

Chapter 7

Clays

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Abstract Clays are ubiquitous constituents of the Earth's crust that serve as raw materials for traditional ceramics. Mineralogically, clays are phyllosilicates or layered aluminosilicates. Bonding is strong within layers, but weak between layers, allowing clays to break into micrometer-sized particles. When mixed with water, clays develop plasticity and can be shaped easily and reproducibly. When heated, clays undergo a series of reactions that ultimately produce crystalline mullite and a silica-rich amorphous phase. Beyond the structure and properties of clays, the science that developed to understand traditional ceramics continues to serve as the framework for the study of advanced ceramics.

1 Introduction and Historic Overview

Products such as bricks, whitewares, cements, glasses, and alumina are considered traditional ceramics because they are derived from either (1) crude minerals taken directly from deposits or (2) refined minerals that have undergone beneficiation to remove mineral impurities and control physical characteristics [1]. Most traditional ceramics are fabricated using substantial amounts of clay. Clays are distinguished from other naturally occurring raw materials by their development of plasticity when mixed with water [2]. As a common mineral constituent of the Earth's crust, clays have been used to fabricate useful objects for countless generations, with earthenware ceramics dating back to at least 5000 B.C. [3]. Clay-based ceramic objects were used by virtually all pre-historic cultures for practical, decorative, and ceremonial purposes. Analysis of shards from these objects is our primary means of gathering information on these civilizations. The hard porcelains produced by the ancient Chinese (~575 A.D. more than 100 years before their European counterparts) stand as the ultimate achievement in the field of ceramics prior to the industrial revolution [4,5]. Clay minerals continue to be widely utilized in the production of traditional ceramics and other products due to their ubiquity and low cost combined with properties that include plasticity during forming, rigidity after drying, and durability after firing [6].

For much of the twentieth century, the ceramics industry centered on the utilization of clays and other silicate minerals. Ceramic engineering educational programs and organizations such as the American Ceramic Society were founded to serve industries

based on the utilization of silicate or aluminosilicate minerals [7]. As clay-based traditional ceramics became commodity items in the middle and latter portions of the twentieth century, the focus of educational programs and industrial development shifted away from mineral utilization and toward advanced ceramics, which include phase-pure oxides, electronic materials, and non-oxide ceramics. The raw materials for these products are classified as industrial inorganic chemicals because they have been chemically processed to improve purity compared with the crude or refined minerals used to produce traditional ceramics [1]. Despite the shift in focus away from traditional ceramics, the production of clays has not fallen significantly over the past 30 years (Fig. 1). At a current average cost of more than \$30 per ton (Fig. 2), clay production was a \$1.3 billion

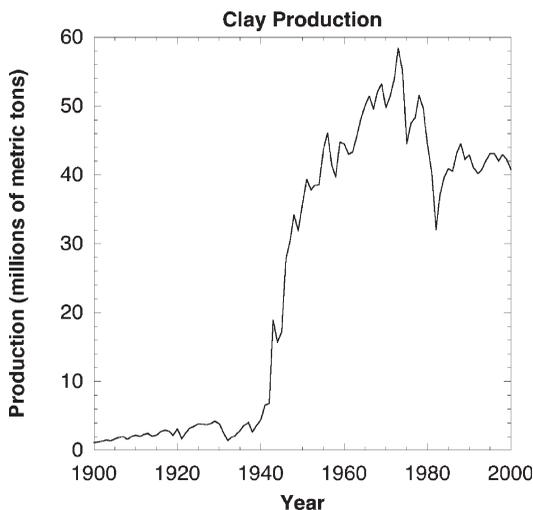


Fig. 1 Clay production from 1900 to 2002 [8]

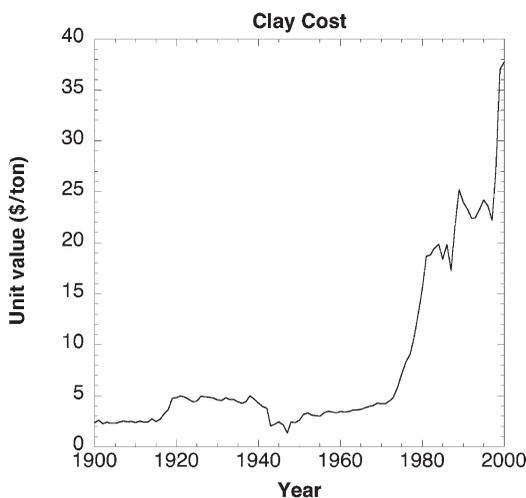


Fig. 2 Cost of clay per ton from 1900 to 2002 [8]

industry in 2002, based on 40.7 million metric tons [8]. Traditional ceramics still account for a significant fraction of the total industry with production in the nonmetallic minerals sector that produced approximately \$95 billion in goods during 2001 [9].

2 Structure, Formation Mechanisms, Types of Deposits, and Use of Clays

This section reviews several of the methods that are used to categorize clays. First, the structure of clay minerals will be discussed. Next, the mechanism of formation for kaolinite will be reviewed followed by a description of the types of deposits in which clays are found. The section will end with a description of the types of clays used in the ceramics industry.

2.1 Structure of Clay Minerals

The outermost layer of our planet, the crust, contains the accessible mineral wealth of the planet. The eight most abundant elements in the crust (Table 1) make up 98.5% of the mass of the crust [10]. The most common metal, silicon, is never found in its elemental form in nature. Instead, silicon is combined in silicate minerals, which make up more than 90% of the mass of the Earth's crust [11]. Depending on the composition and formation conditions, silicate minerals have structures that range from individual clusters (orthosilicates) to three-dimensional networks (tectosilicates) [11]. These minerals can be contained in relatively pure single mineral deposits or, more commonly, in rocks such as granite that are made up of one or more mineral species.

