

POLVERE? NO. ARGILLE! CLASSIFICAZIONE E USI



Il termine “argilla” può essere utilizzato in tre modi:

- Come gruppo di minerali a grana fine. (Fillo)Silicati idrati composti principalmente da silice, allumina ed acqua.
- Come termine relativo alle rocce. Argille e marne.
- Come termine relativo alla granulometria. Include la categoria delle particelle più piccole. Solitamente inferiori a 4 o 2 micron.

TIPI DI ARGILLA

Da un punto di vista commerciale si possono distinguere diverse tipologie di “argille”

- Ball Clay
- Bentonite
- Argille comuni (Common Clay)
- Terra da Follone (Fuller's Earth)
- Caolino
- Palygorskite e Sepiolite (Hormiti)
- Argille refrattarie

La produzione mondiale è di circa (in milioni di tonnellate all'anno):

- Caolino 26
- Bentonite 10,3
- Fuller's earth 3,9
- Ball clay 13
- Hormiti 3

La produzione mondiale totale è di 56 milioni di tonnellate all'anno.

Table 1. World production estimates

Clay Type	2002 World Production, Mt	Reference
Common	Hundreds	Estimate only
Refractory	Possibly more than 20	Estimate only
Kaolin	43 mined	
	26 sold	Virta 2003
Bentonite	10.3 V	irta 2003
Fuller's earth	Uncertain—possibly 10	
Ball	15.5	Chapter on Ball Clays in this volume
Hormites	2.1	Chapter on Palygorskite and Sepiolite in this volume

Table 2. Uses of clay minerals as inert components

Clay Family	Industry	Use
Kaolin	Paper, plastics, rubber	Filler
	Pesticides	Carrier, diluent
Vermiculite	Building	Heat insulation, sound dissipation
	Packaging	Shock-proof materials, thermal protection, liquid absorption
Mica	Foundries	Thermal protection
	Electrical	Insulation
	Paints	UV, heatstable and underwater paints
	Cosmetics	Nacreous pigments
Talcum, pyrophyllite	Coatings	Corrosion proofing, polymer coatings, underseal
	Plastics, rubber, paper	Filler
	Cosmetics, pharmaceuticals	Powders, pastes, ointments, lotions
Palygorskite, sepiolite	Refractories	Refractories
	Pesticides	Carrier for insecticides and herbicides
	Chemicals	Catalyst carrier, filter material, anticaking agent
	Cosmetics, plastics	Filler

that have unique properties leading to their classification as high-quality additives rather than bulk industrial minerals.

In addition, some nonclay minerals—finely ground to have similar properties to some industrial clays—are also frequently included in industrial clay surveys. These minerals include vermiculite, mica, talc, and pyrophyllite. The individual chapters present production statistics of the individual clays. Table 1 summarizes the estimated overall world production of clay minerals by both USGS sources and others.

CLAY USAGE

Clays and clay minerals are very important industrial minerals. They are used in many process industries, in agricultural applications, in engineering and construction, in environmental remediation, and in many other diverse applications (Grim 1962; Grim 1968; van Olphen 1977; Patterson and Murray 1983; Jepson 1984; Odom 1984; Murray 1986, 1999, 2000, 2003; Darley and Gray, 1991; Bundy 1993; Galan 1996; Harvey and Murray 1997; Ravichandran and Sivasankar 1997; and Philippakopoulou, Simonetis, and Economides 2003).

Table 3. Uses of clay minerals based on their rheological properties

Clay Family	Industry	Uses
Common clays	Ceramics	Tiles, bricks, earthenware, stoneware, sewer pipes, sanitary ware, refractory bricks
	Paper	Coating
Kaolins	Ceramics	Porcelain, bone china, vitreous sanitary ware, earthenware
	See Table 4	
Bentonites		
Palygorskite, sepiolite	Paints, chemicals, and mineral oils	Thickening and thixotropic additive, dispersing and antisealing agent, drilling fluids

Clay usage falls into two broad classes:

- Clays are used because their inertness and stability provide specific properties (such as unique rheology) to an industrial use. This leads to large variety of industrial applications.
- Clays are used because of their reactivity, which promotes or catalyzes specific reactions.

Tables 2, 3, 4, and 5 give a brief summary of uses; the individual chapters give a more detailed breakdown.

CLAY MINERAL STRUCTURES

All the clay minerals are basically hydrated aluminum silicates. There are, however, significant structural and chemical differences, which may include substitution of many cations that affect the neutrality or stability of the clay mineral. For example, iron or magnesium may substitute for aluminum; aluminum may substitute for silicon; and in some clay minerals, alkalis and alkaline earth elements are present as essential constituents. The structure of all the clay minerals consists of sheets of silicon tetrahedra and aluminum octahedra arranged in differing patterns for each individual clay mineral.

The physical properties of a particular clay mineral depend on the structure and composition (Murray 2000). Because of their extremely fine particle size, clay minerals were very difficult to identify until the advent of x-ray diffraction in the 1920s. Today, sophisticated analytical equipment is available to fully identify and characterize the clay minerals. The more important analytical methods that are used include x-ray diffraction, x-ray fluorescence, electron microscopy, infrared spectroscopy, and differential thermal analysis.

PHYSICAL AND CHEMICAL PROPERTIES

The important physical and chemical characteristics that relate to the applications of clay minerals are particle size, shape, and distribution; surface chemistry, area, and charge; pH; high and low shear viscosity; filter cake permeability; color and brightness; opacity; plasticity; green, dry, and fired strength; absorption and adsorption; fired color; electrical and heat conductivity; abrasion; cation and anion exchange capacity; refractoriness; dispersability; and thixotropy. The clay chapters each delineate and discuss these and other special properties. In most industrial applications, the clay materials are functional rather than just inert components in the system in which they are used. The common clays are the largest to usage in numerous engineering applications, including road construction, fill, and dam construction, and in waste containment. The mineralogy and particle size distribution in the common clays determine their engineering properties. They contain mixtures of different clay minerals such as illite/smectite minerals, kaolinites,

In una data applicazione industriale le argille sono scelte in base a due caratteristiche:

- Per la loro inerzia chimico-fisica e per la loro stabilità
- Per la loro reattività

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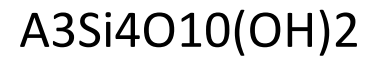
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La struttura di tutti i minerali argillosi (Fillosilicati) è costituita da strati di tetraedri di silicio e ottaedri di alluminio, disposti secondo schemi diversi e tipici per ciascun minerale.

Formule generali



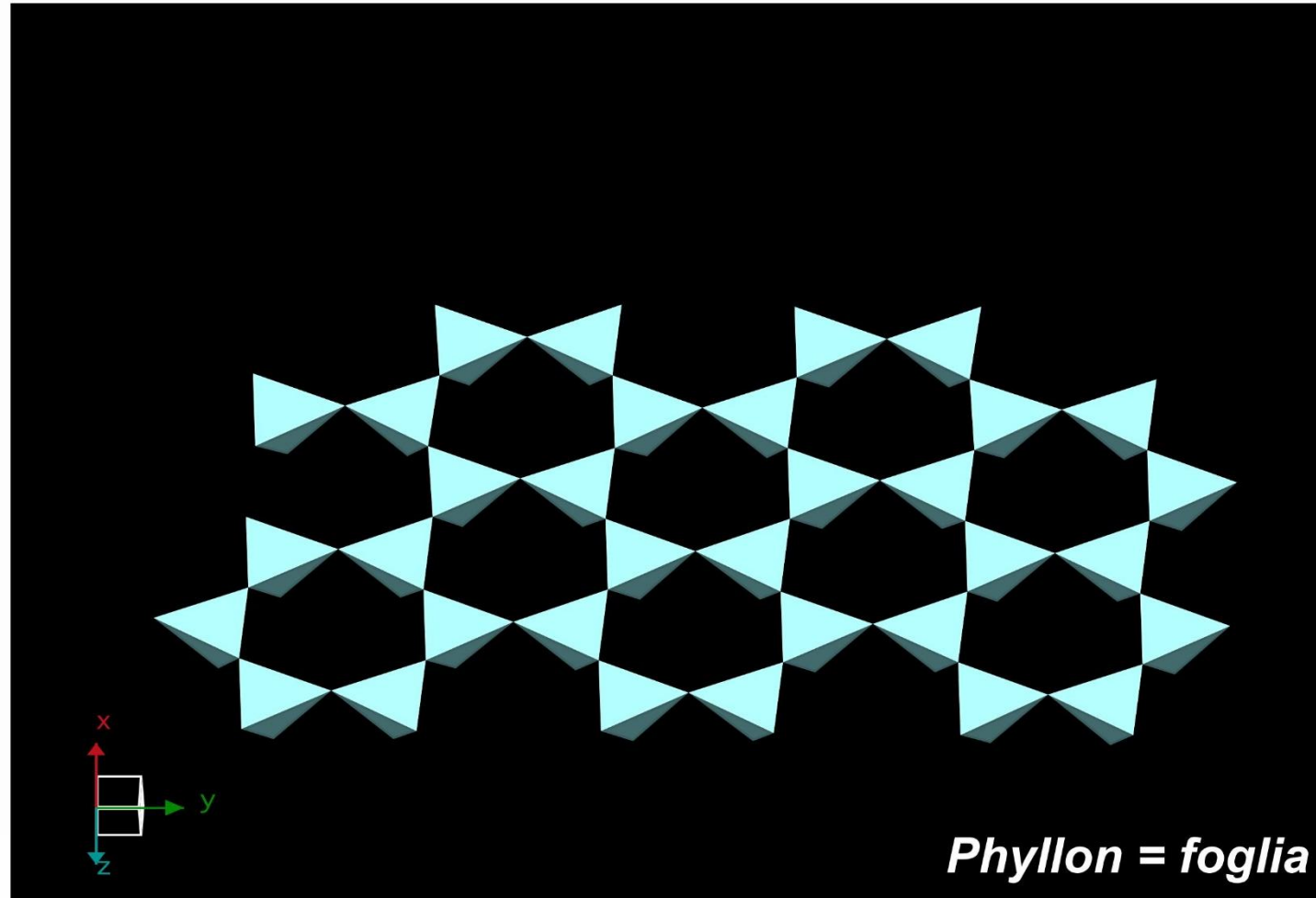
Dove A= Ca, Mg, Al, Na, Fe, Li, Ba

Se l'alluminio sostituisce una parte del silicio nei siti tetraedrici abbiamo i minerali del gruppo delle miche (muscovite, biotite, etc...), altrimenti si formano i minerali argillosi (smectiti, hormiti, montmorilloniti, etc...)

