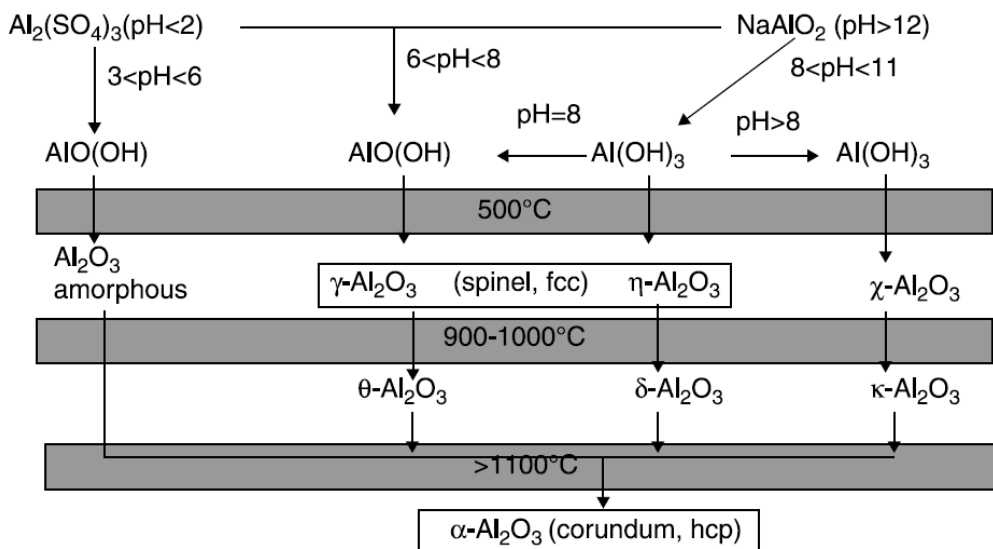


Alumina (Al₂O₃)

Aluminas exhibit good mechanical performances at temperatures as high as 1900 °C provided they are not exposed to thermal shock, impact, or highly corrosive atmospheres. Above 2000 °C, the strength of alumina drops; consequently, many applications are under steady-state, high-temperature conditions, but not where abrupt temperature changes would cause failure arising from thermal shock. Aluminas have good creep resistance up to about 1800 °C, above which other ceramics show a better behavior. In addition, aluminas are susceptible to corrosion from strong acids, steam, and sodium. Alumina is the most versatile engineered ceramic because it can be used up to very high temperature, and because of its chemical, electrical, and mechanical properties. Its relatively low cost and easy fabrication also enhance its use.



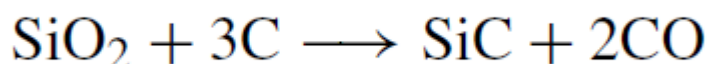
Alumina products range from relatively low-calcined grades of polishing aluminas to the extremely hard, fused alumina and synthetically produced sapphire. The main properties that make alumina valuable in ceramic applications are its high melting point (2050 °C), hardness (9 on the Mohs scale), strength, dimensional stability, chemical inertness, and electrical insulating ability. Together with its availability in large quantities at moderate prices, these properties have led to extensive and varied uses of alumina as a ceramic material. Alumina is currently the most highly developed engineering ceramic. A wide range of high Al₂O₃ ceramics is produced under different trade names, the Al₂O₃ content

usually ranges from 92% to 99.8%, with trace components, particularly silica, enhancing its properties. Strength and temperature capability increase with Al₂O₃ content, but shaping capability decreases with increasing Al₂O₃ content. SiO₂, MgO, and other additives are added to aid shaping and to control sintering temperature. The microstructure of high-Al₂O₃ ceramic also contains some glassy phase arising from the sintering additives. One drawback for its use is a poor thermal shock resistance and the difficulty of machining sintered materials to obtain high-dimensional accuracy of complex-shaped components. Indeed, because of its high hardness, α -Al₂O₃ has long been used in abrasives, either in the form of loose grains or bonded material in grinding wheels. Retention of hardness at high temperature is an important characteristic because the tool temperature can reach values as high as 1000 °C during the machining of ductile materials such as steel. Silicon carbide whiskers can be added to Al₂O₃, increasing its thermal conductivity and, consequently, the resistance to thermal shock. They also significantly increase toughness, which has led to improved tool performance. Sintered Al₂O₃ is also used for missile radomes, external containers for radar, and other equipment. The radome must be transparent to radar signals, thus requiring some particular dielectric properties; in addition, as an external surface, it is also exposed to aerodynamic and thermal effects during flight. It is also widely used for crucibles, tubes, and rods for high-temperature use and for a large number of wear-resistant and corrosion-resistant specialized items. Perhaps the most important single products are spark plugs and the optically translucent polycrystalline alumina lamp hulls for high-temperature sodium vapor street lamps.