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. Each of the

Table 1 Chemical composition of the Earth's crust

Element	Percent by Weight
O	50
Si	26
Al	7.5
Fe	4.7
Ca	3.4
Na	2.6
K	2.4
Mg	1.9
All others	1.5

clay minerals is composed of a unique combination of layers that are made up of either tetrahedral or octahedral structural units that form sheets [13]. Tetrahedral sheets are made up of oriented corner-shared Si–O tetrahedra (Fig. 3) [14]. Each tetrahedron shares three of its corners with three adjacent tetrahedra, resulting in a structural formula of $(\text{Si}_2\text{O}_5)_n$ for the sheet [15]. Likewise, octahedral sheets are composed of Al bonded to O or OH anions, resulting in an effective chemical formula of $\text{AlO}(\text{OH})_2$ [15,16]. The structure of this sheet is shown in Fig. 4 [14]. The simplest clay mineral, kaolinite, is produced when each of the Si–O tetrahedra in the tetrahedral sheet shares an oxygen with an Al–O/OH octahedron from the octahedral sheet, shown as a perspective drawing in Fig. 5. The repeat unit or layer in the resulting structure is

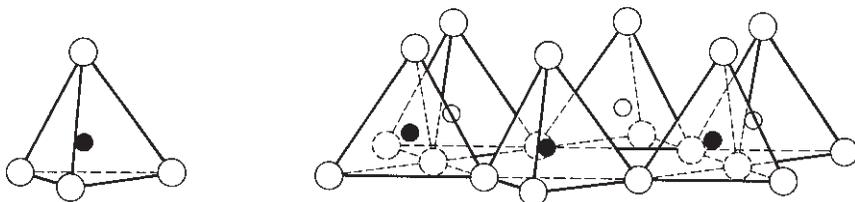


Fig. 3 A single Si–O tetrahedron and the structure of the tetrahedral sheet (Reproduced by permission of the McGraw-Hill companies from R.E. Grim, *Applied Clay Mineralogy*, McGraw-Hill, New York, 1962) [14]

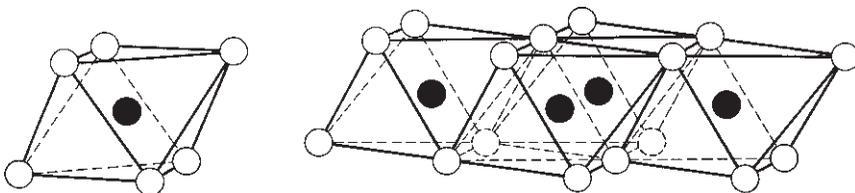


Fig. 4 A single Al–O octahedron and the structure of the octahedral sheet (Reproduced by permission of the McGraw-Hill companies from R.E. Grim, *Applied Clay Mineralogy*, McGraw-Hill, New York, 1962) [14]

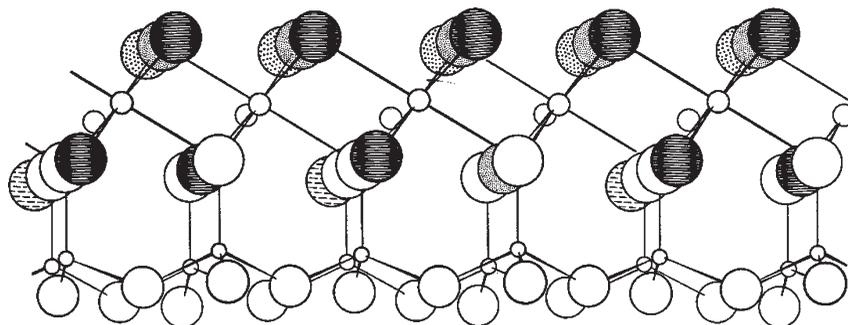


Fig. 5 Perspective drawing of the kaolinite structure taken from Brindley (Reproduced by permission of MIT Press from G.W. Brindley, “Ion Exchange in Clay Minerals,” in *Ceramic Fabrication Processes*, Ed. by W.D. Kingery, John Wiley, New York, 1958, pp. 7–23) [13]

composed of alternating octahedral and tetrahedral sheets. Bonding within each repeat unit is covalent, making the layers strong. In contrast, the bonding between repeat units is relatively weak, allowing the layers to separate when placed in an excess of water or under a mechanical load. The chemical formula for kaolinite, as determined by site occupancy and charge neutrality requirements, is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, which is commonly expressed as the mineral formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. The structure and properties of kaolinite are summarized in Table 2. The repeat units for clay minerals other than kaolinite are produced by altering the stacking order of the octahedral and tetrahedral sheets or by isomorphous substitution of cations such as Mg^{2+} and Fe^{3+} into the octahedral sheets [17].

Conceptually, the next simplest clay mineral is pyrophyllite, which is produced by attaching tetrahedral sheets above and below an octahedral layer (Fig. 6), compared with just one octahedral sheet for kaolin [15]. The resulting chemical composition of pyrophyllite is $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$, which is equivalent to the mineral formula $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$. The structure and properties of pyrophyllite are summarized in Table 2.

Table 2 Composition and crystallography of common clay minerals

	Kaolinite	Pyrophyllite	Mica (Muscovite)
Chemical formula	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$
Mineral formula	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$	$\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
Crystal class	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$C2/c$
Density	2.6 g cm^{-3}	2.8 g cm^{-3}	2.8 g cm^{-3}
c-Lattice parameter	7.2 \AA	18.6 \AA	20.1 \AA

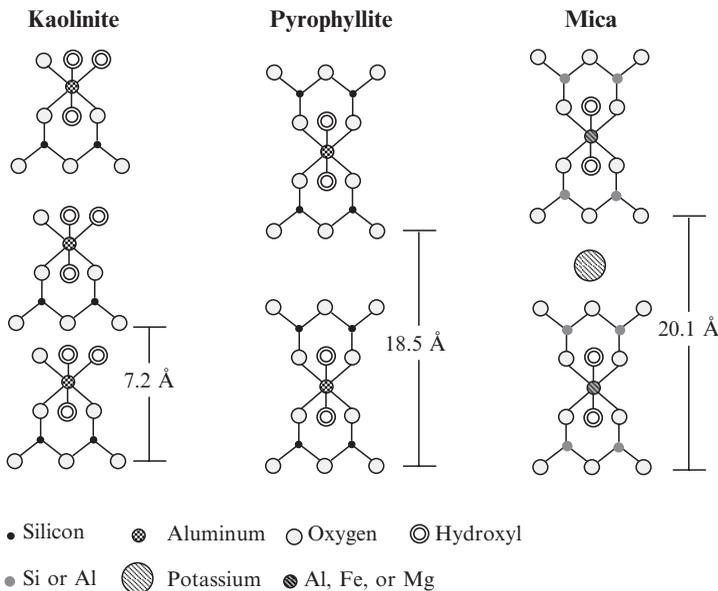


Fig. 6 Schematic representation of the structure of kaolinite, pyrophyllite, and mica (muscovite) after Brindley [13]