Fillosilicati

Sono formati da “fogli” paralleli di tetraedri SiO_4 .

$T = \text{Si}^{4+}, \text{Al}^{3+} (\text{Fe}^{3+}, \text{B}^{3+}, \text{Be}^{2+})$



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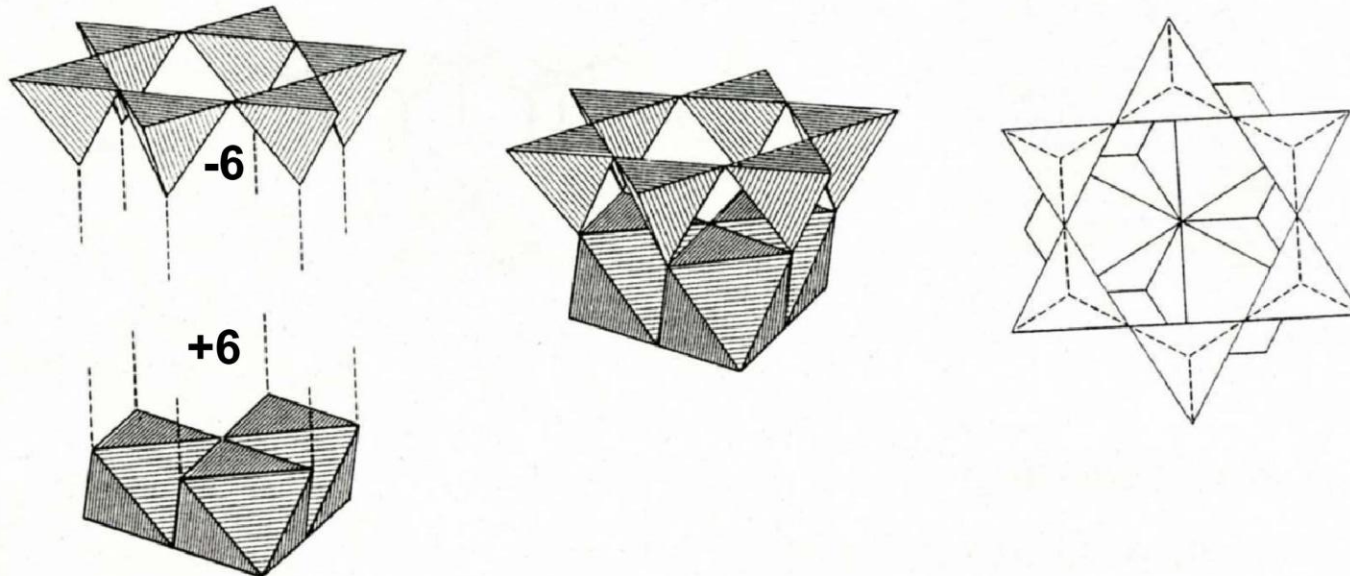
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Fillosilicati

I piani tetraedrici hanno una carica risultante negativa.

Un “foglio” di cationi a coordinazione ottaedrica (6) satura questo sbilancio di carica e “salda” la struttura.

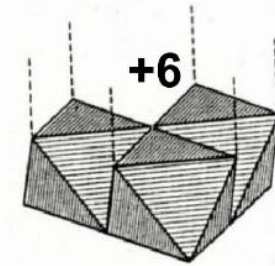
Gli ossigeni/ ossidrili apicali liberi si collegano ai cationi di- trivalenti del piano “ottaedrico”.



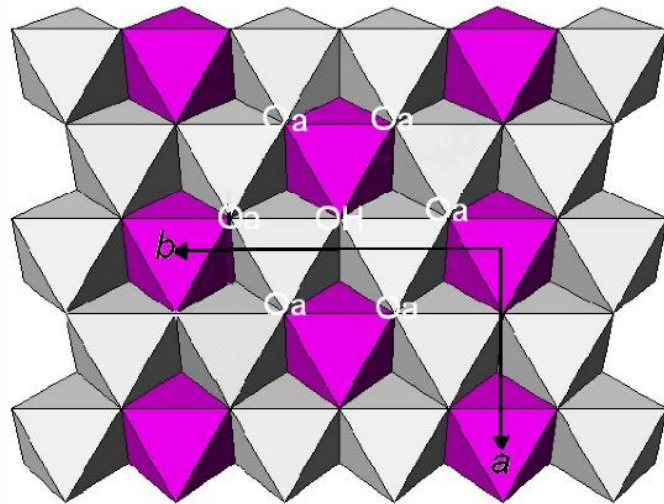
Fillosilicati

La struttura, a seconda del tipo di strato ottaedrico, può essere:

Diottaedrica – Solo 2 delle 3 posizioni a coordinazione ottaedrica sono occupate.



Triottaedrica – Tutte e 3 le posizioni a coordinazione ottaedrica sono occupate.



Strato ottaedrico

M = Mg^{2+} , Fe^{2+} , Al^{3+} , Fe^{3+} , Li^{+} , Ti^{4+} , V^{3+} , Cr^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , □ (vacanza)

Strato Brucitico: $Mg(OH)_2$ (o $Mg_3(OH)_6$)

Strato Gibbsitico: $Al(OH)_3$ (o $Al_2(OH)_6$)

□ occupanza

3/3 = struttura tri-ottaedrica

■ vacanza

2/3 = struttura di-ottaedrica

Fillosilicati

Classificazione dei fillosilicati

Gruppo 1:1 [T-O]

1 strato tetraedrico
1 strato ottaedrico

Gruppo 2:1 [T-O-T]

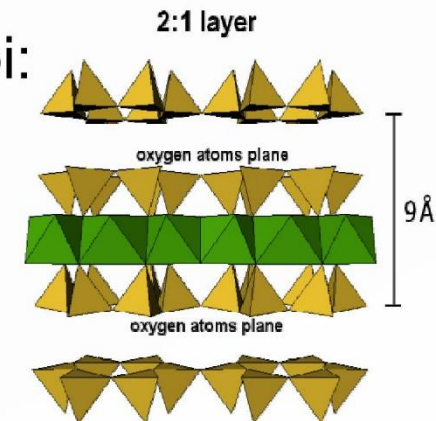
2 strati tetraedrici
1 strato ottaedrico interposto

Gruppo 2:2 [T-O-T +O]

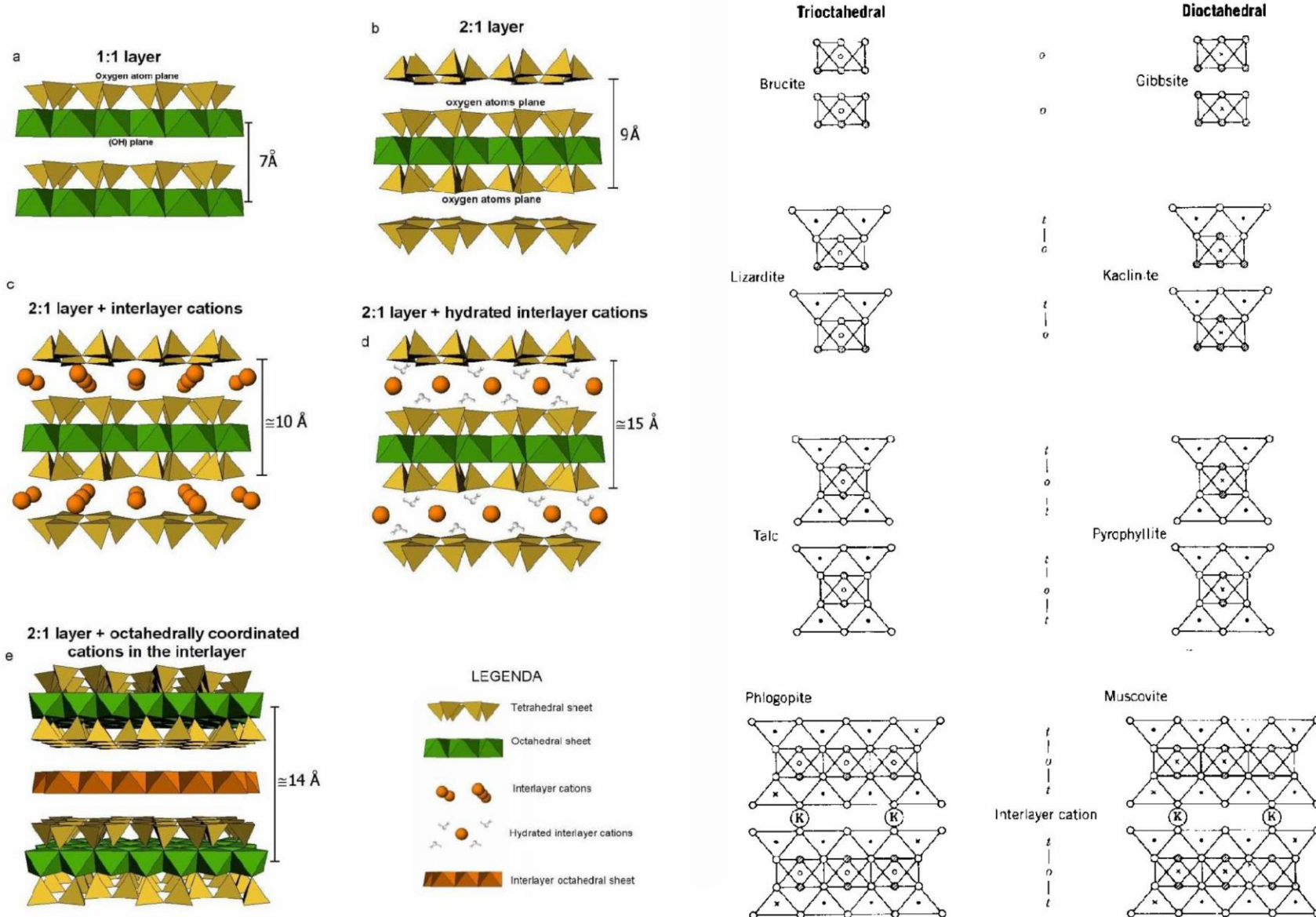
1 pacchetto T-O-T
1 strato brucitico ottaedrico