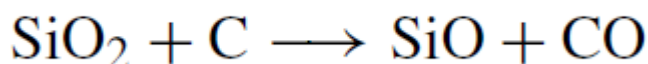
Silicon Carbide (SiC)

Silicon carbide was the first synthetic abrasive invented and commercialized. It was discovered by Acheson in 1891, when he tried to make diamonds by an electric-arc heating process. As Acheson wrongly thought that this compound was a combination of carbon and corundum, he called it “carborundum,” a name maintained even after knowing its real chemical composition. Its chemical formula is SiC, with a composition of 70.05 wt % Si and 29.95 wt % C. Its density is 3.21 g/cm³. It does not exhibit a congruent melting point. In a closed system, i.e., under equilibrium conditions at a total pressure of

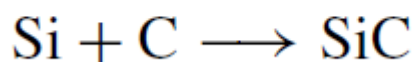
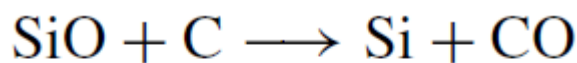
0.1MPa, SiC decomposes at 2830 ± 40 °C into carbon and a silicon-rich melt; in an open system decomposition, it begins at ca. 2300 °C (18). Silicon carbide has special chemical and physical properties, especially a high chemical resistance, a great hardness, and semiconducting properties. It is consequently used in the production of abrasives, refractory materials, heating elements, voltage-dependent electrical resistors, light-emitting diodes, and structural ceramic components. Silicon carbide also has the ability to dissolve in molten iron, and it is therefore used in ferrous metallurgy as an alloying and deoxidizing agent. Silicon carbide has the diamond structure, with C and Si atoms located in alternated positions in the structure, each one having a tetrahedral coordination of atoms of the other type. Silicon carbide exists as both polymorphs and polytypes. As indicated, coordination of both C and Si atoms is tetrahedral. Depending on the plane packing, two forms of silicon carbide may occur: cubic β -SiC and α -SiC, which includes a large number of hexagonal and rhombohedral crystal types. In addition, different polytypes are formed, such as 3C, 4H, 6H, and 15R. β -SiC is metastable and is formed initially in SiC production. It changes into α -SiC above 1900 °C (19). Different packing patterns for these polytypes are shown in Figure 22.13. Silicon carbide is produced industrially from silicon dioxide and carbon, which react according to the overall equation:



The reaction is strongly endothermic with $\Delta H_{298\text{K}} = +618.5$ kJ/mol (20). The reaction in fact takes place in several stages. The initiation step is thermodynamically possible above ca. 1700 °C and in fact starts when SiO₂ melts.



The next steps are



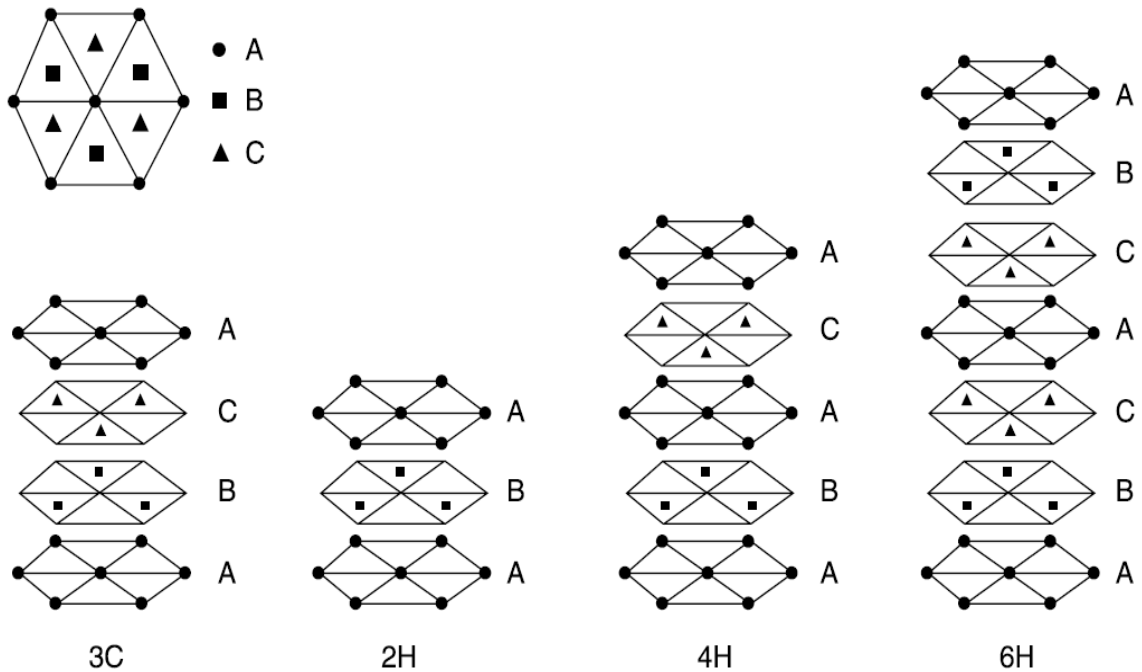
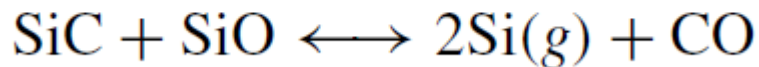


