*
Feldspars	58
Pyroxenes, amphiboles	13
Quartz	11
Micas, chlorites, clay minerals	10
Carbonates, oxides, sulfides, halides	3
Olivines	3
Epidotes, aluminosilicates, garnets, zeolites	2

In recent years, environmental regulations have been placed on the mining of silica sand due to health risks associated with this product.

Quartz, the principal silica mineral, is a constituent of igneous rocks such as granite. It is also found in most metamorphic rocks, comprising a major portion of the sandstones, as well as in the pure form in veins running through other rocks. Optical quality quartz crystals are quite rare, but there are economically viable methods to produce quartz crystals as we will see in Section 29.11.

19.6 SILICATES

We discussed the silicates in Chapter 7. Here we discuss the use of these materials to form commercial ceramics.

Feldspar	70% is used for glass.
Kaolin	It is used in fine china, paper, and rubber.
Mica	Over 200,000 t of low-quality mica is used each year.
Mullite	600,000 t is used each year for refractory furnace blocks.

Feldspar

Feldspars constitute an abundant mineral group and make up an estimated 60% of the earth's crust, as shown in Table 19.3. They are present in many sedimentary deposits and are found in almost all igneous and metamorphic rocks.

The glass industry uses most of the feldspar produced. Feldspar is a source of Al_2O_3, which improves the mechanical properties of glass such as its scratch resistance and its ability to withstand thermal shock. It is also used in whiteware bodies as a flux, which produces a glassy phase during firing increasing the strength and translucency of the body.

The Republic of Korea is the largest producer of feldspar in the world. Annual feldspar production in the United States is about 800,000 t with a value of about $45 million. The largest producing states are North Carolina, Connecticut, and California. The typical procedure for processing feldspar deposits is

- Drilling and blasting at the quarry
- Transporting to a mill for crushing and grinding (physical beneficiation)
- Froth flotation separating the minerals according to their relative wettability in aqueous solution (chemical beneficiation)
- Drying
- Grinding to a No. 20 mesh (841 μm aperture size) for glassmaking and below a No. 200 mesh (aperture size 74 μm) for most other ceramic applications

In the froth flotation process, air is bubbled through a water suspension containing the crushed minerals to form a foam or froth. The wetted particles (those that are hydrophilic) remain in the water suspension, whereas hydrophobic particles collect at the air bubble/water interface and can be removed from the liquid. Various agents, such as amino acids (having a high molecular weight), can be used to enhance the relative wettability of the solids in a mixture; these agents are adsorbed selectively on the surface of certain species in the mixture. The process is carried out in stages:

1. Remove mica
2. Remove iron-bearing minerals, especially garnet
3. Separate feldspar from a residue consisting mainly of quartz

Clays and Kaolin

Clay is the primary ingredient in traditional ceramics and is the general name given to the layer silicates with a grain size < 2 μm. Any of the layer silicates could qualify as a clay mineral. There are six types of commercial clays and these are listed in Table 19.4. They are distinguished by their composition, plasticity, color, and firing characteristics.

Mechanical and chemical weathering of feldspars in igneous and metamorphic rocks forms kaolin, a key ingredient in China clay. It may be disintegrated *in situ* or transported by water or wind and redeposited elsewhere. Primary kaolin deposits are located at the site of the original rock. These typically contain large amounts of quartz and mica, which also formed during weathering. Large, primary kaolin deposits are found in southwest England, the Ukraine, and China.

Secondary kaolins were washed from the original weathering site, naturally beneficiated, and redeposited in large areas of pure kaolin. The major commercial deposits of secondary kaolin in the United States were formed 50 million years ago and occur as a continuous belt stretching along the ancient coastline from Alabama northeast to North Carolina.

Mica

The mica group consists of 37 minerals, known as phyllosilicates, which have a layered or platy texture. The Greek word "phyllon" means leaf. Some of the mica minerals are listed in Table 19.5 together with the location of their principal sources. The micas are classified as either true or brittle.

MICA

The commercially important mica minerals are muscovite and phlogopite.

True micas contain univalent cations (e.g., Na^+ or K^+) between each set of layers and show perfect basal cleavage, allowing the crystals to be split into thin sheets. The cleavage flakes are flexible and elastic.

In brittle micas, the interlayer cations are divalent (e.g., Ca^{2+}). The bond is stronger and although the layered structure still imparts basal cleavage they are more brittle. Brittle micas are uncommon minerals and not of any real interest.