Spessori diversi delle unità strutturali (d) dei 3 gruppi:

1:1	7 Å
2:1	9-15 Å
2:2	14 Å



Fillosilicati



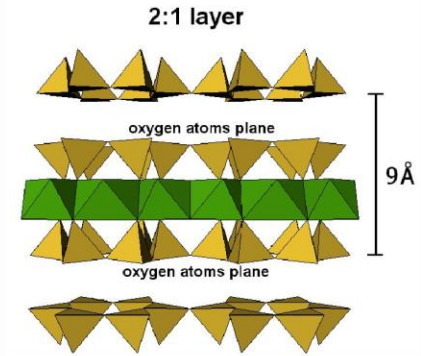
Gruppo 2:1 (T-O-T)

Ulteriore suddivisione in 3 principali sotto-gruppi

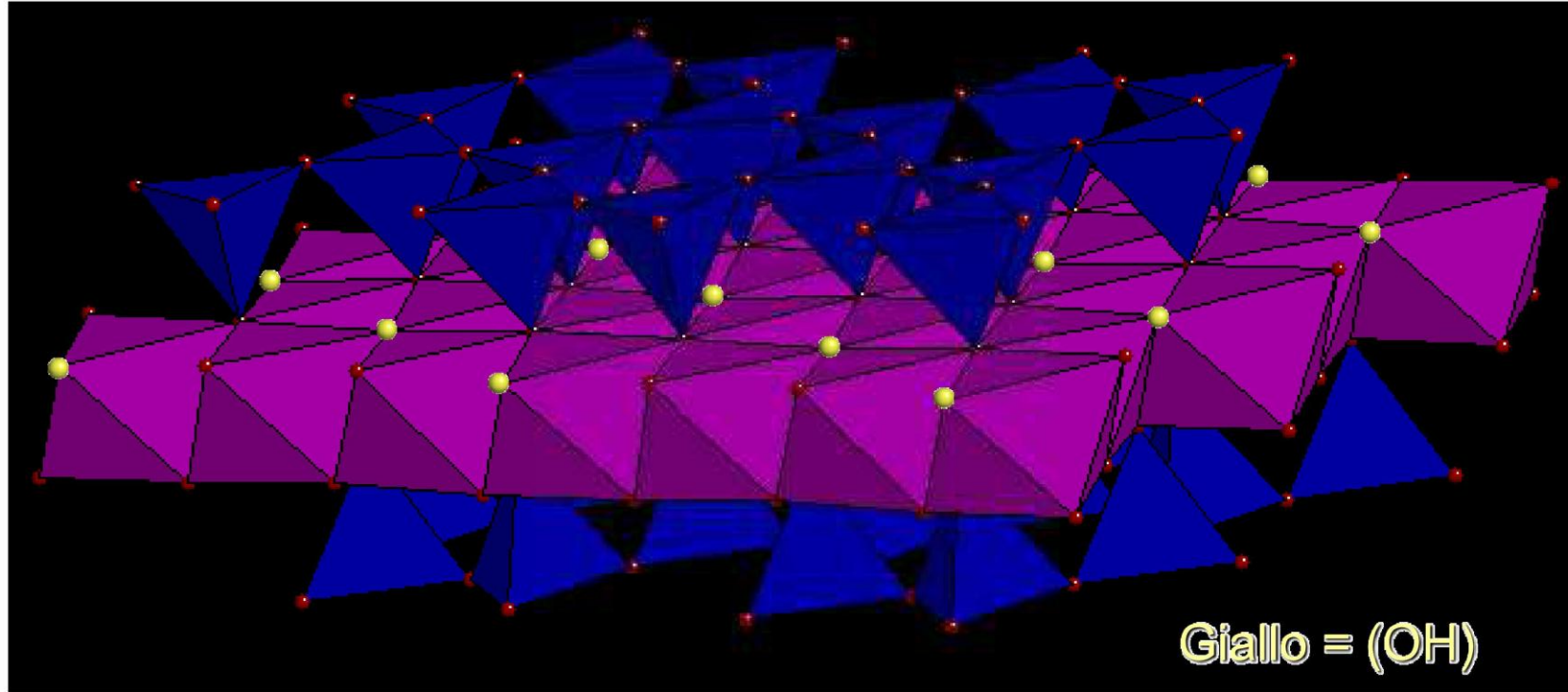
a) Assenza di qualsiasi sostituzione isomorfa (**T-O-T**).

b) Sostituzione isomorfa in T_{sheet} di Si^{4+} da parte di Al^{3+} : comporta una deficit di carica negativa, che viene bilanciato dall'ingresso di cationi interstrato (principalmente K^+ , Na^+) ben legati alla struttura. La coordinazione del **IC** è 12. (**T-O-T + IC**) (IC = interlayer cation).

c) Sostituzioni isomorfe Si/Al in T_{sheet} e /o $\text{M}^{3+}/\text{M}^{2+}$ in O_{sheet} : il deficit di carica viene bilanciato dall'ingresso di cationi interstrato legati molto debolmente alla struttura (coordinazione 12). (**T-O-T + EC**) (EC = Exchangeable Cation).



Fillosilicati



$d = 9 \text{ \AA}$

T
O
T
-
T
O
T
-
T
O
T

Talco: $\text{Mg}_3 [\text{Si}_4\text{O}_{10}] (\text{OH})_2$

Strato **T** - strato **triottaedrico** (Mg^{2+}) - strato **T**

Legami deboli di van der Waals tra i gruppi T-O -T



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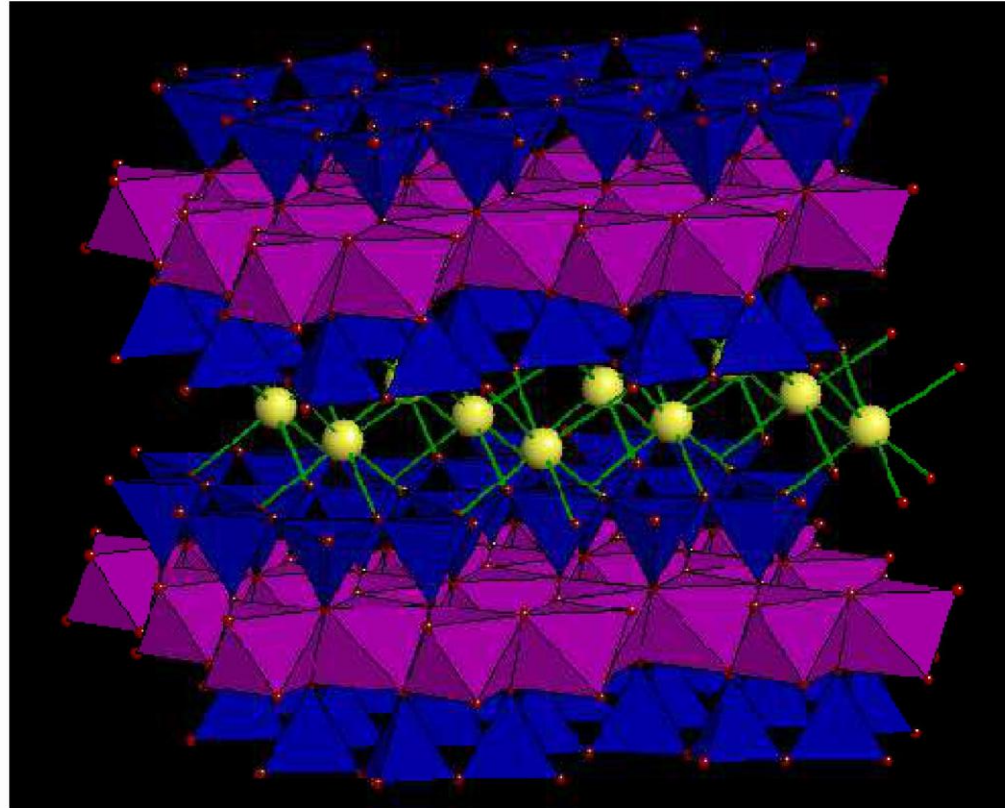


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Fillosilicati

$d = 10 \text{ \AA}$



Muscovite: $K Al_2 [Si_3AlO_{10}] (OH)_2$

Strato **T** - **di**ottaedrico (Al^{3+}) - strato **T** - **K**

K tra i gruppi **T** - **O** - **T** con legami più forti di vdw

Illite ha meno ioni **K** interstrato 0.6-0.8 rispetto alla muscovite (1)