More complex clay minerals are produced when Mg^{2+} or Fe^{3+} substitute onto the octahedral Al^{3+} sites in either the kaolinite or the pyrophyllite structures [17]. Along with the substitution onto the octahedral sites, Al^{3+} can substitute onto the tetrahedral sites. These substitutions produce a net negative charge on the structural units, which, in turn, can be compensated by alkali (Na^+ , K^+) or alkaline earth (Ca^{2+} , Mg^{2+}) cations that attach to the structure either between the layers of the structural units or within the relatively large open space inside the Si–O tetrahedra [13]. Families of clay minerals that contain isomorphous substitutions on Al^{3+} and/or Si^{4+} sites are micas and chlorites. The structure of a potassium compensated mica-type mineral is shown in Fig. 6. The charge-compensating cations in these clays are relatively mobile, giving some clays significant cation exchange capacity [15]. In addition to the distinctly different minerals produced by altering the arrangement of the structural units or by substituting cations into the structure, some clays are susceptible to hydration of the interlayer cations, which can cause swelling in the c -direction. An almost infinite number of clay minerals can be conceived by varying site occupancy and layer orders. These structures can be complex and difficult to determine by experimental methods such as X-ray diffraction. Further complication arises due to the fact that some clays are made up of layers with different structural units (e.g., a random sequence of pure or partially substituted pyrophyllite- and kaolinite-type layers).

An additional structural variant for clay minerals is the chlorite-type structure. Chlorites are similar to the pyrophyllite-type structures with two tetrahedral sheets and an octahedral sheet making up each layer. Instead of alkali or alkaline earth interlayer cations, chlorites contain a brucite (Al–Mg hydroxide) layer between successive pyrophyllite-type layers [18].

The major mineralogical classifications associated with clays are summarized in Fig. 7 [18]. Fortunately as ceramists, we are more concerned with the properties of clays than their mineralogy and most often we classify them by use.

2.2 *Formation Mechanism for Kaolinite*

Geologically, clay minerals can be classified based on the conditions under which they form. Clay minerals can form at or near the surface of the Earth by the action of liquid water that originates either on the surface or ground water that is percolating toward the surface [6]. Clay minerals can also form under pressure at greater depths due to the action of heated (~ 100 – $450^\circ C$) liquid-water or liquid-vapor mixtures [19]. For both formation condition, three different mechanisms have been proposed for the conversion of aluminosilicate minerals to clays: (1) the direct reaction with water, (2) dissolution and removal of carbonate minerals, leaving insoluble clay impurities behind, or (3) the action of water on compacted shale sediments [6]. Only the first of these mechanisms will be discussed as it pertains to formation of clays at or near the surface of the Earth, since this combination has produced the largest volumes of industrially relevant clays. In addition, only the reaction of the most common group of minerals, the feldspars, will be considered, but it is recognized that many other minerals convert to clays. To understand the source of impurities in clays, which will be discussed in the next section, the mineralogy of the rocks that serve as the aluminosilicate source are discussed in this section.

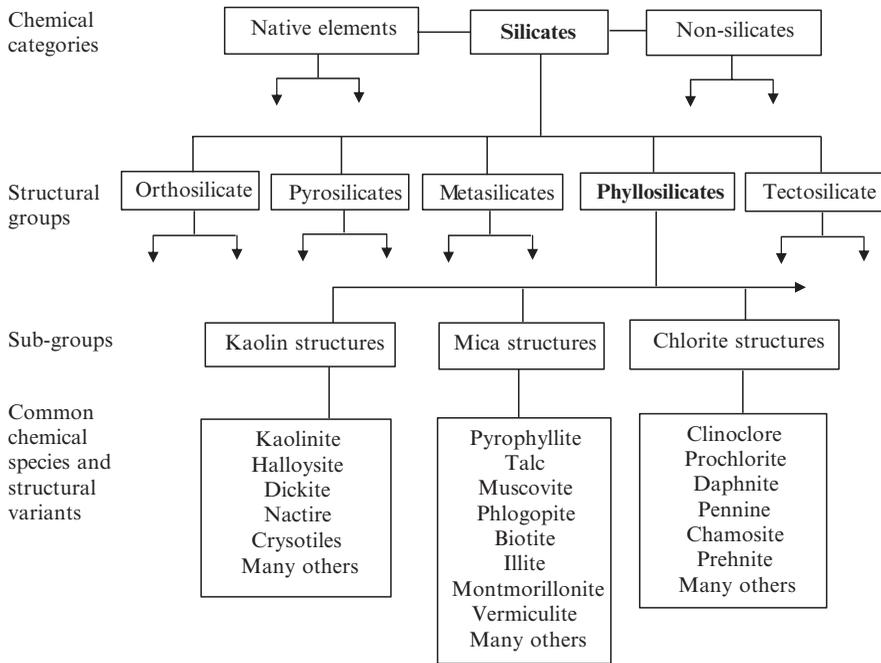
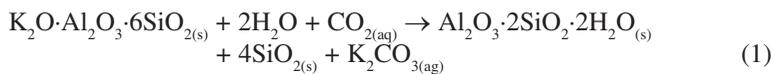


Fig. 7 Mineralogical classifications associated with clay minerals [12,18,22]

Feldspars are common aluminosilicate minerals that are present in many different igneous rocks including granites and rhyolites [11]. When exposed, these rocks are susceptible to physical and chemical attack. Water, along with the sun, plant roots, and other forces physically attack rock formations causing crevice formation and fracture [3]. Water also attacks rocks chemically. Over time, anhydrous aluminosilicate compounds such as those present in igneous minerals react with water to form hydrated species [20]. The classic chemical reaction for clay formation involves the decomposition of potash feldspar due to the action of water-containing dissolved CO_2 to form kaolinite (insoluble) and soluble ionic species (Reaction 1) [14].