Muscovite is the principal mica used because of its abundance and superior electrical properties. Phlogopite

TABLE 19.4 Commercial Clays, Their Main Uses, and Annual U.S. Production

Type	*Main uses*	*Annual U.S. Production (Mt)*	*Comments*
Ball clay	Floor and wall tiles Sanitary ware	1.3	Also called "plastic clay" because it improves workability
Bentonite	Foundry sand bond Absorbents	4.4	The United States imports bentonite from Canada
Common clay	Bricks Cement	26	Also called "brick clay" Red color comes from iron
Fire clay	Refractories	0.3	Fireclay refractories contain 25–45% alumina
Fuller's earth	Absorbents	3.2	Textile workers (or "fullers") cleaned raw wool by kneading it in a mixture of water and fine earth, which adsorbed oil, dirt, and other contaminants
Kaolin	Paper	7.2	Kaolinite is a hydrous aluminum silicate; kaolin is a white firing clay, primarily composed of kaolinite

TABLE 19.5 Principal Sources and Occurrence of Mica Minerals

Mineral	*Chemical formula*	*M, H, or O*	*Type*	*Source*
Muscovite	$KAl_2(Si_3Al)O_{10}(OH)_2$	M	True	United States, India, Brazil, Russia
Phlogopite	$KMg_3(AlSi_3O_{10})(OH,F)_2$	M,H	True	Madagascar, Canada, Mexico, Sri Lanka
Paragonite	$NaAl_2(Si_3Al)O_{10}(OH)_2$	M	True	United States, Switzerland, Italy
Biotite	$K(Mg,Fe)_3(Al,Fe)Si_3O_{10}(OH,F)_2$	M,H	True	United States, Canada, Ireland, Scotland
Lepidolite	$K(Li,Al)_3(Al,Si)_4O_{10}(F,OH)_2$	M,H,O	True	United States, Canada, Brazil, Sweden
Zinnwaldite	$KLiFeAl(AlSi_3)O_{10})(F,OH)_2$	M	True	United States, Brazil, Scotland, Germany
Margarite	$CaAl_2(Al_2Si_2O_{10})(OH)_2$	M	Brittle	United States, Scotland, Italy, Austria
Clintonite	$Ca(Mg,Al)_3(Al_3Si)O_{10}(OH)_2$	M	Brittle	United States, Italy, Finland, Russia

is stable at higher temperatures and is used in applications in which a combination of high heat stability and electrical properties is required. Both are used in sheet and ground forms.

Micas occur in igneous, sedimentary, and metamorphic rocks in a great many contrasting geological environments. The reason for this range of occurrence is their wide thermal stabilities. Figure 19.4 shows a pressure–temperature diagram for muscovite mica. At very high temperatures (>600°C) it becomes unstable, breaking down in the presence of quartz to give potassium feldspar and sillimanite.

$$\underset{\text{Muscovite}}{KAl_2[Si_3AlO_{10}](OH)_2} + \underset{\text{Quartz}}{SiO_2} \rightarrow \underset{\text{K-feldspar}}{KAlSi_3O_8} + \underset{\text{Sillimanite}}{Al_2SiO_5} + H_2O$$

Muscovite occurs in low-grade metamorphic rocks where it forms from pyrophyllite ($Al_4[Si_8O_{20}](OH)_4$) and illite ($K_{1-1.5}Al_4[Si_{7-6.5}Al_{1-1.5}O_{20}](OH)_4$). It also occurs as a primary crystallizing mineral in igneous rocks, such as granites and pegmatites, and is a common constituent of sedimentary rocks, especially the arenites. Muscovite mica is locally common in many parts of the United States.

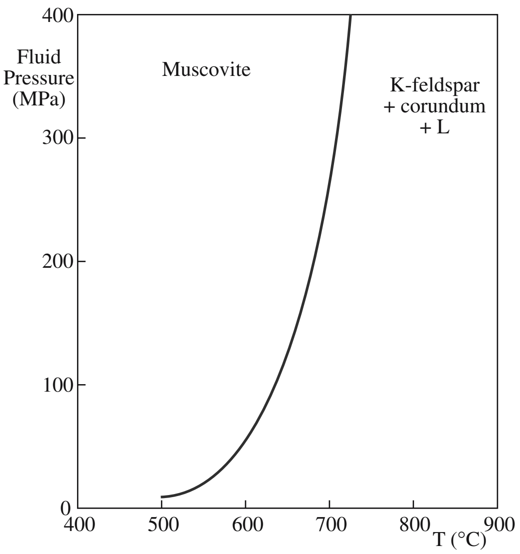

FIGURE 19.4 Pressure–temperature phase relations for the bulk composition $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2$–$2H_2O$.

The largest producer of mica is Russia, which produces about one-third of the world's annual supply of 300,000 t. The United States produces about 75,000 t of scrap and flake mica each year. Although historically the United States was a producer of sheet mica, domestic reserves have declined to zero and commercial production is all scrap and flake.

The principal use for ground mica is as a filler and extender in gypsum wallboard joint compounds where it produces a smooth consistency, improves workability, and prevents cracking. It is also found in paints, molded rubber products including tires, and toothpaste. Mica flakes are being used as a replacement for asbestos in brake linings and clutch facings.

India is the largest producer of muscovite sheet mica. Madagascar is the principal supplier of phlogopite sheet mica. The prices for sheet mica range from less than $1/kg for low-quality material to more than $2,000/kg for the highest quality. High-quality muscovite mica is used as a dielectric in capacitors.