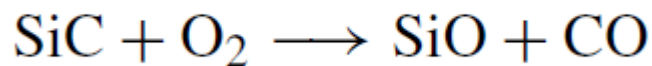
Figure 22.13. Different packing patterns for SiC polytypes.

The SiC thus formed appears as an incrustation on the carbon grains, preventing further formation of SiC, and ultimately causing the reaction to halt. The SiC then reacts further

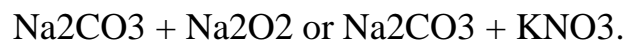


The yield and quality of silicon carbide are seriously affected by any impurities existing in the raw materials. Therefore, high-purity raw materials should be used. The source of silicon is generally very pure, natural silica sand or ground quartz. The SiO₂ content is 99.0–99.9%, preferably >99.7%, depending on the quality of SiC required. The usual impurities are Fe₂O₃ (0.01–0.05%) and Al₂O₃ (0.02–0.50%) (21). The preferred carbon source is low-ash petroleum coke, with a typical composition 93.7% C_{fix}, 6.2% volatiles, and 0.1% ash. Charcoal and anthracite are also used to produce silicon carbide, but these materials are not sufficiently pure to produce the highest quality SiC grades such as green SiC. An important new process is the direct manufacture of sinterable α -SiC powders from the gas phase by decomposing gaseous silicon halides in the presence of hydro-carbons in a plasma jet reactor. In another CVD process, the starting materials are organosilicon compounds. Another method of producing a sinterable α -SiC powder

is the carbothermic reduction of finely divided SiO₂. In addition to its hardness, an important property of silicon carbide is its chemical resistance: It is resistant to organic solvents, alkalis, acids, salt solutions, and even aqua regia and fuming nitric acid. The behavior of silicon carbide toward oxygen and oxygen-containing gases is of industrial importance. Oxidation of pure SiC begins at ca. 600 °C, forming a SiO₂ coating on the surface of the SiC that prevents further oxidation. This is named passive oxidation, and it may be distinguished from the active oxidation, which takes place under oxygen deficient conditions above 1000 °C, leading to decomposition of SiC and formation of SiO, through the following reaction:



Silicon carbide is attacked and decomposed by oxidizing agents if the SiO₂ protective layer is removed, thereby enabling the reaction to proceed unhindered. SiC is decomposed in this way by fused alkalis such as



In the presence of oxygen, fused lead borate causes complete decomposition of SiC. Pb₃O₄ or a mixture of K₂Cr₂O₇ with PbCrO₄ reacts very vigorously on heating with silicon carbide. A mixture of hydrofluoric acid, nitric acid, and sulphuric acid slowly attacks silicon carbide. However, complete dissolution only takes place under pressure and at a high temperature if SiC is very finely divided. Chlorine reacts with SiC above 800 °C, forming silicon tetrachloride and carbon. Silicon carbide behaves toward molten metals in various ways: It is not attacked by molten zinc or zinc vapor, whereas molten aluminum attacks SiC slowly, forming Al₄C₃ and Si. SiC is sensitive to oxygen and oxygen-containing gases such as water vapor. In an oxidizing atmosphere, SiC begins to decompose to SiO₂ and CO or CO₂ at ca. 900 °C. Above ca. 1200 °C, the SiO₂ layer formed on the SiC grains becomes glassy and retards further oxidation. Oxidation can be largely prevented by a dense protective coating (e.g., an Al₂O₃ surface layer). SiC is also sensitive to alkali melts, basic slags, chlorine gas, and metal melts other than lead, zinc, and copper. Alkali resistance can be increased by using a nitride bond. SiC is used in blast furnaces, kiln furniture in the ceramic industry (maximum service temperature, 1500 °C), incinerators, retorts for zinc distillation, aluminum industry (submerged burner tubes), and in tubes for ceramic regenerators.