In nature, the formation of clays is more complex. One complexity is due to the variable composition of feldspar and the other is due to minerals that can react to form clays [11]. Even when only feldspars are considered, the composition can vary significantly among the end-members of the system, which are orthoclase ($\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$), albite ($\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$), and anorthite ($\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) [11]. The different feldspars along with many other aluminosilicate minerals can undergo conversion to kaolinite. Another complexity is due to the fact that feldspars and other aluminosilicates are present in nearly all igneous rocks [12]. Most often, the formation of clay is considered in the context of the decomposition of granite, a rock that contains feldspar, quartz, and mica [20]. Quartz and mica,

which form due to incomplete decomposition of feldspar, are much more resistant to hydration than feldspar and are often left unaltered by the formation of clays from granite. As a result, quartz and mica are common impurities in primary clays.

2.3 Types of Clay Deposits

In nature, clays can be found either in the same location where they were formed or they can be found in a location where they were transported after formation. Clay deposits that are found where they were formed are referred to as primary or residual deposits. Clays that have been transported after formation are said to be in secondary or sedimentary deposits. The discussion in this section will be limited to kaolinite, but will be expanded to other types of clays of significance to the ceramics industry in the following section.

2.3.1 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 Fe_2O_3), TiO_2 , 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

Table 3 Typical compositions (weight percent) of some primary china clays [3,22]

Location	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	H_2O^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

^aCalled “loss on ignition” in most older texts, now considered chemically combined water

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.

2.3.2 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 TiO_2 and Fe_2O_3 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.

2.4 Clays Used in the Ceramics Industry

In this section, clays are categorized based on how they are used in the ceramics industry. The two major types of ceramic clays are china clay and ball clay. Other materials of note include fire clays, bentonite, and talc. Less refractory materials including those classified as shales and stoneware clays are also of interest. The composition, important properties, and uses for these types of clays are discussed in this section.

2.4.1 China Clay

China clays, also referred to as kaolins, are used to produce traditional ceramics when the color of the finished object and its high temperature performance are important.

Table 4 Typical compositions (weight percent) of some secondary china clays [3,22,23]

Location	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	H_2O
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

China clays generally contain large proportions of the mineral kaolinite, but can contain substantial amounts of other clay minerals. In all cases, the content of Fe_2O_3 , TiO_2 , and other potential coloring impurities is low, resulting in bodies that range in color from white to ivory. China clay is found in both residual and secondary deposits. As detailed in Tables 3 and 4, the compositions of most china clays are slightly Al_2O_3 poor compared with the composition expected based on the mineralogical composition of kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ is 46.6 wt% silica, 39.5 wt% alumina, and 13.9 wt% water) due to the presence of impurities. China clays tend to have a moderate particle size (1–2 μm). Because of the particle size, china clays produce moderate plasticity during forming compared with other clays. Drying and firing shrinkage also tend to be moderate. China clays are used in many traditional ceramics, including pottery and stoneware, along with refractories and finer ceramics such as hard porcelains.

2.4.2 Ball Clay

Ball clays are remarkable because of their high plasticity when mixed with water. The plasticity is a result of fine particle size (0.1–1 μm), which is stabilized by a substantial content of organic matter (up to 2 wt%). Typical compositional data for ball clays are given in Table 5 [24]. Because of the fine particle size, the water demand for ball clays is higher than for most china clays. The fine particle size also gives ball clay bodies higher green strength and higher fired strength than other clays. In the raw state, ball clays range in color from light brown to nearly black, depending heavily on the organic content. After firing, the higher Fe_2O_3 and TiO_2 contents give ball clays, compared to china clays, an ivory to buff color. Ball clays are used extensively in whitewares, pottery, and traditional ceramics due to the workability and strength. However, their use in hard porcelains or other applications where color is important is minimal.

2.4.3 Fire Clay

Though no standard definition exists, the term fire clay refers to secondary clays that are not ball clays or china clays, but can be used to produce refractory bodies [3]. Fire clays are often found in proximity to coal deposits, but this is not true for all fire clays or for all coal deposits [6]. The main sub-types of fire clays, in the order of increasing alumina content, are plastic fire clays, flint fire clays, and high-alumina fire clays. The compositions of typical fire clays are summarized in Table 6 [22]. Among the attributes common to the different varieties of fire clays are their relatively low concentration of fluxing impurities (alkalis, alkaline earths) and their non-white color after firing. Through the 1970s, refractories made from fire clays set the standard for performance in metal processing applications due to their low cost, high corrosion

Table 5 Typical compositions (weight percent) of some ball clays [3,24]

Location	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	H_2O
Tennessee	57.6	28.1	1.1	1.4	Trace	Trace	0.9	0.1	10.6
Tennessee	51.7	31.2	1.2	1.7	0.2	0.5	0.4	0.6	12.1
Kentucky	57.7	28.5	1.2	1.5	0.2	0.2	0.1	1.2	9.5

Table 6 Typical compositions (weight percent) of common types of fire clays [22]

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

resistance, and excellent thermal stability. However, higher processing temperatures and increasingly stringent batch chemistry requirements have driven most industries to alternative refractory linings such as high-alumina castables, basic brick, or carbon containing materials. In spite of the shift in industry needs, fire clay refractories are still used extensively. Current uses for fire clay refractories include insulation behind hot-face materials, low heat duty furnace linings, and specialty applications such as laboratory crucibles and setters.

Plastic fire clays have a composition similar to china and ball clays, except for the elevated Fe₂O₃ and TiO₂ 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 Fe₂O₃ and TiO₂ (Table 6) [22]. 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 diasporite, 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.

2.4.4 Bentonite

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

Table 7 Typical compositions (weight percent) of other commonly used clays

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

firing shrinkages, bentonites are rarely used as a major constituent of traditional ceramics; applications are confined to additives in a variety of processes. The typical composition of a bentonite is given in Table 7 [6].

2.4.5 Talc

Talc is the magnesium silicate structural analog to pyrophyllite. Its properties are nearly identical to pyrophyllite, except that Al³⁺ cations have been replaced by Mg²⁺ cations [25]. Talc occurs in secondary deposits and is formed by the weathering of magnesium silicate minerals such as olivine and pyroxene [2]. In bulk form, talc is also called soapstone and steatite. A typical composition for talc is given in Table 7 [22]. Historically, talc has been used extensively in electrical insulator applications, in paints, and as talcum powder [2].

2.4.6 Shales

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 [22]. A typical shale composition is given in Table 7 [22].