Mullite

Mullite ($3Al_2O_3 \cdot 2SiO_2$) does not exist in nature in large quantities and must be produced synthetically. It has many properties that make it suitable for high-temperature applications. Mullite has a very small coefficient of thermal expansion (giving it good thermal shock resistance) and is creep resistant at high temperature. Most importantly, it does not react readily with molten glass or with molten metal slags and is stable in the corrosive furnace atmosphere. Hence it is used as a furnace lining and other refractory applications in the iron, steel making, and glass industries.

There are two commercial approaches to producing mullite:

- Sintering
- Fusing

Sintered mullite may be obtained from a mixture of kyanite (Al_2OSiO_4), a naturally occurring mineral found in metamorphic rocks, bauxite, and kaolin. This mixture (in the correct ratio) is sintered at temperatures up to about 1600°C. The sintered quality contains 85–90% mullite with the balance being mainly glass and cristobalite (a crystalline polymorph of SiO_2). South Africa is the major producer of kyanite, about 165,000 t/year. The United States has the largest resource of kyanite and these are located mainly in the Applachian Mountains region and in Idaho. Andalusite and sillimanite are other aluminosilicate minerals, similar to kyanite, that can be used as a raw material for mullite.

By fusing the appropriate amounts of alumina and kaolin together in an electric-arc furnace at about 1750ºC a higher purity mullite can be made. The fused product contains >95% mullite, the rest being a mixture of alumina and glass.

19.7 OXIDES

The raw materials used for oxide ceramics are almost entirely produced by chemical processes to achieve a high chemical purity and to obtain the most suitable powders for component fabrication. The important oxides are summarized in Table 19.6 and are discussed individually.

FIGURE 19.5 Alcoa refinery in Wagerup, Western Australia that supplies 15% of the world's alumina.

Alumina

Aluminum oxide (Al_2O_3, alumina, corundum) is the most widely used inorganic chemical for ceramics and is produced from the mineral bauxite using the Bayer process. Bauxite is a mixture of hydrated aluminum oxide with iron oxide (Fe_2O_3), silica (SiO_2), and titania (TiO_2) impurities. It results from the decay and weathering of aluminous rocks, often igneous, under tropical conditions. Like kaolin, bauxite occurs as both primary deposits and secondary deposits.

The Bayer process produces a nominal 99.5% Al_2O_3 product. The alumina can be prepared in a range of grades to suit specific applications. The grades differ by the size and shape of the crystals and the impurity content. The dominant impurity, accounting for up to 0.5%, is Na_2O. The crystal size can be adjusted to measure between 0.1 and 25 μm. Figure 19.5 shows a refinery that produces alumina from bauxite using the Bayer process.

The steps in the Bayer process are as follows:

Physical beneficiation: The bauxite from the mine is first ground, fairly coarsely, to a particle size of <1 mm. Grinding increases the total surface area of the particles, leading to a reduction in the processing time for the chemical reaction in the following step.

TABLE 19.6 Oxide Raw Materials

Alumina	Refractories, abrasives, substrates
Ceria	Catalysts, fuel cells, polishing (CMP)
Ferrites	Magnets
Magnesia	Refractories
Rutile and anatase	Paints
Zincite	Rubber, adhesives, varistors
Zirconia	Additives, furnace components

Digestion: The coarsely ground bauxite is treated with a sodium hydroxide (NaOH) solution at 150–160ºC and 0.5 MPa total pressure. Most of the hydrated alumina goes into solution as sodium aluminate:

$$Al(OH)_3\ (s) + NaOH\ (aq) \rightarrow Na^+\ (aq) + Al(OH)_4^-\ (aq)$$

Filtration: The solid impurities, mainly SiO_2, TiO_2, and Fe_2O_3, remain undissolved and are separated by filtration.

Precipitation: After cooling, the filtered sodium aluminate solution is seeded with very fine gibbsite [a naturally occurring hydrated alumina, α-$Al(OH)_3$] and at the lower temperature the aluminum hydroxide reforms as the stable phase. Reducing the pH by bubbling CO_2 through the solution encourages precipitation.

Washing: The precipitate is filtered and washed to reduce the sodium content.

Calcination: The powder is calcined at temperatures in the range 1100–1200ºC to convert the hydroxide to the oxide:

$$2\,Al(OH)_3\ (s) \rightarrow Al_2O_3\ (s) + H_2O\ (g)$$

At this stage the alumina is in the form of agglomerates of small grains about 5–10 μm in diameter.

Milling: The powder is then milled to give the desired particle size and particle size distribution. The alumina produced in this way contains ≥99.5% Al_2O_3 and, as mentioned earlier, the major impurity is Na_2O. The powder may also contain small amounts, on the order of 0.001%, SiO_2. This level of purity is sufficient for many

TABLE 19.7 Composition of Calcined Aluminas

	Normal Na_2O (wt%)	*Low Na_2O (wt%)*	*Reactive (wt%)*
Al_2O_3	98.9–99.7	99.5–99.8	>99.5
SiO_2	0.02–0.05	0.07–0.12	0.04–0.08
Fe_2O_3	0.04–0.05	0.04–0.06	0.01–0.02
Na_2O	0.3–0.6	<0.13	0.08

applications. Careful control of the precipitation conditions, thorough washing of the precipitate, and control of the calcination/milling conditions can give aluminas of up to 99.99% purity. The cost of normal calcined alumina is about $0.60/kg and can go up to over $2.00/kg for higher purity calcined aluminas. The price for metallurgical-grade (suitable for conversion into Al) alumina is around $150/t.