T
O
T
K
T
O
T
K
T
O
T



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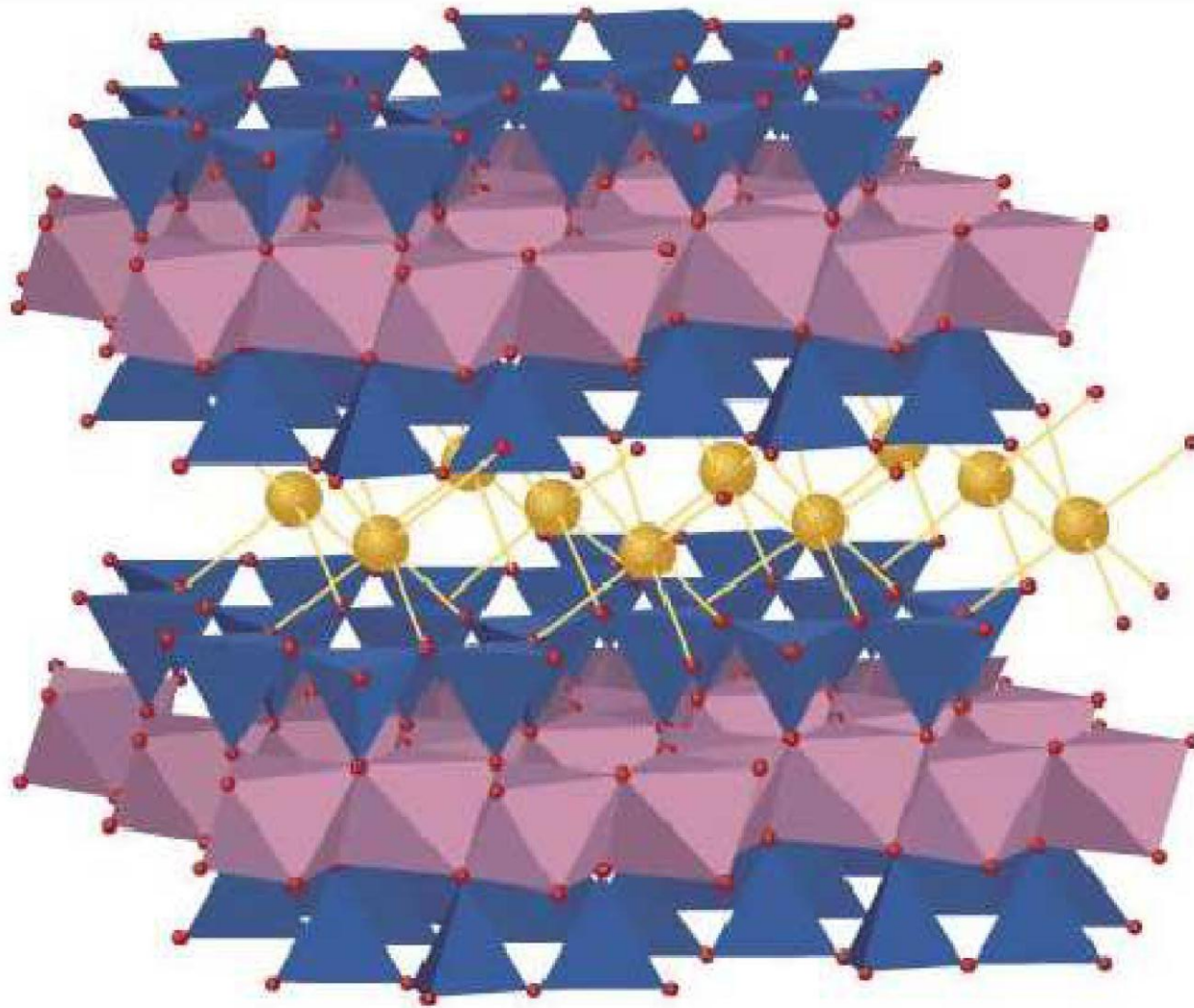
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The molecular structure of smectite clays consists of 2 silicon-centered tetrahedral layers (blue) and one aluminum octahedral layer (purple) form crystalline sheets.



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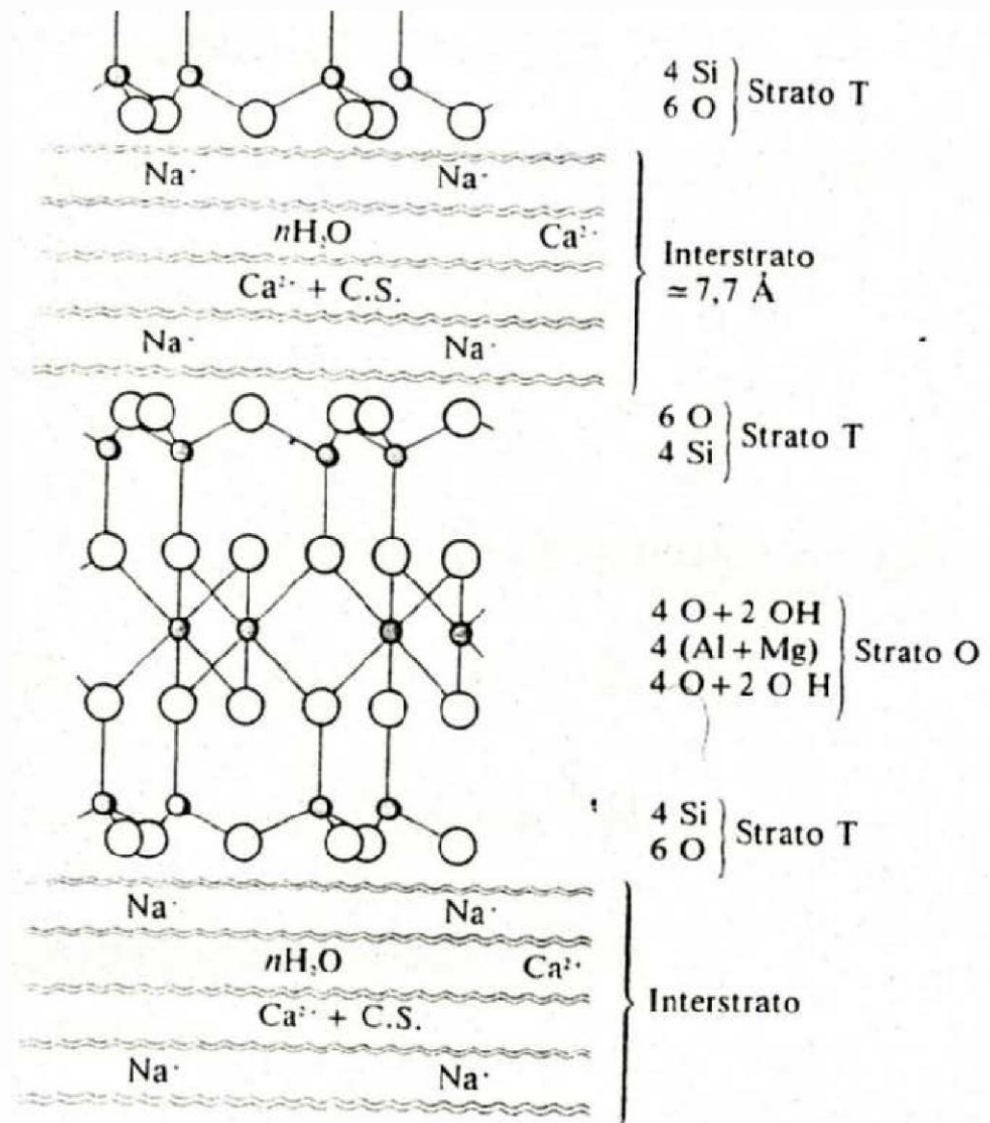
$d \approx 15 \text{ \AA}$ (if EC = Ca)

$T = 400^\circ\text{C}$ $9.4 \text{ \AA} < d < 10 \text{ \AA}$

Con trattamento :

- glicole etilenico 17 \AA
- glicerolo 15 \AA

d = spessore dell'unità strutturale = pacchetto

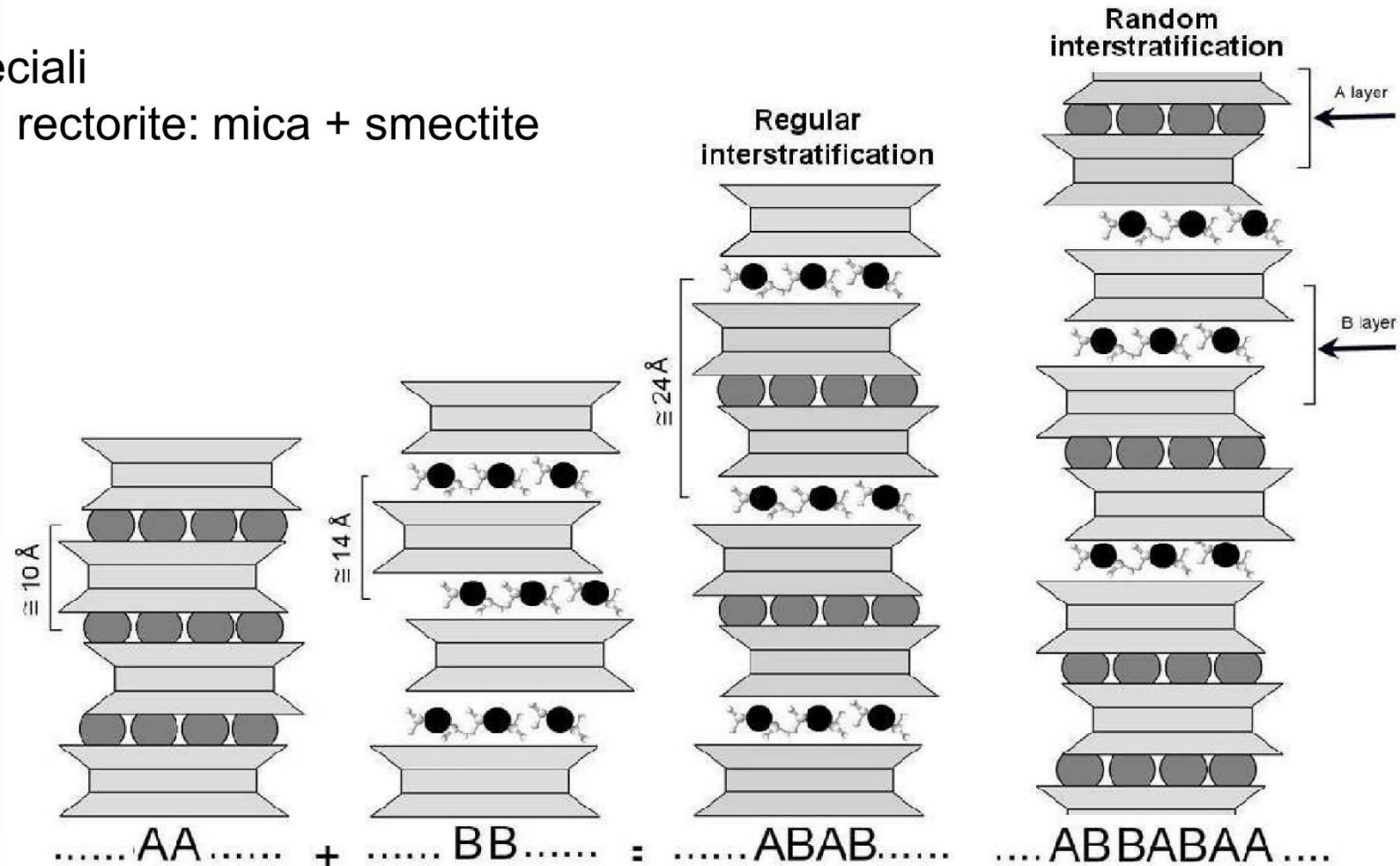


Fillosilicati

Strati misti: sono il mix di due o più periodicità
mix di diversi strati

Nomi speciali

Esempio: rectorite: mica + smectite



Le caratteristiche fisiche e chimiche di interesse per uno specifico prodotto commerciale, in relazione alle applicazioni industriali dei minerali argillosi sono:

- la dimensione del granulo di minerale
- la forma e la distribuzione granulometrica delle particelle
- la struttura chimica della superficie
- il rapporto tra superficie e volume e la carica elettrica
- il pH
- la viscosità ad alto e basso regime di sforzo
- la resistenza allo sforzo allo stato naturale, secco e dopo cottura
- l'assorbimento e l'adsorbimento di sostanze
- il colore dopo la cottura
- la conducibilità elettrica e termica
- l'abrasività
- la capacità di scambio cationico e anionico
- la refrattarietà
- la disperdibilità
- la tissotropia

Nella maggior parte delle applicazioni industriali, i materiali argillosi entrano come componenti funzionali piuttosto che semplici componenti inerti del prodotto in cui vengono utilizzati.

Table 4. Uses of bentonites based on their rheological properties

Industry	Uses	Activation ^a
Agriculture, horticulture	Soil improvement	r, s
Building	Supporting dispersions for cut-off diaphragm wall construction, shield tunneling, subsoil sealing, antifriction agents for pipejacking and shaft sinking	r, s
	Additions to concrete and mortar	r, s
Ceramics	Plasticizing of organic masses, improvement of strength, fluxing agents	r, a
	Binding agents for molding and core sands	r, s
Foundries	Binding agents for anhydrous casting sands	o
	Thickening of blackwashes	o
Mineral oil	Drilling fluids	r, a, o
	Thickening of greases	o
Paints, varnishes	Thickening, thixotroping, stabilizing, antisetling agents	s, o
	Coating materials, sealing cement, additives for waxes and adhesives	s, o
Cosmetics, pharmaceuticals	Bases of creams, ointments, and cosmetics	r, a, s
	Stabilization of emulsions	r, o
Tar exploitation	Emulsification and thixotroping of tar-water emulsions	a, o
	Tar and asphalt coatings, additives for bitumen	

^a Bentonites are used as raw materials or in activated form: r = raw bentonite, a = acid-activated bentonite, s = soda-activated bentonite, o = organo-bentonite.

smectites, micas, and accessory minerals. A second class is termed *industrial kaolins*, which are recognized by their relatively high contents of kaolinite (kaolins) or sometimes a small proportion of high-quality kaolin minerals. Ball clays have very fine particle size and are composed predominantly of kaolin. A fourth class is clay that has a high montmorillonite (smectite) content (bentonites). A fifth class is the palygorskite and sepiolite clays (hornites), which have many similarities to bentonites and are used specifically for their surface properties and reactivity.

CLAY MINERAL SOCIETIES AND PUBLICATIONS

Several scientific societies and groups are devoted to the science and applications of clays. The major societies and groups that are currently active in clay science are as follows:

- The Clay Minerals Society in the United States
- The European Clay Group, which includes most of the European countries
- The Clay Science Society of Japan
- The Association Internationale pour l'Étude des Argiles (AIPEA)

Many of the individual clay groups in European countries hold meetings periodically. The Clay Minerals Society hosts an annual conference in the United States and publishes the journal *Clays and Clay Minerals*, plus special publications and workshop proceedings. The European Clay Group holds a Euroclay Conference every 2 years and publishes the journal *Clay Minerals*. The Clay Science Society of Japan sponsors an annual conference and publishes the journal *Clay Science*. AIPEA sponsors the International Clay Conference every 4 years and publishes the proceedings. The journal *Applied Clay Science* is published by Elsevier. Other organizations

Table 5. Uses of clay minerals based on their adsorption properties and reactivity

Clay Family	Industry	Uses
Kaolin	Fiberglass	Source of alumina
	Petrochemicals	Catalyst support
	Chemicals	Zeolite synthesis
Bentonite	Building	Additive in cement
	Agriculture, horticulture	Soil improvement, composting Adsorption of mycotoxins
Chemicals		Sulfur production: refining, decoloration, bitumen extraction Catalysts
		Carriers for pesticides Dehydrating agents Adsorbents for radioactive materials
Cleaning		Regeneration of organic fluids for dry cleaning Polishes and dressings
		Additives for washing and cleaning agents and soap production
Environmental technology		Forest and water conservation: fire extinguishing powders, binding agents for oil on water Animal husbandry, manure treatment, cat litter
		Water and wastewater purification Sewage sludge pelletizing Barriers
Food		Refining, decoloration, and stabilization of vegetable and animal oils and fats Fining of wine, must, and juices, beer stabilization, purification of saccharine juice and syrup
	Mineral oil	Refining, decoloration, purification, and stabilization of mineral oils, fats, waxes, and paraffins
Papermaking		Pigment and color developer for carbonless copying paper Adsorption of impurities in circulation water
		De-inking in wastepaper recycling
Cosmetics, pharmaceuticals		Powders, tablets, drug carrier, odor control, liquid absorption
	Palygorskite, sepiolite	Chemicals Adsorbent, carrier, bleaching, decoloration, anticaking agent
Environmental technology		Cigarette filters (sepiolite), cat litter

and publications that feature articles on clays are the American Ceramic Society (annual meetings and monthly bulletin); SME (annual meetings, preprints, *Mining Engineering* magazine, books, and transactions); and *Industrial Minerals* magazine.

The scientific and technological publications pertaining to clays are too numerous to cover in this chapter. Therefore, the rest of this chapter summarizes the subject matter and, where possible, indicates by bibliographic reference where more detailed information is available. For example, Bicker (1970) is a bulletin containing only summary information on the economic geology of bentonite in Mississippi, but it contains references to virtually all published reports on bentonite in that state.

Categorie di argille industriali

A livello di giacimenti possiamo distinguere quattro categorie:

- Categoria 1 – argille di alta qualità. Ad esempio, argille caoliniche
- Categoria 2 – argille speciali con proprietà uniche a livello mondiale.

Risorse relativamente rare e uniche di minerali argillosi industriali insoliti, ma preziosi per usi “di nicchia”. Halloysite, Hectorite, Bentonite bianca

- Categoria 3 – argille “a basso contenuto tecnologico”, adatte per mercati locali
- Categoria 4 – argille di qualità variabile

Per depositi di categoria 1 ad un giacimento è richiesta una vita utile minima di 20 anni con una produzione di almeno 300.000 tonnellate all'anno, quindi la risorsa deve essere di dimensioni sufficienti a produrre 6 milioni di tonnellate di prodotto. I giacimenti di categoria superiore all'1 ovviamente devono possedere quantità estraibili ancora maggiori per poter essere economicamente sfruttabili, in considerazione ad esempio del minor prezzo per tonnellata spuntabile sul mercato.

I progetti di categoria 1 richiedono un significativo investimento iniziale o capitale di rischio.

Il livello di confidenza nella caratterizzazione (sia qualitativa che quantitativa) della risorsa e nel trovare mercati adatti deve essere molto elevato, il che richiede un livello di investimento significativo che può anche superare 1 milione di dollari.

Il tempo di ammortamento di tale investimento può essere di almeno 5 anni, a causa del tempo necessario per passare dalla fase di esplorazione alla messa in servizio.

Gli addetti agli acquisti del potenziale cliente finale devono essere convinti della compatibilità del prodotto con le loro formulazioni commerciali e, inoltre, della costanza nella qualità e nella quantità della fornitura.

Una volta individuato un giacimento, è necessario effettuare almeno 100 perforazioni per

BALL CLAY

Le ball clay sono argille sedimentarie caoliniche che rappresentano un ingrediente importante nella maggior parte degli impasti ceramici, in quanto gli conferiscono resistenza e plasticità.

I due componenti principali delle ball clay sono la caolinite e il quarzo. Molte delle proprietà importanti per gli utilizzatori finali sono legate alle percentuali relative di questi due minerali.

L'argilla deve essere di colore bianco, pesca o rosa dopo la cottura.

La genesi delle ball clay è legata ad inondazioni stagionali che causano lo spostamento dell'alveo dei fiumi, lasciando dietro di sé ambienti abbandonati a bassa energia noti come "anse fluviali". Questi canali abbandonati od anse fluviali diventano ambienti ideali a bassa energia per la deposizione di argille a grana fine.

Si ritiene che il termine "*ball clay*" derivi dall'antico metodo di lavorazione dell'argilla, dove essa veniva tagliata in cubi del peso di 13-18 kg. Data la natura plastica dell'argilla, questi assumevano rapidamente una forma sferica durante la

La produzione di ball clay è stata stimata in 15,5 milioni di tonnellate all'anno. Nove paesi: Cina, Germania, Indonesia, Malesia, Spagna, Turchia, Ucraina, Stati Uniti e Regno Unito, rappresentano l'83% della produzione mondiale. Il prodotto proveniente dall'Ucraina è principalmente utilizzato dalle aziende italiane nella produzione di Gres Porcellanato.