2.4.7 Other Clays

An enormous variety of other grades of clay minerals have been used commercially. The names of these clays can be based on the ultimate application (stoneware clay, brick clay) or the fired properties (red firing clay, vitrifying clay) [25]. The compositions of these clays are highly variable, but in general they contain high amounts of alkalis and high amounts of Fe₂O₃, TiO₂, and other impurities. A few of these clays (earthenware, stoneware, and brick clays) are mentioned here, but interested readers should consult references [3,6,14,22, 25] for information on other categorizations as well as chemical composition information. Keep in mind that the designations are not based on mineralogy, composition, or any specific property. A particular clay may fall under one or more categories depending on how it is gathered, its beneficiation, or its intended use.

Earthenware refers to products produced from unbeneficiated clays with no other additives. Earthenware clays are formed by incomplete conversion of the parent mineral formation and they contain substantial amounts of residual feldspar and quartz, giving a composition similar to a triaxial whiteware [3]. Earthenware bodies are typically formed by throwing or modeling [22]. Earthenwares are self-fluxing during firing due to the alkali content. Fired earthenware bodies typically have high absorption (10–15%) and are fired at moderate temperatures (cone 5–6) [22]. Fired earthenware bodies are usually red and find use as decorative objects, as tiles, or as tableware [26].

Stoneware clays can be used without beneficiation or additives to produce ware with low absorption (0–5%) at relatively low temperatures (cone 8–9) [22]. Fired stoneware objects usually have a buff or gray color and are used as electrical insulators, cookware, decorative items, drain pipe, tiles, and tableware [26]. Stoneware can be formed by casting, throwing, or pressing. The major difference between stoneware clays and earthenware clays is Fe_2O_3 content, with stoneware clays usually having lower Fe_2O_3 than earthenware.

Brick clays tend to be high in alkalis and iron, but low in alumina [14]. The clays usually have moderate to high plasticity, which facilitates forming [25]. Often, brick clays are actually shales [14]. These clays fire at moderate temperatures (cone 1–5) and the resulting fired bodies are dark red. Clays with similar properties but different colors upon firing can be used to produce other products such as sewer tile and roofing tile [6]. Nearly any red burning clay can be classified as brick clay.

3 Processing Methods for Clay-Based Ceramics

The study of clay-based ceramics has an enduring legacy due to the science that developed to understand the rheological behavior of clay–water pastes. As stated repeatedly in this chapter, clays develop plasticity when mixed with water. Plasticity, as defined by Grim, is “the property of a material which permits it to be deformed under stress without rupturing and to retain the shape produced after the stress is removed” [14]. For countless generations, clay-based ceramics were formed by mixing clay and other ingredients with some amount of water (determined by trial and error and/or experience) to get a consistency (i.e., rheology) that was acceptable for the forming method of choice. As new analytical tools were developed throughout the twentieth century, ceramists used them to examine the structure of clay minerals and to understand how clays interacted with water. Even though the emphasis in the field of ceramic engineering has shifted away from traditional ceramics to advanced materials, processing science still focuses on processing methods (dry pressing, extrusion, tape casting, and slip casting) that rely on controlled plastic deformation during forming, thus mimicking the behavior of clay–water pastes [1]. The key difference is that advanced materials use organic additives to promote plasticity whereas plasticity develops naturally when water is added to clays.

3.1 Clay–Water Interactions

The processing methods for clay-based ceramics can be categorized by the water content and the resulting rheological behavior. The methods that will be discussed in

this section, in order of increasing water content, are: (1) dry pressing (2) stiff plastic forming, (3) soft plastic forming, and (4) casting. Most clay compositions can be fabricated using any of the forming processes by simply changing the water content of the batch. As such, the choice of forming methods is often dictated by the desired shape of the product and will be discussed in that context. Water contents and shape limitations for the four forming methods are summarized in Table 8. The overlap in the water contents for the different techniques is due to the varying water requirements for different clays, which is caused by differences in composition, structure, and physical characteristics of the clays.

Forming techniques used for clay-based ceramics require control of water content in the batch. Water content, in turn, affects the response of the clay during forming [27]. As the water content of the batch increases, the yield point of the clay–water mixture, and thus the force required to form the desired shape, generally decreases [26]. However, the relationship is complex and depends on the composition of the clay, its structure, additives to the batch, and other factors [14]. One method for quantifying the behavior of clay–water pastes is to measure the plastic yield point as a function of water content [14]. The water contents and maximum yield points in torsion are compared for several clays in Table 9. Kaolins and plastic fire clays require the least amount of water to develop their maximum plasticity, ball clays require an intermediate amount, and bentonite requires the most.

The interactions between water and ceramic particles are complex and important for processes ranging from the rheology of slurries to the drying of particulate solids. An in-depth discussion of water–particle interactions is beyond the scope of this chapter. For the discussions that follow, it is sufficient to understand the forms that water takes within a particulate ceramic [27]. At the lowest contents, water is present as partial, complete, or multiple layers adsorbed (physical) on the surface of the particles. After the surfaces are covered with a continuous adsorbed film, liquid water can condense in the pores between particles. Finally, at the highest water

Table 8 Water contents and pressure range used during the four common forming methods used for clay-based ceramics [22,26]

Method	Water (wt%)	Pressure range (MPa)
Dry pressing	0–15	100–400
Stiff plastic	12–20	3–50
Soft plastic	20–30	0.1–0.75
Slip casting	25–35	None

Table 9 Water content and maximum yield point for different types of clays [14]

Clay	Water content (wt%) ^a	Yield torque (g cm ⁻¹)
Kaolin	19.2	472
Plastic fire clay	19.0	442
Ball clay	34.4	358
Bentonite	41.9	254

^aDetermined as weight of water added to clay dried at 105°C for 24 h

contents, free water that does not interact with particle surfaces begins to separate individual particles, eventually leading to a stable dispersion of fine, separated particles.

3.2 Dry Pressing

Dry pressing refers to forming methods that require up to 15 wt% water in which plastic deformation of the clay–water mixture is minimal. At the lower end of the water contents, water is present as a partially adsorbed layer. At the higher end, the particle surfaces will be completely covered by the adsorbed layer and some water will condense in fine pores. The amount of water needed for a pressing operation varies depending on the pressing characteristics desired, the state of hydration of the clay, how the clay interacts with water, and the particle size of the clay [1,22]. In dry pressing, water acts mainly as a binder that promotes green strength in a compacted body.