Zirconia (ZrO₂)

Among the families of engineering ceramic materials, zirconias provide the best combination of mechanical properties; for instance, they show the highest mechanical strength and toughness at room temperature. At higher temperatures where the mechanical strength of metals would plummet, the drop-off in the strength of engineering ceramics is more gradual. Zirconias have better wear-resistant properties than metals, are usually resistant to corrosion, and possess a thermal expansion coefficient close to those of many metals. The use of zirconium oxides in technical ceramics is well established, notably for their electrical, wear, and heat-resistant properties. Zirconia and yttria-stabilized zirconia materials are vital ingredients in a huge range of industrial and domestic products, including capacitors, microwave telecommunications, piezoelectrics, wear part ceramics, molten metal filters, fibre optic ferrules, and oxygen sensors. Zirconia is very resistant to acids and bases, but it slowly dissolves in concentrated hydrofluoric acid or hot concentrated sulphuric acid. It is also resistant to many fluxes, molten glasses, or melts, silicate, phosphate, or borate, but it is attacked by fluoride or alkaline melts. Zirconium oxide and alkaline oxides or caustic substances can be fired together to form solid-solution oxides, known as zirconate compounds, or a mixture of both. Because of its high melting temperature (2764 °C), zirconia can be used for structural applications at higher temperatures than alumina (12).

Zirconium oxide is extracted from two commercial ores: baddeleyite (natural form of zirconia, containing ~2% HfO₂ and other impurities) and zircon (ZrO₂·SiO₂). Various undesired elements should be removed from these ores, silica in the case of zircon and low-level impurities of other compounds, such as titanium and iron oxides, from baddeleyite. The breakdown of zircon and baddeleyite through reaction with sodium hydroxide is the most common method for chemical production of the pure oxide. Sodium hydroxide and zircon react above 600 °C to form sodium zirconate, sodium zirconate silicate, and sodium silicate. Careful control of the zircon/sodium hydroxide ratio, temperature, and reaction conditions (particularly the surrounding atmosphere) can yield nearly complete conversion. When sodium carbonate is used, reactions require higher temperatures and depend on the sodium carbonate to zircon ratio. Three polymorphs of ZrO₂ are stable at atmospheric pressure: the cubic one above 2370 °C, the tetragonal phase above 1170 °C, and the monoclinic one below 1000 °C. The cubic form has the fluorite structure, and the tetragonal and monoclinic structures are also known. Transformation of the monoclinic phase to the tetragonal phase begins at ca. 1050 °C and is completed at ca. 1170 °C. This transformation is accompanied by a volume shrinkage of 3–5% and shows thermal hysteresis: On gradual cooling, the tetragonal phase is stable to ca. 1000 °C and the conversion to the monoclinic one is only completed at ca. 800 °C. Upon rapid quenching, the tetragonal

phase is metastable to room temperature. Only the tetragonal phase provides ceramic materials with satisfactory properties, but the mechanical behavior limits its use. The cubic phase shows moderate mechanical properties, whereas the monoclinic phase weakens the mechanical performance and simultaneously reduces the cohesion among the particles and thus the density. Consequently, the percentage of the monoclinic phase in a mixture should be as small as possible for structural ceramics. Some properties of these phases are summarized on Table 22.4.

TABLE 22.4. Some Properties of Zirconia Polymorphs (12).

	Monoclinic	Tetragonal	Cubic
Space Group	P21/c	P42/nmc	Fm3m
a (Å)	5.156	5.094	–
b (Å)	5.191	5.177	
c (Å)	5.304		
β (°)	98.9		
Density (g/cm ³)	5.830	6.100 (calculated)	6.090 (calculated)

The monoclinic–tetragonal transformation is accompanied by a volume change of a. 7% together with considerable hysteresis, resulting in stress and cracking in pure ZrO₂ ceramics. Consequently, such ceramics cannot be manufactured. The addition of suitable metal oxides (mainly CaO, MgO, and Y₂O₃ in solid solution with ZrO₂ for refractory purposes) leads to stabilization of the cubic modification down to room temperature. A fully stabilized ZrO₂ can be achieved by the addition of a 5–10% stabilizer. Partially stabilized zirconia raw materials with a 3–6% stabilizer added are now used in most cases. This leads to smaller volume changes on heating and provides the additional advantage of creating microcracks, which increases the thermal shock resistance of the brick (1). The volume expansion during the tetragonal-to-monoclinic phase transition can be used as an advantage to improve both the strength and the toughness of ceramics:

Zirconia particles within a critical size range are introduced into the ceramic, and the constraining pressure exerted by the surrounding matrix retains zirconia in the tetragonal structure. If a crack grows in such a ceramic, the tensile stress around the advancing crack tip allows the tetragonal–monoclinic transformation to take place. The resulting expansion introduces a compressive stress around the crack tip, thereby reducing its tendency to propagate. The addition of 15 vol%ZrO₂ to Al₂O₃ improves fracture toughness to 12 Mpam^{1/2}; this material is used commercially in modern Al₂O₃ cutting tools. Transformation toughening in ZrO₂ is achieved by isothermally aging a partially stabilized (3% MgO) ZrO₂ at 1400 °C to develop small tetragonal precipitates within the cubic