I principali mercati per le ball clay sono nella produzione di sanitari, piastrelle per pareti e pavimenti.

L'argilla viene utilizzata anche in pannelli acustici per soffitti, stoviglie, porcellana per applicazioni elettriche, materiali refrattari, ceramica per hobbisti, catrame di carbone/asfalto, fibra di vetro, gomma, rivestimenti e sigillanti.

La ball clay grezza viene lavorata e fornita al cliente in quattro diverse tipologie commerciali: sminuzzata, essiccata meccanicamente, classificata in corrente d'aria (in polvere) ed in sospensione acquosa.

Alcuni giacimenti contengono sei o più strati di argilla con caratteristiche diverse. Ciascuna deve essere estratta con precisione e conservata separatamente per la successiva miscelazione. I dati dei campioni di miniera vengono utilizzati per realizzare miscele precise di diverse argille "base", al fine di ottenere la combinazione di proprietà desiderata e concordata con il cliente.

L'utilizzo ceramico delle ball clay comprende piastrelle per pareti e pavimenti, sanitari e altri usi. Un impasto tipico contiene dal 20 al 60% di argilla e il resto è costituito da quantità variabili di Pirofillite, Feldspato, sabbia micacea e Talco. L'argilla nell'impasto della piastrella ne consente la formatura e conferisce resistenza allo stato grezzo, in modo che una volta pressata mantenga la sua forma. Un tipico impasto per sanitari è composto per il 35% da ball clay, per il 15% da Caolino e per il 50% da materiali non plastici come feldspato e sabbia silicea. In Ucraina, l'azienda Keramet produceva prima della guerra circa 500.000 tonnellate all'anno di argilla caolinica, di cui l'80% veniva esportato in Italia. Le esportazioni dall'Ucraina sono cresciute rapidamente grazie alla sua idoneità per la produzione di piastrelle in Gres Porcellanato.



Figure 13. Map of the ball clay deposits of Europe

and the main basin is divided into a number of topographic and generic basins that are controlled by earlier fault patterns. Clay-bearing sequences were laid down in subsidence hollows in the Tertiary period, some 25–40 Ma.

The largest company in Germany is WBB Fuchs, which extracts and processes a wide range of plastic clays and kaolins from deposits in the Westerwald region and other areas of the country. Fuchs'sche Tongruben (Fuchs-Ton) was established as a family company in 1838 and grew into one of the country's leading clay suppliers, becoming part of the WBB Group in 1974. WBB Fuchs-Keramische Massen is a market leader in prepared ceramic bodies, with two dedicated plants at Ransbach and Kannenbäckerland in Höhr-Grenzhausen. WBB Fuchs produces approximately 2 Mtpy. A large range of ball clay products come from the Westerwald; these consist mainly of disordered kaolinite, illite, and quartz with good forming properties and range from red-firing to white-firing clays. The Italian floor-tile market accounts for more than 30% of the Fuchs Westerwald ball clay sales. This market, however, has been attacked by increasing imports of ball clay from Ukraine. Clays having good plasticity and high strength are also sourced from the Eifel region.

Spain

Ball clays used in Spain are mainly domestic (67%) with the rest imported from the United Kingdom, Germany, France, and Ukraine (Regueiro 2004). Total ball clay consumption in Spain

reached 1.2 Mtpy in 2003 and was worth about €36 million (2003 currency; Sanchez and Regueiro 2004).

Formed in 1999, WBB España SA is the market leader in the supply of red-firing clays to the Spanish ceramic tile industry. WBB extracts more than 4.5 Mt of clay, kaolin, and silica sand annually from four main quarries: Sant Joan de Moró near Castellón, Galve near Teruel, and from Madroño and La Yesa near Valencia. WBB also has two other smaller operations in the Castellón Area—Morella and El Campillo—and a kaolin and silica sand plant in Higuerauelas near Valencia. WBB España's clays are relatively low in calcium carbonate content and are ideally suited for the manufacture of single-fired floor tiles. The Spanish ceramic tile industry uses almost all of the output from WBB's quarries and produces about 650 million m² of tiles each year; the industry is in the Castellón region.

Euroacre, a subsidiary of the Samca Group, is the major ball clay body producer operating in Spain. The company developed a wet-purification system to produce 115,000 tpy for use in sanitary ware, glazes, and engobes, and has its own spray drying plant with a capacity of 475,000 tpy of ceramic bodies for floor and wall tiles. Euroacre has a quarry in Teruel that produces about 600,000 tpy of ball clays using a very selective extraction technology. These are ground and blended in a 350,000-tpy homogenization facility to produce illitic-kaolinitic clays for the ceramic industry. Minera Sabater is the second Spanish producer from three quarries in Teruel, reaching 250,000 tpy. Potome produces 90,000 tpy of ball clays consumed

BENTONITE

La bentonite è un'argilla composta essenzialmente da minerali del gruppo delle Smectiti, indipendentemente dalla sua provenienza od origine. Le bentoniti sono generalmente classificate come sodiche (rigonfianti) o calciche (non rigonfianti) in base al tipo di cationi presenti nell'interstrato ed alla conseguente capacità di gonfiarsi in acqua.

Il componente minerale predominante della bentonite è costituito da minerali del gruppo delle Smectiti (Beidellite, Montmorillonite, Hectorite, Nontronite e Saponite). La struttura generale è di tipo TOT (Tetraedro-Ottaedro-Tetraedro) con uno spessore tipico degli strati di 1 micrometro.

I minerali smectitici si dividono in due gruppi: diottaedrici e triottaedrici, a seconda che tutti e tre i siti ottaedrici della cella elementare siano occupati o solo due. Entrambe le classi di smectiti presentano sostituzioni solide all'interno degli strati ottaedrici e tetraedrici, ed è proprio questa sostituzione a essere in parte responsabile delle loro peculiari proprietà fisiche e chimiche. L'entità e la distribuzione della carica superficiale sono in gran parte determinate dal numero e dal tipo di sostituzioni all'interno degli strati tetraedrici e ottaedrici. La sostituzione di cationi con carica maggiore con cationi a carica minore (ad esempio la sostituzione di Al e Si) determina una carica netta negativa dello strato. I cationi scambiabili più comuni nelle smectiti sono sodio, calcio, magnesio, idrogeno e potassio. La capacità di scambiare cationi è descritta come capacità di scambio cationico (CSC) ed è tipicamente espressa in milliequivalenti per 100 g di argilla. Le smectiti presentano una CSC compresa tra 60 e 170, con valori tipici tra 100 e 120.

Le bentoniti si trovano sia in ambienti marini che non marini, dal Giurassico al Pelistocene. Questi strati possono essere molto estesi geograficamente, con spessori che variano da pochi centimetri a decine di metri e sono solitamente paralleli agli strati sovrastanti e sottostanti.

La modalità di formazione più comune della bentonite è l'alterazione in situ di ceneri vulcaniche o tufi. L'alterazione delle ceneri vulcaniche in Smectite è una reazione di idratazione che richiede magnesio e produce un eccesso di silice e ioni alcalini. L'alterazione delle ceneri vulcaniche a contatto con l'acqua di mare è l'ambiente di deposizione più comune delle bentoniti commercialmente sfruttabili. Considerando questi fattori, un tipico ambiente di formazione della bentonite sarà un'area di passata attività vulcanica situata in prossimità di un corpo idrico di dimensioni considerevoli.

In Europa esistono giacimenti di minerale di bentonite in Grecia (isola di Milos, con giacimenti molto estesi), Sardegna e Turchia, da dove le bentoniti bianche vengono esportate principalmente come lettieri per animali domestici, essiccanti e nella produzione di detersivo in polvere o granulato.

Negli Stati Uniti occidentali, lo spessore dello “sterile” al di sopra dello strato di bentonite varia da zero a 10 m. Gli strati di bentonite estraibile hanno uno spessore che varia da meno di 1 m a 2 m. Una regola generale per il recupero economicamente vantaggioso della bentonite richiede che il rapporto tra lo spessore dello sterile in copertura e quello dell'argilla sia inferiore a 10:1.

Table 1. Bentonite sold or used by producers in the United States, by use, *kt*¹

Use	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002
Domestic										
Absorbents										
Pet waste absorbents	302	455	574	607	604	773	788	862	902	899
Other absorbents	66	91	88	91	W†	W	W	W	W	W
Adhesives	W	W	W	11	15	13	14	6	2	2
Animal feed	78	97	98	65	110	77	74	47	52	42
Ceramics (except refractories)†	24	W	W	W	W	W	W	W	W	W
Drilling mud	476	586	627	572	789	665	667	654	787	762
Filler and extender applications‡	31	30	70	34	41	49	25	35	49	46
Filtering, clarifying, decolorizing	13	W	W	W	82	104	81	94	92	127
Foundry sand	733	712	745	772	901	869	888	835	746	762
Pelletizing (iron ore)**	466	509	646	674	536	529	540	500	522	536
Miscellaneous refractories	58	32	22	17	8	3	2	4	W	W
Miscellaneous††	2	55	288	242	126	80	83	67	91	117
Waterproofing and sealing	213	287	228	227	267	236	268	254	283	269
Total	2460	2850	3390	3310	3479	3398	3430	3358	3526	3562
Exports										
Drilling mud	90	34	87	102	150	65	69	56	73	59
Foundry sand	243	321	256	278	293	239	251	233	244	244
Other††	72	81	89	46	101	123	121	115	129	106
Total	405	436	431	426	544	427	441	404	446	409
Grand total	2870	3290	3820	3740	4023	3825	3871	3762	3972	3971

Source: USGS Minerals Yearbooks.

¹ Data rounded to nearest thousand tons and may not add to totals shown.

† W = withheld to avoid disclosing company proprietary data; included with "Miscellaneous."

‡ Includes catalysts and pottery.

§ Includes cosmetics, ink, medical, paint, paperfilling, pesticides and related products, pharmaceutical, and plastics.