Table 19.7 gives typical compositions of the main forms of calcined aluminas. The presence of Na_2O can be unacceptable. For example, the Na^+ ion is mobile in an electric field and causes degradation of electrical insulation. Also during high-temperature processing a sodium β-alumina ($Na_2O \cdot 11Al_2O_3$) phase can form that leads to a reduction in density, strength, thermal shock resistance, and corrosion resistance of the final product. Table 19.8 shows the Na_2O content required for various applications of calcined alumina prepared by the Bayer process.

Australia is the world's largest producer of bauxite, producing almost 60 Mt per year. The major regional producer of bauxite in the United States is Arkansas, with smaller deposits in Georgia, Alabama, and Mississippi. Domestic mines supply less than 1% of the U.S. bauxite requirement and hence the United States is a major importer of bauxite, importing over 10 Mt/year.

Of all the bauxite mined about 95% is converted to alumina. World production of alumina is about 50 Mt/year. The majority (about 90%) of the alumina is used for the production of aluminum; most of the rest goes into nonmetal uses such as specialty aluminas. It is this latter quantity that is of interest to us in ceramics. The primary suppliers of specialty aluminas in the United States are Alcoa, Alcan, Aluchem, LaRoche, and Reynolds.

TABLE 19.8 Soda Contents Required of Calcined Aluminas in Commercial Applications

Application	*Median crystal size (μm)*	*Na_2O content range (%)*
Electronic ceramics	<0.5–5	<0.02–0.1
Sodium vapor lamps	<0.5	<0.02–0.1
Structural ceramics	<0.5–5	0.02–>0.4
Fused abrasives	<0.5–1	0.2–>0.4
Ceramic fibers	<0.5–1	0.2–>0.4
High-technology refractories	0.5–3	<0.1–0.25
Spark plugs	2.5–>5	0.02–0.2

High-purity aluminas can also be prepared directly from aluminum metal, of which there are several routes as shown in Figure 19.6.

Magnesia

Magnesium oxide (MgO, magnesia) occurs naturally as the mineral periclase, a metamorphic mineral formed by the breakdown of dolomite, $CaMg(CO_3)_2$, and other magnesium minerals. Occurrences of periclase are rare and are of no commercial importance. The principal commercial sources of MgO are magnesite ($MgCO_3$) and magnesium hydroxide [$Mg(OH)_2$].

Major deposits of magnesite occur in many countries including China, Turkey, and Russia. The magnesite contains varying amounts of impurities including silica, iron, aluminum, manganese, and calcium, usually present in the form of various minerals, for example, quartz, talc, mica, and magnetite. After mining the ores must be beneficiated. The methods for beneficiation vary, for example, crushing, screening, washing, magnetic separation, and froth floatation.

After the impurities have been separated the magnesium carbonate is calcined. Calcining at temperatures between 800 and 900°C produces a very reactive fine-grained MgO called caustic magnesia. Sintered, or dead burned, magnesia is obtained by calcining the magnesium carbonate at temperatures above 1700°C. During this process the reactive crystals grow and lose their activated state.

Magnesia can be produced from seawater and magnesium-rich brines. About 60% of the U.S. production

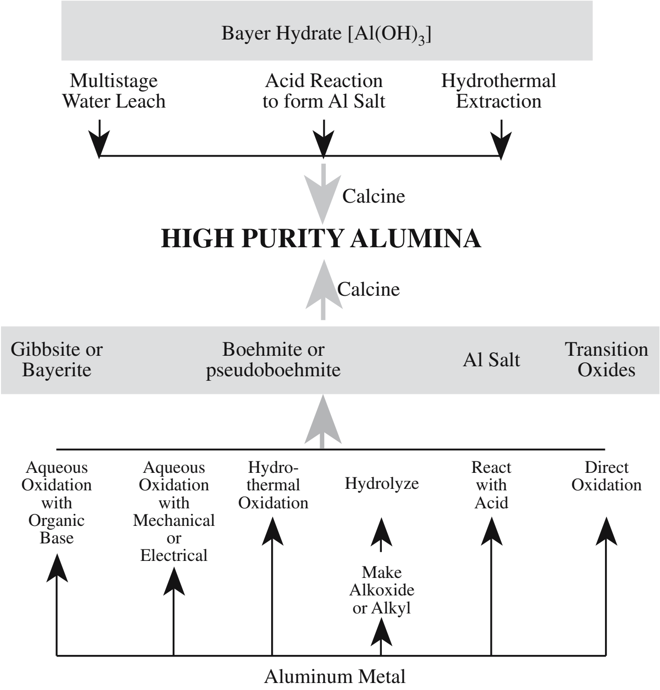

FIGURE 19.6 High-purity alumina production routes.

of magnesium compounds is from these sources. Seawater contains about 1.28 g Mg^{2+}/kg. The most important process for the production of MgO from seawater is precipitation of magnesium hydroxide [$Mg(OH)_2$] from solutions of magnesium salts by a strong base:

$$Mg^{2+}\ (aq) + 2(OH)^-\ (aq) \rightarrow Mg(OH)_2\ (s)$$

The $Mg(OH)_2$ precipitate is washed, filtered, and calcined to produce MgO.