matrix. This material is used for cutting and slitting industrial materials; the insulating potential in automotive engine parts, where the low thermal conductivity is advantageous, is currently being evaluated. The low thermal conductivity of ZrO_2 has also resulted in its use in coating jet engine components (1). As indicated, to improve its properties, zirconia is extensively modified by the addition of elements that stabilize the cubic structure (13). The amount of these oxides added may produce a partially stabilized zirconia (PSZ) or form a zirconia modification that maintains the cubic structure from its melting point to room temperature, namely, fully stabilized zirconia (FSZ). The oxides more widely used to stabilize zirconia are MgO , CaO , Y_2O_3 , and rare-earth oxides, giving rise to novel and innovative ceramic materials that have brought about considerable technological change. The acronyms frequently used to denote zirconia ceramic alloys are summarized in Table 22.5.

TABLE 22.5. Acronyms for Zirconia Ceramics Alloys.

TZP	tetragonal zirconia polycrystals
PSZ	partially stabilized zirconia
FSZ	fully stabilized zirconia
TTC	transformation toughened ceramics
ZTA	zirconia toughened alumina
TTZ	transformation toughened zirconia

Usually, the molar percentage and symbol of the added, stabilizing element used are also written in the acronym. Stabilized zirconium oxides contain from 3% yttria to 8% calcia. They have the same crystal structure from room temperature to melting, avoiding the catastrophic mechanical failure shown by pure zirconia ceramic parts on transforming from the tetragonal to monoclinic phase while cooling. Partially stabilized zirconias can be thermally cycled to precipitate metastable tetragonal zirconia within the grains of cubic zirconia. These materials have higher toughness than fully stabilized zirconias. The increased toughness of PSZ is the result of stress-induced martensitic transformation of the metastable tetragonal grains to the monoclinic form in the stress field of a propagating crack. This leads to development of an entirely tetragonal zirconia, known as tetragonal zirconia polycrystal (TZP). The orthorhombic structure can be stabilized at atmospheric

pressure by addition of >12 mol % of niobia or tantala or a mixture thereof (2). Y-TZP is very hard, and it has been the ceramic of choice for most uses. However, this material is prone to environmental degradation under humid conditions. Also Mg-TZP and Ca-TZP undergo continuous leaching of the Mg^{2+} and Ca^{2+} cations in aqueous environments, in addition to requiring critical control during annealing. These problems have led us to pay more attention to Ce-TZP, which is more stable under environmental conditions and less prone to leaching and degradation of mechanical properties in aqueous environments. This is possible because the ceria content is larger than 10 mole %. Besides, Ce-TZP has an attractive yellowish-green lustre and is cheaper than Y-TZP (2). To prepare zirconium oxides with satisfactory stability, the presence of yttrium oxide is necessary, the ideal content being 5.15 wt.%. The most common impurity when preparing zirconia is alumina, which should be less than 0.5 wt.%. The ISO requirements for ceramic zirconia, both for chemical composition and for some properties, are summarized in Table 22.6. When using zirconia for special optical and ophthalmic glasses, the requirements are even more strict. Some applications of zirconia ceramics have been already indicated, and others are listed in Table 22.7. Although stabilized zirconias are insulators at room temperature, at elevated temperatures, the vacancies in the anion lattice allow O^{2-} ions to diffuse and the zirconia becomes a solid electrolyte with applications in oxygen sensors and high-temperature fuel cells. Some stabilized zirconias can also be used as resistors or susceptors. Inductively heated yttria-stabilized zirconia cylinders are used as heat sources to melt quartz boules for the drawing of quartz optical fibres. Zirconia is a constituent of lead zirconate titanate (PZT) used in piezoelectric ceramics for applications as gas furnace and barbeque igniters, microphone and phonograph crystals, ultrasonic transducers for medical ultrasound imaging, for agitation in cleaning tanks, and for underwater sonar. With the further addition of lanthanum (PLZT), ferroelectric optically active transparent ceramics have become available..

Clays Used in the Ceramics Industry

1. China Clay
2. Ball Clay
3. Fire Clay
4. Bentonite
5. Talc
6. Shales
7. Other Clays

Shale is a term that refers to sedimentary deposits that have been altered by compaction and, in some cases, the cementation of grains by deposition of other minerals such as

sericite (a fine grained muscovite) [6]. Shales are identical structurally and chemically to clays, although the water content of shales tends to be significantly lower. However, when they are mixed with water, shales develop plasticity similar to clays and can be used interchangeably [22]. In fact, weathering of shales is one method for the formation of clays [2]. Shales often contain high levels of iron, giving them a red color when fired.