Dry pressing is defined as the simultaneous shaping and compaction of a powder in either a rigid die or a flexible container [28]. Common variations on the technique include uniaxial pressing and isostatic pressing [29]. The water content must be sufficient to promote binding of the clay particles without forming a continuous water film that would allow for excessive plastic deformation under an applied load. Dry pressing is the most common forming technique used in the ceramics industry and it is used to form a variety of clay-based ceramics including floor and wall tile, bricks, and electrical insulators [29]. Shapes with a low aspect ratio (height to diameter) are commonly formed by pressing operations [29]. A schematic representation of a die used for uniaxial dry pressing, along with the resulting forces on the powder compact, is shown in Fig. 8. Compaction pressures range from 20 to 400 MPa (3–60 ksi) with an upper pressure limit of around 100 MPa for uniaxial pressing. Fabrication of parts with high aspect ratios or the use of pressing pressures above 100 MPa can lead to the development of pressure gradients (Fig. 9) and other defects that affect the quality of parts after pressing and after firing [29]. As a side note, most nonclay ceramics require the addition of binders and plasticizers as

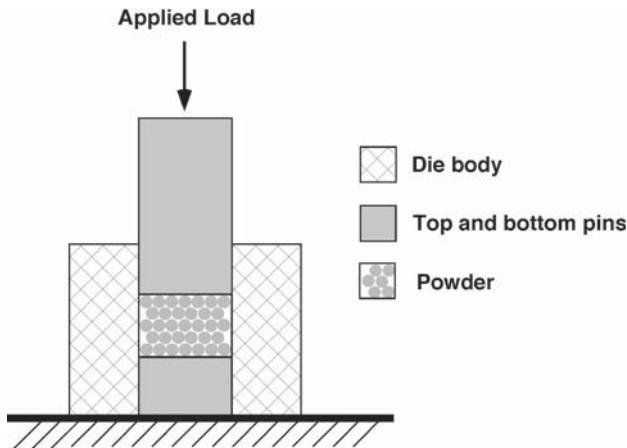


Fig. 8 Schematic representation of a common die geometry for dry pressing [1]

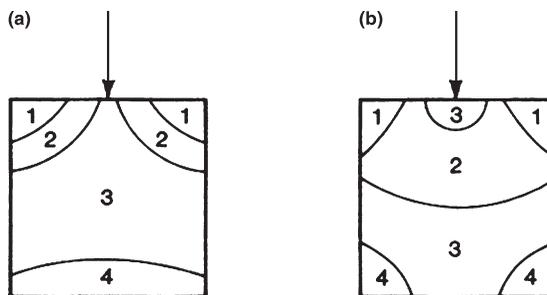


Fig. 9 Schematic representation of pressure gradients that are present in uniaxially pressed clay-based ceramics after pressing at (a) low and (b) high pressure (Reproduced by permission of John Wiley from J.S. Reed, *Principles of Ceramic Processing*, 2nd Edition, John Wiley, New York, 1995) [1]

forming aids [1]. Organic additives are commonly used as binders and plasticizers, but clays such as bentonites are also used as binders/plasticizers in many applications [14].

3.3 Stiff Plastic Forming

The water content for stiff plastic forming techniques is between 12 and 20 wt%, which produces partial or full filling of pores by water [1,25]. Extrusion is the most common stiff plastic forming technique, although injection molding can also fall under this category [22]. The pressures required for stiff plastic forming are lower than dry pressing, ranging from ~3 to 50 MPa (~0.5–10 ksi) due to the higher water content, which results in lower plastic yield points [26]. Extrusion is used to form clay-based products with a uniform cross section such as pipe, tubes, rods, and bricks [1]. In addition, thin-walled products with fine structure details such as honeycomb supports for catalytic converters can be extruded [1]. Extrusion processes can either be continuous or batch type [30]. Continuous auger extruders mix raw materials in a pug mill, shred and de-air the resulting plastic mass, and then force it through a die (Fig. 10a) [30]. The shape of the die opening and the positioning of “spiders” or other tooling in the throat of the die determine the shape of the extruded part [1]. The piston extruders used for batch processes can be used to form the same shapes as continuous auger extruders and they have a much simpler design (Fig. 10b). However, piston extruders can only produce limited quantities of product from a premixed plastic mass [30]. Common defects in extruded parts include laminations caused by wall friction and crow’s foot cracks around rigid inclusions [1]. Nonclay ceramics can also be formed by extrusion, but require formulation of suitable binder/plasticizer combinations [1].

3.4 Soft Plastic Forming

The water content for soft plastic forming methods ranges from 20 to 30 wt%, which produces complete filling of pores by water and can result in some additional free water that separates the particles in the structure [22,31]. Soft plastic forming techniques include high-volume mechanical techniques such as jiggering, jollying, and ram pressing

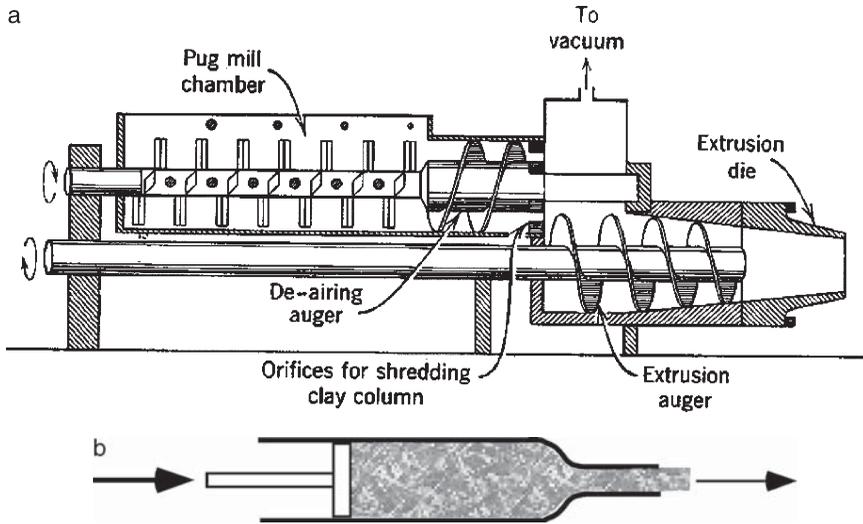


Fig. 10 Augur (a) and piston (b) type extruders used for stiff plastic forming of clay-based ceramics. (a reproduced by permission of John Wiley from W.D. Kingery, *Introduction to Ceramics*, 1st Edition, John Wiley, New York, 1960; b reproduced by permission of the McGraw-Hill Companies from F.H. Norton, *Fine Ceramics*, McGraw Hill, New York, 1970) [25,3]