Another means of obtaining magnesia is from brines. This process is based on the decomposition of $MgCl_2$ at 600–800°C:

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$$

World magnesia production capacity is about 10 Mt/year: ~9.0 Mt from natural magnesite and ~1.5 Mt from seawater and brines. Prices for magnesia range from \$150/t to more than \$1200/t depending on purity.

The major application for magnesia is as a refractory lining in furnaces. In lesser quantities, it is made into a well-known milky solution and ingested. It is also used to manufacture other ceramics such as chrome-free spinels. Nonchrome spinel is not available in nature on an industrial scale. At Asahi Glass, spinel is produced by electrofusing magnesia with alumina.

Zirconia

Zirconium dioxide (ZrO_2, zirconia) is principally derived from zircon, $ZrSiO_4$, which occurs in igneous rocks such as granites and pegmatites. Decomposed pegmatites have been worked for zircon in Madagascar and Brazil. Zircon is also a constituent of some metamorphic rocks and also occurs as secondary deposits in beach sands in Australia, Brazil, India, and Florida. In these secondary deposits, which have been worked commercially, the zircon occurs together with other minerals such as ilmentite, rutile, and monazite.

There are a number of commercial approaches to producing pure zirconia from zircon. Zircon dissociates above 1750°C into ZrO_2 and SiO_2. Injection of zircon sand into a plasma (at temperatures >6000°C) results in dissociation and melting. The zirconia solidifies first, in the form of dendrites, and the silica solidifies as a glassy coating on the zirconia. The silica may be removed by leaching in boiling sodium hydroxide solution. The residue is washed and the zirconia is removed by centrifuging.

The main production method for zirconium oxide is electric arc melting of zircon between 2100 and 2300°C. Dissociation still occurs at these lower temperatures, but solid zirconia is produced along with liquid silica. The purity of the ZrO_2 produced is about 99%.

Another, although commercially less significant, source of zirconia is baddeleyite (impure monoclinic ZrO_2). Baddeleyite is found in small deposits and usually contains contaminants such as silica, iron oxide, and titania. Baddeleyite deposits are mined commercially in Brazil and South Africa.

Zirconium ores all contain varying amounts of hafnium, typically 1.5–3 wt% of the Zr content. As a result of the chemical similarity of Hf to Zr, separation techniques are expensive. Unless specifically required separation is not performed and technical grade zirconia is sold containing up to 3 wt% Hf.

Zincite

Zinc oxide (ZnO) occurs naturally as the mineral zincite. Chemically pure ZnO is white. Zincite is red because it contains up to 10% Mn; traces of FeO are usually also present. Naturally occurring sources of zincite are not commercially important. There are two production methods for forming zinc oxide:

- Oxidation of vaporized zinc metal in air
- Reduction of sphalerite (ZnS) with carbon and CO

Sphalerite is a naturally occurring mineral and the most important ore of zinc. Large deposits are found in limestone of the Mississippi Valley, around Joplin, MO and Galena, IL. Significant deposits are also found in France, Mexico, Spain, Sweden, and the UK.

The largest consumers of ZnO are the rubber and adhesives industries. Zinc oxide is also found in some latex paints, tiles, glazes, and porcelain enamels, and is the most widely used material in the manufacture of varistors.

Rutile and Anatase

Rutile (TiO_2, titania) occurs as a constituent of igneous rocks such as granites and also in metamorphic derivatives such as gneiss. It also occurs as fine needles in slates, biotite mica, quartz, and feldspar. Economically the most important deposits are segregations in igneous rocks as found in Virginia, Canada, and Norway. Rutile is also an important constituent of beach sands resulting from denudation of rutile-bearing rocks, as in Australia, Florida, and India.

Titania is also produced by reacting ilmenite $FeTiO_3$ with sulfuric acid at 150–180°C to form titanyl sulfate, $TiOSO_4$:

$$\begin{gathered} FeTiO_3\ (s) + 2H_2SO_4\ (aq) + 5H_2O\ (l) \rightarrow \\ FeSO_4 \cdot 7H_2O\ (s) + TiOSO_4\ (aq) \end{gathered}$$

Titanyl sulfate is soluble in water and can be separated from undissolved impurities and the precipitated iron sulfate by filtration. Hydrolyzing at 90°C causes the hydroxide $TiO(OH)_2$ to precipitate:

$$TiOSO_4\ (aq) + 2H_2O\ (l) \rightarrow TiO(OH)_2\ (s) + H_2SO_4\ (aq)$$

The titanyl hydroxide is calcined at about 1000°C to produce titania TiO_2.