Talc is the magnesium silicate structural analog to pyrophyllite. Its properties are nearly identical to pyrophyllite, except that Al^{3+} cations have been replaced by Mg^{2+} cations. Talc occurs in secondary deposits and is formed by the weathering of magnesium silicate minerals such as olivine and pyroxene. In bulk form, talc is also called soapstone and steatite. A typical composition for talc is given in Table 7. Historically, talc has been used extensively in electrical insulator applications, in paints, and as talcum powder.

Bentonites are highly plastic secondary clays that are used in small amounts as absorbents or as binders/plasticizers in batches of other materials [3]. Bentonites are formed from volcanic ash or tuff rather than igneous rocks [6]. The most significant commercial deposits of bentonite in the U.S. are in Wyoming, but bentonite deposits are widespread. The main crystalline constituent of bentonites is montmorillonite, with Mg and Fe substitution onto the octahedral sites (Fig. 6). Bentonites swell significantly when mixed with water. Also, bentonites form highly thixotropic gels, even in low concentration [14]. Because of swelling and extremely high drying and firing shrinkages, bentonites are rarely used as a major constituent of traditional ceramics; applications are confined to additives in a variety of processes

Type	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O + Na ₂ O	H ₂ O
Bentonite	49.6	15.1	3.4	0.4	1.1	7.8	–	23.0
Talc	56.3	3.2	5.4	–	0.4	27.9	0.9	5.7
Shale	54.6	14.6	5.7	–	5.2	2.9	5.9	4.7

Primary Clays

Primary clay deposits are formed when a rock formation is chemically attacked by water. The size and shape of the deposit depends on the size and shape of the parent rock [6]. The mineral constituents and impurities of a primary clay deposit are also determined by the composition of the parent rock, the degree of completion of the reaction, the impurities that are removed by solution during or after reaction, and the impurities brought in during or after formation [3]. The residual clay deposits formed by conversion of feldspar almost always contains silica (quartz) and mica as major mineral impurities. The soluble cations such as potassium, sodium, and calcium are dissolved and removed during or after conversion [2]. Most primary deposits contain a high proportion of impurity phases, with typical clay contents ranging from 10 to

40% by volume [21]. However, primary deposits tend to be low in iron-bearing impurities (reported subsequently as Fe₂O₃), TiO₂, and organics. The major mineral impurities can be removed by beneficiation techniques such as air or water flotation to yield usable clay, while removal of other impurities may require more involved treatment processes [1]. Though not mineralogically correct, clays that are white in color and have minimal iron-based impurities are often referred to as “kaolin,” regardless of the crystalline phases present. To avoid confusion, the term “china clay” will be used for iron-free, white burning clays in this article. Most of the commercially important primary clay deposits are considered as china clays. Industrially significant primary clay deposits in the United States are found in North Carolina with minor deposits in Pennsylvania, California, and Missouri [22]. Perhaps the most famous primary china clay deposits are those found in Cornwall, England, the source of English china clay [22]. Typical compositions of some primary china clays (after removal of accessory minerals) are given in Table 3 [3,22]. In the raw state, high purity clays can be nearly white in color, although commercial deposits vary in color from white to ivory. Likewise, the color upon firing varies from white to ivory depending upon the impurity content. The highest quality clays are termed “white burning” because of the lack of coloring from impurities after heating.

Location	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	H ₂ O ^a
North Carolina	46.2	38.4	0.6	Trace	0.4	0.4	0.6	0.1	13.3
California	45.3	38.6	0.3	Trace	0.1	0.2	1.0	1.4	13.3
England	48.3	37.6	0.5	0.2	0.2	Trace	1.3	0.3	12.0

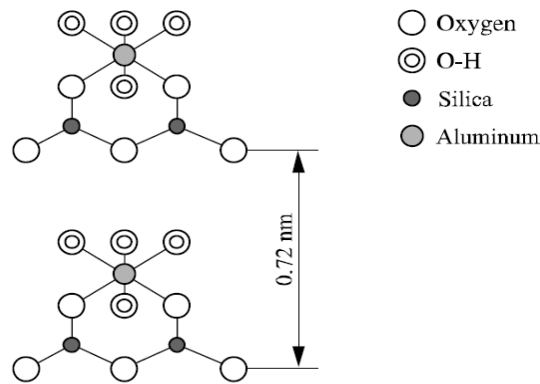
Secondary Clays

Secondary or sedimentary clays are formed in one location and then transported to the location of the deposit by the action of wind or water. Often, mineral impurities present in the primary deposit are left behind during transport. Impurity minerals such as quartz and mica are almost completely removed in some cases. However, other impurities such as TiO₂ and Fe₂O₃ are often picked up during transport [3]. Secondary clay deposits tend to have distinct layers due to repeated cycles of active deposition and inactivity [6]. Secondary deposits can also be significantly larger than primary deposits and contain a wider variety of clay mineral types, since clay can be transported in from different primary deposits [6]. Major U.S. commercial deposits of secondary china clays are found in Georgia, Florida, and South Carolina, with additional deposits in Alabama and Tennessee. Typical compositions of secondary clays are given in Table 4 [22,23]. As with primary clays, the color of raw secondary clays varies with the impurities. Many deposits are white