** Excludes shipments to Canada.

†† Includes chemical manufacturing, heavy clay products, and other unknown uses.

‡‡ Includes absorbents, fillers and extender, miscellaneous refractories, pelletizing, and other unknown uses.

HISTORY AND USE

Most of today's major uses of bentonite were developed in the 20th century. In the United States bentonite finds major uses in iron ore pelletizing, drilling muds, pet litters, and foundry sands (Table 1). Overall, global consumption follows similar trends to U.S. consumption, with the exception that use in pet litters is less, especially in developing countries. Significant secondary uses include waterproofing and sealing applications, animal feed additives, oil and grease absorbents, agricultural carriers, and filtering, clarifying, and decolorizing agents. Still smaller specialty uses of bentonite include asphalt emulsions, catalysts, paints, plastics, inks, greases, cosmetics, and pharmaceuticals.

The use of calcium bentonites can be traced back as early as 5000 BC, when they were used to cleanse and thicken woolen cloths in Cyprus (Robertson 1986). It is from this ancient use that calcium bentonites derive the name *fuller's earth*.

In the last century it was discovered that some calcium bentonites are effective at decolorizing or "bleaching" vegetable, animal, and mineral oils (Nutting 1943). This is especially true when calcium bentonites have been acid activated to improve their bleaching efficiency (Rich 1960; Torok and Thompson 1972). Acid-activated bentonites have grown in use relative to unactivated bentonites, especially for oils that are more difficult to bleach or when more highly refined oils are desired.

As used today, fuller's earth is a general descriptive term for clay or other fine-grained earthy material that is used in bleaching,

absorbent, and other related applications (for more details, see the chapter on fuller's earth in this volume). The name does not carry any specific mineralogical or compositional meaning and applies equally to minerals such as attapulgite and sepiolite. Each of these different minerals, however, is not equally suited to all applications in which fuller's earths are used. Premium products for decolorizing edible oils are largely based on acid-activated calcium bentonites.

In the United States, mining of natural sodium bentonite began in 1888 on the Taylor Ranch near Rock River, Wyoming, and in 1903 a mine was opened in Upton, Wyoming, within the bentonite beds surrounding the Black Hills. Mining of calcium bentonite began on a significant scale in the United States in Mississippi in the early 1930s (Bicker 1970). Today there are five major producers and 10 production facilities in Wyoming and South Dakota.

Significant use of bentonite as a sand bonding agent in foundries and as a drilling mud in the oil industry began in the late 1920s. The suspension and fluid loss control properties of western bentonites make them especially suitable for water-based drilling applications (Darley and Gray 1988). As a bonding agent in greensand molding, bentonite has the advantage of producing good compressive strengths when wet or dry (Anon. 1962, 1963, 1994; Sanders 1973). The natural sodium bentonites from the western United States also perform well at the elevated temperatures encountered during the pouring of molten iron and steel, resulting in good clay utilization and fewer casting defects.

La maggior parte della bentonite trova impiego nella pellettizzazione del minerale di ferro per le fonderie, nei fanghi di perforazione per l'industria della trivellazione, nelle lettiere per animali domestici e nelle sabbie per fonderia. Tra gli usi secondari più significativi si annoverano applicazioni di impermeabilizzazione e sigillatura, additivi per mangimi animali, assorbenti di oli e grassi, vettori di fertilizzanti ed antiparassitari per uso agricolo, agenti filtranti, chiarificanti e decoloranti. Ulteriori usi di nicchia della bentonite includono emulsioni bituminose per lavori stradali, catalizzatori, vernici, materie plastiche, inchiostri, grassi, cosmetici e prodotti farmaceutici.

Le bentoniti di sodio naturali provenienti dagli Stati Uniti occidentali si comportano bene anche alle alte temperature raggiunte durante una colata di ferro e acciaio fusi, con conseguente utilizzo ottimale dell'argilla e minori difetti di fusione sul pezzo finito.

Utilizzate anche come rivestimenti geosintetici per discariche e depositi di scorie e rifiuti.

Chiarificazione di vino, olio e succhi di frutta. La natura colloidale e l'elevata superficie specifica della bentonite vengono sfruttate in queste applicazioni per rimuovere proteine ed altre sostanze microscopiche che conferiscono colore e opacità al prodotto. Le bentoniti di sodio sono utilizzate molto più frequentemente delle bentoniti di calcio.

L'industria ceramica utilizza le bentoniti per modificare le proprietà reologiche degli smalti e

Nelle applicazioni cosmetiche e farmaceutiche, le bentoniti svolgono una funzione simile a quella ricercata negli inchiostri e nelle vernici. Agisce come agente sospensivante in shampoo, lozioni e gel e la sua elevata resistenza allo snervamento ed il comportamento pseudoplastico consentono la creazione di fluidi che non gocciolano né colano, ma scorrono facilmente quando vengono applicati.

Le bentoniti sono utilizzate come catalizzatori in numerosi processi chimici, ad esempio per il recupero di composti di benzene, toluene e xilene.

Argille organiche. Le argille smectitiche possono essere modificate (Mastergel) per renderle più compatibili in soluzioni contenenti solventi a bassa polarità come oli e gasolio. Ciò avviene tramite lo scambio di cationi di Ca e Na con tensioattivi cationici, in particolare ammine quaternarie.

Nelle vernici e nei rivestimenti, i mastergel svolgono tre funzioni principali: antisedimentazione, antigoccia e anti-sgocciolamento. Negli inchiostri da stampa, garantiscono una viscosità stabile, controllano la nebulizzazione e possono migliorare la resistenza all'acqua. Sono impiegati nella produzione di grassi da utilizzare ad alta temperatura grazie alla loro stabilità termica. Trovano impiego nelle applicazioni di trivellazione per la perforazione profonda di giacimenti di idrocarburi, sempre grazie alla loro stabilità termica. Vengono utilizzati come leganti nella produzione di alcuni tipi di mattoni refrattari e monolitici. Sono utilizzati nei cosmetici e nei

ARGILLE COMUNI (COMMON CLAY)

Le argille comuni sono materiali naturali a grana fine, composti prevalentemente da silicati di alluminio idrati. Questo materiale può quindi essere modellato nelle forme desiderate e cotto per produrre un prodotto con una durezza simile a quella della roccia.

Le argille comuni si trovano in una notevole varietà di ambienti e si formano a partire da molti tipi di roccia diversi in tutti i periodi geologici. Dal punto di vista mineralogico, le argille comuni sono molto variabili, sebbene il costituente più comune sia solitamente uno dei membri del gruppo dei minerali micacei (Illite, Sericite, Muscovite e Biotite). Altri minerali argillosi frequentemente presenti nelle argille comuni sono la Caolinite e le Smectiti. Il quarzo ed altri minerali detritici sono tipici minerali non argillosi.

L'Illite è un minerale che si forma a bassa temperatura sulla superficie terrestre. È un silicato idrato di potassio e alluminio, in cui il ferro è solitamente sostituito all'alluminio nella struttura cristallina.

Common Clays and Shale

Karan S. Keith and Haydn H. Murray

INTRODUCTION

Common clays are a naturally occurring, fine-grained material composed predominately of hydrous aluminum silicates. The term *common clay* encompasses a wide variety of clay types, including fine-grained rocks such as shale. Common clays and shale are a useful geologic material because they typically exhibit plastic behavior when wet. This material can then be formed into desired shapes and fired to produce a product with rock-like hardness. Common clays and shale are the most widespread ceramic materials. Products made from these clays include items such as structural and face brick, drain tile, vitrified pipe, quarry tile, flue tile, conduit, pottery, stoneware, and roofing tile. Large quantities of common clays are also used to make construction materials such as lightweight aggregate and portland cement. They are used as filler in paint and other products, for packing dynamite blast holes, and for plugging oil and gas wells that are no longer in use.

GEOLOGY

Mineralogy

Common clays occur in a variety of environments and in many different rock types across all time periods of the geologic record. The source material includes glacial clay, soils, alluvium, loess, shale, weathered and fresh schist, slate, and argillite. Fireclay and kaolin are sometimes considered common clays, particularly when used in the manufacture of structural clay products. Mineralogically, common clays are highly varied, although the most common constituent is usually one of the members of the mica mineral group. Mica clays include illite, sericite, muscovite, and biotite. Other frequently occurring clay mineral components of common clays are kaolinite, smectite, mixed-layer clays, and chlorite. Quartz and other detrital minerals are typical nonclay minerals present in rocks mined for common clay.

Illite is one of the most abundant clay minerals found in sediments and sedimentary rocks and one of the most prevalent minerals in common clay resources. *Illite*, a term introduced by Grim, Bray, and Bradley (1937), is mica-type clay mineral that was named after an abbreviation for Illinois. Illite is a low-temperature mineral formed at the earth's surface. It is a hydrous potassium aluminum silicate (Figure 1) in which some iron is usually substituted for aluminum in the structure. Illite is similar in structure to smectite, the main difference being that in illite the interlayer cation is potassium and in smectite it is sodium, calcium, or magnesium.

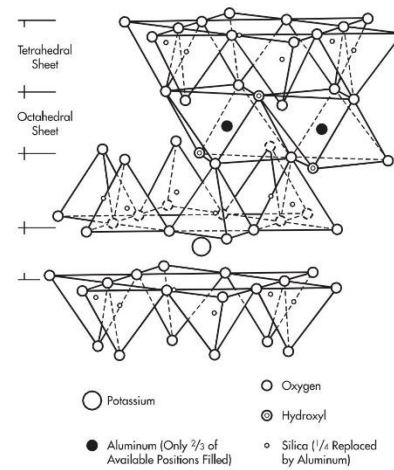


Figure 1. Structure of illite

Because of the similarity in structure, it is common to have smectite interlayered with illite, which is termed a *mixed-layer* clay. Smectite is an expandable clay, and if the mixed-layer clay material contains significant quantities of smectite, its presence can lead to excessive shrinkage during drying, in addition to other problems.