19.8 NONOXIDES

Most of the important nonoxide ceramics do not occur naturally and therefore must be synthesized. The synthesis route is usually one of the following:

- Combine the metal directly with the nonmetal at high temperatures.
- Reduce the oxide with carbon at high temperature (carbothermal reduction) and subsequently react it with the nonmetal.

In this section we look at several important nonoxide ceramics. To show the variety of nonoxide ceramics we have taken examples of carbides, nitrides, and borides. There are of course many other nonoxide ceramics that are of interest.

SiC	Abrasives, harsh-environment electronic packing
TiC	Bearings, cutting tools
AlN	Electronic packaging, crucibles
Si_3N_4	Future gas-turbine and diesel engine components
ZrB_2	Crucibles and thermowell tubes (steel)
WC	Abrasives, cutting tools
C	Graphite: solid lubricant; diamond: abrasive

Silicon Carbide

Silicon carbide (SiC) is the most widely used nonoxide ceramic. Its major application is in abrasives because of its hardness (surpassed only by diamond, cubic boron nitride, and boron carbide). Silicon carbide does not occur in nature and therefore must be synthesized. It occurs in two crystalline forms: the cubic β phase, which is formed in the range 1400–1800°C, and the hexagonal α phase, formed at >2000°C.

Silicon carbide is synthesized commercially by the Acheson process, which involves mixing high-quality silica sand (99.5% SiO_2) with coke (carbon) in a large elongated mound and placing carbon electrodes in opposite ends. Each mound, or furnace, consists of about 3000 t of material. An electric current is passed between the electrodes resistively heating the coke in the mound to about 2200°C. The total electrical energy consumed during a standard furnace run is about 2 million kWh (about 7 TJ). The average power input during the furnace run is 9000–10,000 kW.

At the high temperatures the coke reacts with the SiO_2 to produce SiC plus CO:

$$SiO_2\ (s) + 3C\ (s) \rightarrow SiC\ (s) + 2CO\ (g)$$

Heating is continued (2–20 days depending on the size of the transformer and the furnace) until the reaction is completed on the inside of the mound. After cooling, the mound is broken up and sorted. The core contains high-purity green hexagonal SiC crystals suitable for electronic applications. The purity of the SiC can be determined based on the color of the crystals.

FIGURE 19.7 SiC produced by the Acheson process.

- Light green 99.8% pure
- Dark green 99% pure
- Black 98.5%

Around the core is a zone of lower purity (≥97.5%), which is suitable for abrasives. The outer layer consists of a mixture of SiC, unreacted SiO_2, and C that is reused in the next batch. Figure 19.7 shows examples of SiC crystals produced by the Acheson process.

The world's largest producer of SiC is China, which produces about 450,000 t/year. The largest U.S.-based manufacturer for SiC is Exolon in Hennepin, IL, which produces about 40,000 t of SiC annually. Figure 19.8 shows several of the furnaces at the Hennepin plant in various stages of production. The cost for SiC powders produced by the Acheson process is in the range \$10–\$40/kg.

Titanium Carbide

Titanium carbide (TiC) is another nonoxide ceramic that is not available in nature. It is prepared either by the carbothermal reduction of TiO_2 or by direct reaction between the elements titanium and carbon. As in many of these reactions high temperatures are required. The carburization temperature is between 2100 and 2300°C.

Aluminum Nitride

There are several large-scale methods for producing AlN, two of which are currently used in industry. One method is direct nitridation of aluminum:

FIGURE 19.8 The Exolon plant in Hennepin, IL. This plant is one of the newest SiC facilities in the world, producing both high-quality metallurgical and crystalline SiC annually. It is North America's only manufacturer of SiC. The plant features 16 furnaces operating off of four transformers.

$$Al\ (l) + 1/2N_2\ (g) \rightarrow AlN\ (s)$$

Al powders are converted directly to the nitride at temperatures above the melting point of the metal. Careful process control is necessary to avoid coalescence of the metal prior to nitridation.

Reducing alumina using nitrogen or ammonia in the presence of carbon is another method to produce AlN:

$$2Al_2O_3\ (s) + 3C\ (s) + 2N_2 \rightarrow 4AlN\ (s) + 3CO_2\ (g)$$

The mixture of alumina and carbon is reacted with a nitrogen-containing atmosphere above 1400°C. Fine powders and extremely good control of mixing are required to result in complete conversion to AlN.

In both processes the major impurities are O (~1.0 wt%) and C (<0.07 wt%). Other impurities are silicon, iron, and calcium, which typically occur at levels <50 ppm each.

The main vendors for AlN powders are Advanced Refractory Technologies (in the United States); H.C. Starck and Elf Atochem (Europe); and Toyo Aluminum and Tokuyama Soda (Japan). The world market for AlN powder is about 200 t/year. Prices range from \$20/kg to \$180/kg depending on supplier, powder characteristics, and quantity.