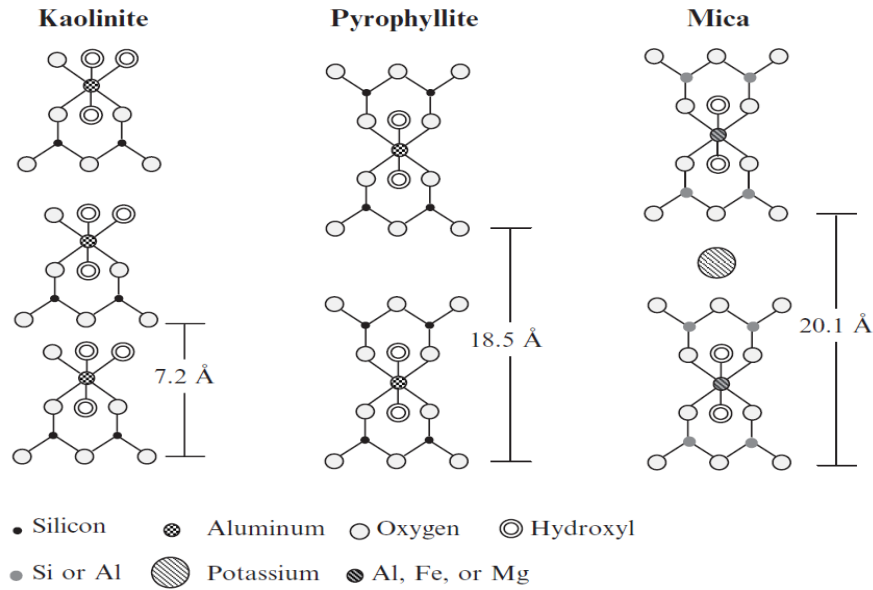
to ivory colored, but secondary clays can also be red or brown due to other impurities. Likewise after firing, color depends strongly on the impurities present.

Location	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	H ₂ O
Georgia	45.8	38.5	0.7	1.4	Trace	Trace	Trace	Trace	13.6
Florida	45.7	37.6	0.8	0.4	0.2	0.1	0.3	0.1	13.9
South Carolina	45.2	37.8	1.0	2.0	0.1	0.1	0.2	0.2	13.7

Kaolinite, Si₂Al₂O₅(OH)₄ or Al₂O₃·2SiO₂·2H₂O, is the most common among the argillaceous minerals used in ceramics. A projection of its crystalline structure is represented in Figure 4.2. It consists of an alternate stacking of [Si₂O₅]²⁻ and [Al₂(OH)₄]²⁺ layers, which confer to it a lamellate character favorable to the development of plates. The degree of crystallinity of the kaolinite present in clays is highly variable. It depends largely on the genesis conditions and the content of impurities introduced into the crystalline lattice.



	Kaolinite	Pyrophyllite	Mica (Muscovite)
Chemical formula	Al ₂ Si ₂ O ₅ (OH) ₄	Al ₂ Si ₄ O ₁₀ (OH) ₂	KAl ₃ Si ₃ O ₁₀ (OH) ₂
Mineral formula	Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O	Al ₂ O ₃ ·4SiO ₂ ·H ₂ O	K ₂ O·3Al ₂ O ₃ ·6SiO ₂ ·2H ₂ O
Crystal class	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
Density	2.6 g cm ⁻³	2.8 g cm ⁻³	2.8 g cm ⁻³
<i>c</i> -Lattice parameter	7.2 Å	18.6 Å	20.1 Å



Plastic fire clays have a composition similar to china and ball clays, except for the elevated Fe_2O_3 and TiO_2 contents. Because of their composition, plastic fire clays have similar plasticity, dried strength, and fired strength when compared with china clays. Plastic fire clays range in color from gray to red or even black in the raw state. Like other fire clays, plastic fire clays produce buff-colored bodies when fired. Flint fire clays have a higher alumina content than plastic fire clays, ball clays, and china clays, in addition to having slightly elevated levels of Fe_2O_3 and TiO_2 .

Flint fire clays have lower plasticity (compared with china clays) when mixed with water and, consequently, develop lower dried and fired strengths. Because of the lower plasticity, the drying and firing shrinkages tend to be very low [25]. Processing of flint fire clays can require plastic additives such as ball clays or bentonites. In the raw state, flint fire clays range in color from gray to red and flint fire clay deposits tend to be harder than other clays [3].