and low-volume hand techniques such as throwing and wheel turning [27]. The imposed pressure range for soft plastic forming is 0.1–0.75 MPa (15–110 psi) [26]. The soft plastic forming techniques of jiggering and jollying are used to form objects that have a center of radial symmetry conducive to forming by rotation, such as dinner plates, cups, mugs, and flowerpots. During jiggering, the plastic mass is placed on a rotating form that determines the profile of the product and a tool is brought down to cut away excess material from the back (Fig. 11a) [31]. Jollying is similar to jiggering, except that in this case the tool determines the inner profile of the product and the form serves as a physical support [26]. Typically, objects such as dinner plates are formed by jiggering, while objects such as teacups and mugs are formed by jollying. Similarly, ram pressing employs two forms that are pressed together, but without rotating tooling [26]. Ram pressing can be used to form a variety of shapes including dinner plates (Fig. 11b).

3.5 Casting

Slip casting is used to produce clay-based ceramics from clay–water slurries containing 25 wt% water or more [26]. For casting slips, the water content is high enough so that all of the particles in the system are separated by free water. Most often, slip casting requires no applied pressure, although many industrial shops have switched to pressure casting (slip casting with an applied pressure) to improve productivity and reproducibility. Slip casting requires a well-dispersed, stable suspension of ceramic particles and a porous mold, which is most often gypsum (hydrated plaster of Paris) [22]. When the slurry is poured into the mold, the pores in the mold draw water out of the slurry, causing particles to deposit on the mold surface (Fig. 12) [15]. When the cast layer has sufficient thickness, the excess slip is poured out, leaving a thin, negative replica of the mold. The replica is partially dried in the mold until it pulls away

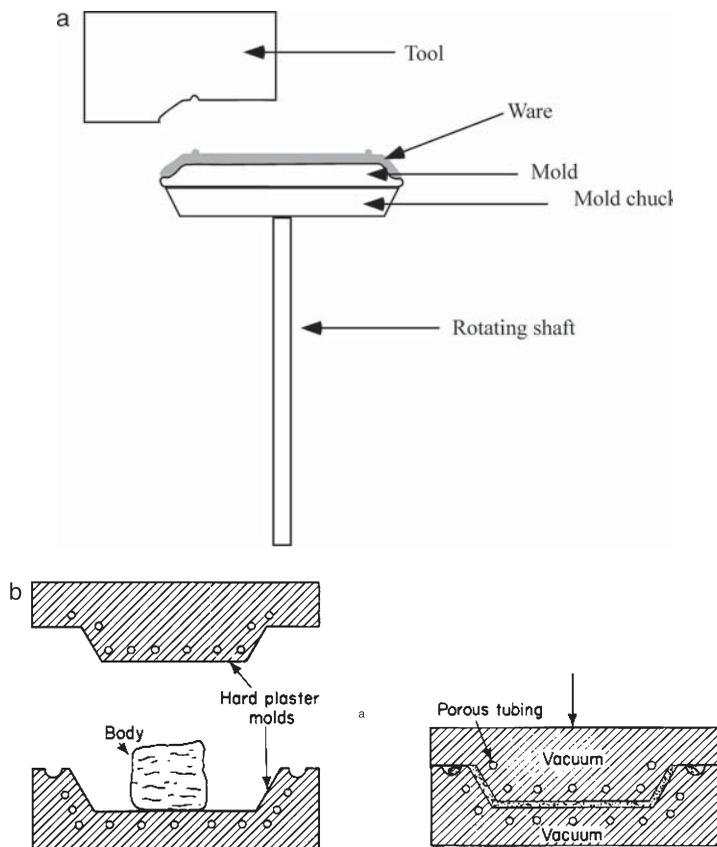


Fig. 11 Schematic illustrations of the processes of (a) jiggering and (b) ram pressing used for soft plastic forming of clay-based ceramics (a reprinted by permission of Addison-Wesley from F.H. Norton, *Elements of Ceramics*, Addison-Wesley Publishing, Reading, MA, 1952; b reprinted by permission of the McGraw-Hill Companies from F.H. Norton, *Fine Ceramics*, McGraw Hill, New York, 1970) [22,3]

from the sides of the mold and is rigid enough to be removed without deformation. Slip casting is used to form objects that are not conducive to jiggering or jollying because of a lack of radial symmetry or those with complex surface details such as decorative figurines. Slip casting is also used to form objects that are difficult to form by other techniques because of their size such as radomes, large crucibles, and large diameter furnace tubes [25]. Slip casting does not work as well with solid objects due to the problem of removing water uniformly and differential shrinkage [1].

4 Kaolinite to Mullite Reaction Sequence

When heated, kaolinite undergoes a complex series of chemical and physical changes that transform the layered mineral to a combination of crystalline mullite and an amorphous siliceous phase. Though simple conceptually, the study of this reaction sequence

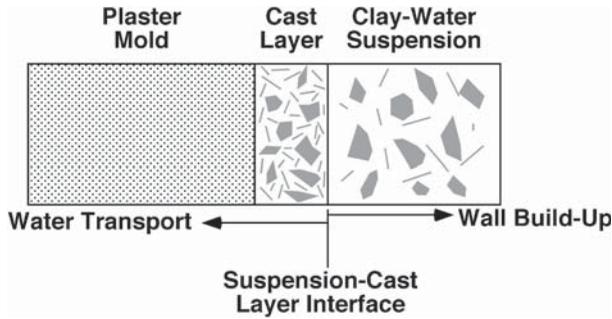


Fig. 12 Schematic representation of the build up of a cast layer (wall) from a suspension of clay particles (slip) in contact with a gypsum (hydrated plaster of Paris) mold (reproduced by permission of Addison-Wesley from F.H. Norton, *Elements of Ceramics*, Addison-Wesley Publishing, Reading, MA, 1952) [22]

continues to draw interest from the materials research community due to on-going controversies related to the composition and structure of the intermediate phases. Notable studies of the reaction of clays during heating have been conducted by LeChatelier [32], Brindley [33], and MacKenzie [34]. In an interesting parallel to the connection between the processing of clay-based ceramics and advanced processing methods, the characterization protocols used in modern ceramic science draw heavily on the work of these authors who were among the first in the field of materials to apply characterization techniques that are now considered routine. LeChatelier used thermal analysis, Brindley employed a combination of transmission electron microscopy and diffraction, and MacKenzie made use of nuclear magnetic resonance spectroscopy.