Many of the applications of AlN require it to be in consolidated in the form of substrates or crucibles. It is an electrical insulator and has a high thermal conductivity (better than Fe), which makes it attractive for use in electronic packaging. Aluminum nitride crucibles are used to contain metal melts and molten salts.

Silicon Nitride

Silicon nitride (Si_3N_4) is another synthetic mineral. It occurs in two crystalline forms. The lower temperature α form is usually preferred as a raw material because the transformation to the β form during sintering favors the development of an elongated crystal structure. Several routes are available for the synthesis of Si_3N_4 powder, similar to those used to form AlN:

- Nitridation of Si powder
- Carbothermal reduction of silica in N_2
- Vapor phase reaction of $SiCl_4$ or silane (SiH_4) with ammonia

Most commercially available powder is made by reacting silicon powder with nitrogen at temperatures from 1250 to 1400°C according to the reaction

$$3Si\ (s) + 2N_2\ (g) \rightarrow Si_3N_4\ (s)$$

The powder generally consists of a 90:10 mixture of α-Si_3N_4 and β-Si_3N_4 polymorphs. Seeds of Si_3N_4 powder are often mixed with the silicon to hasten the reaction and to help prevent the formation of the undesired β phase. Nitrided powder contains impurities such as Fe, Ca, and Al originally present in the Si or picked up during subsequent milling. Higher purity Si_3N_4 powder can be made by carbothermal reduction in the range 1200–1550°C:

$$3SiO_2\ (s) + 6C\ (s) + 2N_2\ (g) \rightarrow Si_3N_4\ (s) + 6CO\ (g)$$

Although this process leads to powders with residual carbon and oxygen it produces high surface area powder with a high α content. Si_3N_4 seeds may again be used to speed up the reaction.

High-purity powders are also made via vapor phase reactions such as

$$SiCl_4\ (g) + 6NH_3\ (g) \rightarrow Si(NH)_2\ (s) + 4NH_4Cl\ (g)$$

$$Si(NH)_2\ (s) \rightarrow Si_3N_4\ (s) + 2NH_3\ (g)$$

$$3SiH_4\ (g) + 4NH_3\ (g) \rightarrow Si_3N_4\ (s) + 12H_2\ (g)$$

Powder from these reactions is amorphous, but the product on heating to 1400°C is mostly α-Si_3N_4.

Worldwide production of Si_3N_4 is about 500 t/year; Japan is the primary market. The cost for this powder is between \$30/kg and \$150/kg depending on the particle size and the quantity ordered.

Silicon nitride exhibits high strength at elevated temperatures and excellent thermal shock, creep, and oxidation resistance in hostile environments, which makes it ideal for gas turbine and diesel engine applications. The SiAlONs are variations on this theme. For example, SiAlON is being combined with boron nitride (BN) to produce a composite material that is reported to have incomparable thermal shock resistance.

Zirconium Diboride

ZrB_2 is useful as a crucible material for metal melts because of its excellent corrosion resistance. It is also used in Hall–Heroult cells (for Al production) as a cathode and in steel refining where it is used as thermowell tubes.

Several different processes can be used to produce ZrB_2; these are similar to those used to form carbides and nitrides. Commercially, either a direct reaction between zirconium and boron

$$\mathrm{Zr + 2B \rightarrow ZrB_2\ (s)}$$

or carbothermal reduction of zirconia is used:

$$\mathrm{2ZrO_2 + C + B_4C \rightarrow 2ZrB_2 + 2CO_2}$$

$$\mathrm{2ZrO_2 + 5C + 2B_2O_3 \rightarrow 2ZrB_2 + 5CO_2}$$

All these reactions must be carried out at high temperature in an inert atmosphere or in vacuum. The typical price of ZrB_2 powder is \$60–\$100/kg.

Tungsten Carbide

Tungsten carbide is a wear-resistant material used in the metalworking, mining, and construction industries for machine parts and dies that are subject to severe service conditions. It is produced by carburization of tungsten powder. The United States uses about 5500 t of WC each year.

Carbon

Graphite is one of three crystalline forms of carbon, the others being diamond and fullerenes. Graphite is unlike most of the nonoxide ceramics in that it occurs naturally in metamorphic rocks such as marble.

The graphite used in industry comes both from natural sources where it is mined in open pit and underground operations. The largest producers of natural graphite are China and India and total world production is around 1 Mt/year. Graphite is not currently mined in the United States, although the United States does produce about 300,000 t of synthetic graphite annually with a value of almost \$1 billion.

There are several methods used to produce synthetic graphite. Many of these involve heating nongraphitic carbons above 2500°C. For example, a high-purity form is produced by heating a calcined mix of petroleum coke and coal tar pitch to 3000°C. The high temperature allows the carbon atoms to order into the graphite structure. Synthetic graphite can also be obtained by chemical vapor deposition from hydrocarbons at lower temperatures (~1800°C).