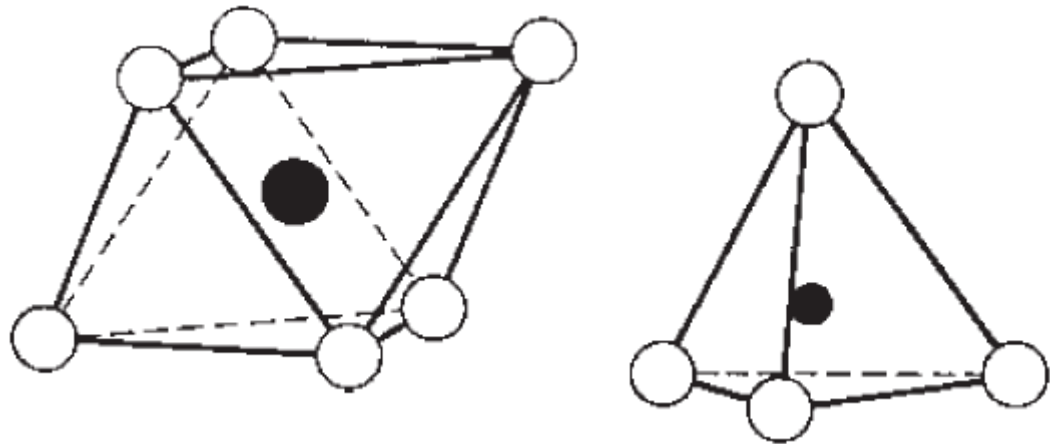
High-alumina fire clays found in the U.S. contain substantial amounts of alumina minerals such as diaspore, in addition to the aluminosilicate clay minerals present. High-alumina fire clays can have much higher alumina content than other common clays (Table 6). These clays produce refractory bodies when fired, but have comparatively low plasticity when mixed with water. Like flint fire clays, high-alumina fire clays undergo little shrinkage when dried or fired. In addition, the dried strength of bodies produced from high-alumina fire clays is poor. High-alumina fire clays tend to

be gray to reddish-brown or brown in the raw state and produce buff-colored objects when fired.

Type	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	H ₂ O
Plastic fire clay	58.1	23.1	2.4	1.4	0.8	1.0	1.9	0.3	8.0
Flint fire clay	33.8	49.4	1.9	2.6	–	–	–	–	12.0
Diasporitic fire clay	29.2	53.3	1.9	2.7	–	–	–	–	12.0

Clays

The term clay refers to fine-grained aluminosilicates that have a platy habit and become plastic when mixed with water [11]. Dozens of minerals fall under the classification of clays and a single clay deposit can contain a variety of individual clay minerals along with impurities. Clay minerals are classified as phyllosilicates because of their layered structure [12]. The most common clay mineral is kaolinite, although others such as talc, montmorillonite, and vermiculite are also abundant.



Common characteristics

Clays are hydrated silico-aluminous minerals whose structure is made up of a stacking of two types of layers containing, respectively, aluminum in an octahedral environment and silicon in tetrahedral coordination. Their large specific surface (10 to 100 m²g⁻¹), their plate-like structure and the physicochemical nature of their surface enable clays to form, with water, colloidal suspensions and plastic pastes. This characteristic is largely used during the manufacture of silicate ceramics insofar as it makes it possible to prepare homogenous and stable suspensions, suitable for casting, pastes easy to manipulate and green parts with good mechanical strength. By extension, the term clay is often used to denote all raw materials with proven plastic properties containing at least one argillaceous

mineral. The impurities present in these natural products contribute to a large extent to the coloring of the shard.

During the heat treatment, kaolinite undergoes a whole series of transformations. The variations of exchanged heat and the corresponding mass changes are indicated in Figure 4.3. The departure of water, which occurs from 450°C onwards, is a very endothermic phenomenon. The amorphous metakaolin, $\text{Al}_2\text{O}_3, 2\text{SiO}_2$ then formed, exhibits a structural organization directly derived from that of kaolinite. The exothermic transformation observed between 960 and 990°C is a structural reorganization of the amorphous metakaolin, sometimes associated with the formation of phases of spinel structure like $\text{Al}_8(\text{Al}_{13,33}\square_{2,67})\text{O}_{32}$ (γ variety of Al_2O_3) or $\text{Si}_8(\text{Al}_{10,67}\square_{5,33})\text{O}_{32}$. In these formulae, \square represents a cation vacancy. Between 1,000 and 1,100°C (often around 1,075°C), these phases are transformed into mullite stoichiometry ranging between $3\text{Al}_2\text{O}_3, 2\text{SiO}_2$ and $2\text{Al}_2\text{O}_3, \text{SiO}_2$. During this reaction, amorphous silica is released. The surplus amorphous silica starts to crystallize in the form of cristobalite from 1,200°C onwards. It should be noted that the impurities present, the degree of crystallinity (see Figure 4.3) and the speed of heating influence each of these transformations.