4.1 Loss of Adsorbed Water

At temperatures below 150°C, water that is physically attached to clays evaporates. Physically attached water can be present as water adsorbed onto the surface of particles or between the layers of the clay structure. The loss of water is endothermic and results in measurable weight loss. For kaolinite, the weight loss is usually minor, on the order of a percent or less. However, other clays, particularly those that swell when exposed to water such as bentonite can have considerable weight loss in this temperature regime (4–8 wt%) [6]. For kaolinite, the changes due to loss of physical water do not alter the structure as determined by X-ray diffraction.

4.2 Metakaolin

Around 450°C, the chemically combined water in clays is released, resulting in the formation of metakaolin. As with the loss of physically adsorbed water, the loss of the chemical water is an endothermic process that is accompanied by weight loss [33]. The magnitude of the weight loss depends on the amount of chemically combined water in the clay. For kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, the weight loss due to chemically

combined water should be 13.9 wt%, which is similar to reported water contents for high-purity secondary kaolins (Table 4). After dehydration, metakaolin appears amorphous on X-ray diffraction, but the short range ordering of the cations within the sheets that make up the kaolinite structure is retained [33,34]. Brindley has speculated that disruption of the order perpendicular to the sheets causes the change in the X-ray diffraction pattern [33]. Thus, metakaolin is a homogeneous molecular-level mixture of noncrystalline alumina and silica. Metakaolin does not spontaneously rehydrate when it is exposed to water and it remains stable up to approximately 980°C.

4.3 Spinel

As metakaolin is heated, it undergoes a structural transformation around 980°C, a temperature of significant interest in the synthesis of mullite ceramics [35]. Brindley, among others, has observed the formation of spinel, an amorphous siliceous phase, and a small amount of nanocrystalline mullite at 980°C [33]. This process is exothermic with no accompanying weight loss. The observed heat of reaction comes mainly from spinel formation [33]. Investigators are in general agreement that the spinel phase is similar in structure to the cubic transitional alumina γ -Al₂O₃ and that it contains most of the alumina from the original kaolin. The amorphous phase is mainly silica, but it also contains a small amount of alumina plus most of the impurities from the original clay. The mullite phase makes up only a small volume fraction of the total volume after heating to 980°C and is composed of submicrometer needle-like mullite grains. Questions remain regarding the composition of the spinel phase, with proposed compositions ranging from pure γ -Al₂O₃ to 2Al₂O₃·3SiO₂, which includes the mullite composition, 3Al₂O₃·2SiO₂ [33,36]. It seems unlikely that spinel is pure γ -Al₂O₃, since mixtures of γ -Al₂O₃ and silica prepared from colloidal particles form α -Al₂O₃ and amorphous silica around 1200°C prior to mullite formation at higher temperatures [37]. It also seems unlikely that spinel is poorly crystalline mullite, at least after heating to 980°C, since a second mullite crystallization event is recorded at higher temperatures [37]. Recent studies using nuclear magnetic resonance spectroscopy indicate that the spinel phase formed at 980°C may contain just a few weight percent silica [38]. Logically, the composition of the spinel phase probably lies between that of metakaolin (Al₂O₃·2SiO₂) and mullite (3Al₂O₃·2SiO₂) and is part of a phase separation process that leads to the eventual formation of mullite and an amorphous silica-rich phase [33].

4.4 Mullitization

As kaolinite is heated beyond 980°C, the small fraction of mullite crystals that formed at 980°C continue to grow, albeit at a slow rate. Mullite growth is accompanied by the disappearance of the spinel phase, although the amount of mullite formed is lower than expected based on the spinel loss [33]. Mullite formation does not approach completion until a second exothermic event occurs at approximately 1200°C, as recorded by differential thermal analysis [33]. When formed by solid-state reaction, mullite has

a composition of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, approximately 72 wt% alumina and 28 wt% silica [39]. According to Brindley, the mullite formed by heating to 1200°C contains all of the alumina from the original clay, while the silica is distributed between the mullite phase and an amorphous phase [33]. Further heating alters the size of the needle-like mullite grains and can result in crystallization of the silica to cristobalite [22]. Heating to 1200°C is generally sufficient to fully densify clay-based ceramic bodies.

5 General Outlook

Clays will continue to be an important industrial mineral for the foreseeable future. Clays continue to be used widely as raw materials for refractories and other traditional ceramics because of their availability, low cost, and ease of processing. However, a majority of applications for clay minerals lie outside the field of ceramics, as summarized in Tables 10 and 11 and described in detail in several of the references [8,14,21]. Because of this breadth of applications and continued availability of easily-mined, high-quality clay deposits, the current level of production and utilization of clay minerals should continue [8]. Production is currently stabilized around 40 million metric tons per year with an average price of approximately \$30 per ton [8]. More importantly for the modern materials community, understanding the processing and characterization of traditional ceramics can provide significant insight into the structure of the materials curriculum and the methods used to process and characterize advanced ceramic materials.

Table 10 Important applications for clay minerals grouped by clay type and application [8]

Clay	Application	Important Property(ies)
Kaolin	Paper	Absorbency, color
	Refractories	High temperature stability
Ball Clay	Traditional ceramics	Plasticity, fired strength
	Traditional ceramics	Plasticity, fired strength
Bentonite	Kitty litter	Absorbency
	Foundry sand	Binding ability
	Iron ore palletizing	Binding ability
	Petroleum drilling mud	Viscosity control, thixotropy
Fire Clay	Refractories	High temperature stability

Table 11 Other applications for clay minerals

Application	Reason for use
Absorbent	Water affinity
Adhesive	Viscosity control, inert filler
Aggregate	Low cost, low density
Cement	Al_2O_3 source
Clarification of beverages	Surface charge characteristics
Paint	Pigment, inert filler, viscosity control
Paper	Brightness, absorbency
Petroleum refining	Catalytic activity

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