Most of the synthetic graphite produced in the United States (>60%) is used in the massive electrodes in carbon-arc furnaces to melt steel and in much smaller battery electrodes. Other major applications include lubricants and carbon raisers in steelmaking. Synthetic graphite is used in replacement heart valves, an application we describe in Chapter 35.

The largest uses for natural graphite are in refractories (45%) and brake linings (20%). Natural graphite costs around \$500/t, whereas synthetic graphite costs over \$2000/t.

The quantity of industrial diamonds produced in the United States is much smaller than the amount of synthetic graphite. About 300 million carats or 60 t are produced each year with major applications in stone cutting and highway/building repair.

The fullerenes were discovered in 1985 and the related carbon nanotubes in 1991. Both are now available in commercial quantities, but at present they are very expensive and the applications are limited to specialty products such as Nanodesu bowling balls, which use fullerenes as an additive in a polymer coating.

CHAPTER SUMMARY

This chapter described the processes used to obtain the raw materials necessary to make ceramics. The significant points to remember from this chapter as you continue your study of ceramics are as follows:

- Where and how we get the raw materials will determine impurity concentrations in the final powder (e.g., Na is the major impurity in Bayer alumina).
- The abundance of a mineral may affect the cost of the final ceramic component (e.g., SiO_2 comes from sand; it is abundant and inexpensive. Glass bottles are cheap; the cost of an Si wafer is not related to the cost of sand).
- If the raw materials are not oxides then they have almost certainly been synthesized [e.g., we use 0.5 Mt of SiC (mostly for abrasives), which must be synthesized. The cost of the powder depends on how pure it is].
- Gemstones are found during mining, but are not abundant (e.g., about 200 mg of diamonds will come from 1 ton of ore; the market price of diamonds can justify this dilution).

PEOPLE & HISTORY

Acheson, Edward Goodrich (1856–1931), was an American chemist who worked with Thomas Edison before establishing his own laboratory. He developed a process for producing silicon carbide while trying to make synthetic diamonds. In 1891 he founded The Carborundum Co. to produce SiC for abrasives and was granted a patent in 1893 for SiC. In 1926, the U.S. Patent Office named his patent for SiC one of the 22 patents most responsible for the industrial age.

Bauxite is named after the small French town of Les Baux de Provence, which is near Arles.

Bayer, Karl Joseph (1847–1904) was an Austrian chemist (born in (Bielitz) who described the Bayer process in 1888.

Dana, James Dwight (1813–1895) was educated at Yale University and made contributions to the fields of geology, mineralogy, and zoology. He developed classification systems that are still in use in these fields today.

Graphite. The word is derived from the Greek word *graphein*, to write. Graphite is used as the "lead" in pencils among many other applications.

Kaolin refers to an area of Jiangxi province, which is why it is also called China clay.

Moissan, Ferdinand Frédéric-Henri (1852–1907) is known in the field of ceramics for his unsuccessful attempts at diamond synthesis (he actually produced SiC). Moissan was awarded the 1906 Nobel Prize in Chemistry for isolating fluorine on June 26, 1886. It was in Moissan's laboratory at the University of Paris in France that tungsten carbide was first made.

Mullite is named after the Isle of Mull off the west coast of Scotland where the rare mineral is found.

Muscovite mica was first used in 1850 by James Dwight Dana and is derived from the term "Muscovy glass," by which it was previously known because of its widespread use as a window-glass substitute in the old Russian state of Muscovy.

Phlogopite mica comes from the Greek word *phologopos* meaning *fiery* in reference to the reddish color seen on some specimens of this mica.

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WWW

www.usgs.gov

U.S. Geological Survey. The Mineral Commodity Summaries and the Minerals Yearbook are here, and so much more.

EXERCISES

19.1 How many pounds of mullite are there in 1 ton of the material? How many kilograms?

19.2 What are the major impurities you would expect to find in high-quality deposits of silica sand?

19.3 Why do you think rock quartz is not used widely as a source of silica?

19.4 In the brief description of Edward Acheson we noted that the U.S. Patent Office named silicon carbide as one of the 22 patents most responsible for the industrial age. Why do you think this was such an important material?

19.5 What factors do you think contribute most to feldspar sales in the United States?

19.6 Why are magnesia sales related to steel production?

19.7 What is the difference between zircon and zirconia? Which of these, in single crystal form, is the diamond simulant?

19.8 A commercial supplier of ceramic powders sells 1 g of HfO_2 (purity 99%) for about $2, but charges only 15 cents for the same amount of ZrO_2 (purity 99%). Both powders come from the ore zircon. Explain the differences in the price.

19.9 Quartz, basalt, and obsidian are all formed when magma cools (they are all igneous). Relate the microstructure of each of these materials to the expected relative rate of cooling of the magma. (We described obsidian in Chapter 2, you may need to look in a geology book for the microstructure of basalt.)

19.10 Synthetic graphite is used primarily for electrodes and as a carbon raiser in steel production, whereas the major applications of natural graphite are refractories and brake linings. Why does the source of graphite matter and what are some of the considerations end users might make in deciding where to buy their graphite?