Clays and shale from the Pennsylvanian strata in the central and eastern portions of the United States have an excellent range of properties for making structural ceramics and low-grade refractory shapes. Commonly these strata have a refractory underclay or fireclay beneath a coal bed and a red-firing, illite-chlorite-rich roof shale above the coal (Hughes 1993). The roof shale is sometimes up and coarsening, which allows producers to create shale or fireclay blends

Le argille comuni presentano un'ampia gamma di proprietà fisiche, che le rendono adatte alla realizzazione di numerosi prodotti “strutturali”. Queste proprietà includono plasticità, resistenza allo stato naturale ed a secco, ritiro in fase di essiccazione e cottura, temperatura di vetrificazione e colore dopo la cottura.

Le proprietà desiderate variano a seconda del prodotto strutturale in argilla che si intende realizzare. Ad esempio, l'argilla utilizzata per la produzione di pannelli per condotti deve essere molto plastica, possedere elevata resistenza allo stato naturale e dopo essiccazione ed un coefficiente di ritiro uniforme.

Le argille comuni sono ampiamente diffuse e generalmente facili da reperire e vengono spesso utilizzate in prodotti che non richiedano lavorazioni complesse per la loro commercializzazione. Solitamente sia la materia prima che i prodotti finiti sono pesanti ed il margine di profitto è basso, pertanto è fondamentale limitare i costi di produzione.

La produzione di argille comuni è di 23,3 milioni di tonnellate. I principali mercati sono i mattoni da costruzione (12,8 milioni di tonnellate), la produzione di aggregati leggeri quali i blocchi di cemento (4 milioni di tonnellate) e la produzione di clinker di cemento Portland (3,95 milioni di tonnellate).

Fuller's Earth

Fuller's earth (Terra da Follone) è un termine generico che indica una Smectite (quindi con una struttura tipo TOT) costituita da Palygorskite o Sepiolite (Hormiti). È un prodotto versatile a livello industriale, caratterizzato da un'elevata superficie specifica e da forti proprietà assorbenti, leganti, gelificanti, addensanti e decoloranti. Veniva già anticamente utilizzata per la follatura, ovvero la pulizia della lana grezza, al fine di rimuovere la lanolina grassa e lo sporco prima della filatura, tintura e tessitura.

La Fuller's earth è una sostanza terrosa a grana molto fine, con un'elevata capacità di assorbimento dell'acqua e la capacità di raffinare e decolorare gli oli alimentari. Si differenzia dall'argilla comune per la maggiore percentuale di acqua contenuta nella struttura cristallina e per la scarsa plasticità. È adatta per usi sbiancanti e adsorbenti.

I depositi di Fuller's earth negli Stati Uniti si trovano ad esempio in unità sedimentarie marine marginali che si sono formate in condizioni anossiche, superficiali, a bassa energia riducente e spesso ipersaline. Tali ambienti deposizionali favoriscono la formazione di Montmorillonite magnesiacca, Palygorskite, Attapulgitite o Sepiolite.

La mineralogia delle Fuller's earth ne determina il potenziale utilizzo: altamente assorbente una volta essiccato, questo minerale viene utilizzato nelle lettiere granulari per animali, nei composti per la pulizia dei pavimenti e come vettore per insetticidi, erbicidi e così via.

peaked at about 317,000 st in 1930. At that time, this was about 90% of total U.S. fuller's earth production. After 1930, the use of fuller's earth for petroleum refining decreased because of the availability of alternative oil refining methods.

After that time, U.S. oil refining use of fuller's earth declined until it reached a uniform rate of 35,000 to 40,000 st y for edible oils only. Using fuller's earth as a waste oil absorbent and floor-sweep type of clean-up agent, however, began before World War II and, by the 1950s, its use as a carrier for herbicides and pesticides had become more prominent. Cat litter production began in 1952, and it has grown rapidly since then.

In the district between Quincy, Florida, and Attapulgus, Georgia, the excellent gelling properties of palygorskite (attapulgite) fuller's earth were discovered and developed for salt water drilling mud, as a joint binder tapping compound for sealing the seams of construction wallboard, and for other applications requiring a thickened gelling clay. These uses for gelling fuller's earth products developed to replace sales lost when use for petroleum refining declined. The Florida-Georgia mining district today is the world center for gelling fuller's earth clay production.

What is now by far the most prominent American use for fuller's earth, as a pet waste absorbent product (cat litter), began to grow rapidly in the 1950s. At first, cat litter was made from oil absorbent product that had been crushed to finer than $\frac{3}{4}$ -in. size, semicalcined in countercurrent rotary kilns, milled and screened, and packaged for retail sale. Today, cat litter is typically dried to only 4% to 15% moisture, which results in improved absorption, reduced dusting, and lower energy cost.

In the early 1990s, clumping cat litter became very popular. Blending western bentonite or clumping agents with eastern fuller's earth causes liquid waste to form clumps that can easily and neatly be taken from the litter box with a perforated scoop. This leaves only unused clean granules in the litter box, minimizing waste and enabling easy handling of a formerly messy and unsanitary chore. Today, many clumping cat litter products are up to 100% western sodium bentonites.

GEOLOGY

Mineralogy

Typically, fuller's earth is a marine or semi marine sedimentary clay variably composed of the clay mineral groups smectite and hornite. Tables 4 and 5 summarize these closely similar types of clay minerals.

In 1862, Savchenkov first used the term *palygorskite* to define a vein-type hydrothermal "mountain leather" clay mineral from the Palyorsk locality in the Ural Mountains of Russia (Hey 1975), where it was mistaken at first for a variety of asbestos.

J. de Lapparent first termed the highly absorptive gelling clays from Decatur County, Georgia (United States), and also those from an area near Mormoiron, France, with the mineral name *attapulgite*, because he thought those clays quite different from palygorskite. The new name was applied to gelling clays occurring near the small southern Georgia town of Attapulgus. More recently, however, x-ray diffraction proved the two clay types to be the same mineral (Bailey et al. 1971). Although first applied later than palygorskite, the name attapulgite is still in common informal use in the Florida-Georgia mining district where the crystal length-to-diameter ratio does not exceed 10:1 (Merkl 1989).

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Table 3. World production of fuller's earth, 2002

Producing Nation*	Production, t
Algeria	3,521
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Australia, attapulgite	6,000
Germany (unprocessed)†	500,000
Italy	30,000
Mexico	150,000
Morocco, smectite	42,243
Pakistan	15,000
Senegal, attapulgite	176,454
South Africa, attapulgite	7,900
Spain, attapulgite, estimated	90,000
United Kingdom, estimated product	140,000
United States	2,730,000
Rounded world total	3,890,000

Source: Virta 2004.

* Excludes centrally planned economy countries.

† Crude rather than processed product tons of clay.

Table 4. Smectite group minerals

End-Member Mineral	Crystal System	Chemical Composition
Montmorillonite	Monoclinic	(Na,Ca) _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ •nH ₂ O
Bidellite	Monoclinic	(Na,Ca _{0.65}) _{0.33} Al[Al,Si] ₄ O ₁₀ (OH) ₂ •nH ₂ O
Nontronite	Monoclinic	Na _{0.33} Fe ₂ (Si,Al) ₁₀ (OH) ₂ •nH ₂ O
Hectorite	Monoclinic	Na _{0.33} (Mg,Li) ₃ Si ₄ O ₁₀ (F,OH) ₂
Saponite	Monoclinic	(Ca/2,Na) _{0.33} (Mg,Fe) ₃ (Si,Al) ₄ O ₁₀ •4H ₂ O

Source: Roberts, Campbell, and Rapp 1990.

Table 5. Hornite group minerals

End-Member Mineral	Crystal System	Chemical Composition
Palygorskite*	Orthorhombic and monoclinic	(Mg,Al) ₂ Si ₄ O ₁₀ (OH) ₂ •4H ₂ O
Sepiolite	Orthorhombic	Mg ₄ Si ₆ O ₁₅ (OH) ₂ •H ₂ O

Source: Roberts, Campbell, and Rapp 1990.

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known as sepiolite and is found more abundantly in the northern extent of the Florida-Georgia basin than more southerly concentrations of attapulgite near Quincy.

The reader is referred to the Bentonite, and Palygorskite and Sepiolite chapters of this book for a more detailed discussion of the mineralogy of the smectite group and hornite minerals, respectively.

Origin

Fuller's earth clay deposits in the eastern United States are found in marginal marine sedimentary units that formed in restricted, anoxic, shallow, low-energy, reducing, and often hypersaline conditions. Such depositional environments favor formation of magnesian montmorillonite, palygorskite (attapulgite), or sepiolite.

Alternatively, sorptive calcium montmorillonite fuller's earth deposits have been formed in Pliocene freshwater lakes with as much as 40% siliceous diatom tests. In south-central

L'uso è progressivamente cambiato nel tempo:

- nell'antichità veniva utilizzata per la pulizia e la follatura della lana
- verso la fine del XIX secolo per decolorare e purificare oli minerali e alimentari
- all'inizio del XX secolo per la raffinazione del petrolio
- nella seconda metà del XX secolo come assorbente per oli, lettieri per gatti e granuli veicolanti per prodotti chimici agricoli, sostituendo la raffinazione del petrolio come utilizzo principale.
- tra la metà e la fine del XX secolo, sono iniziate ad essere ampiamente utilizzate a scopo assorbente, sia come argilla naturale che attivata con acido o per sbiancare oli minerali o alimentari.

La produzione mondiale annua di Fuller's earth si aggira intorno ai 3,9 milioni di tonnellate.

L'utilizzo più diffuso delle Fuller's earth come assorbente per i rifiuti degli animali domestici è nelle lettieri per gatti: mescolando la bentonite sodica con alcuni agenti agglomeranti e con la Terra da Follone, i rifiuti liquidi formano grumi che possono essere rimossi facilmente e senza sporcare dalla lettiera con l'ausilio di paletta forata.

Utile per aumentare l'adesività e promuovere un'elevata resistenza allo stato grezzo nelle

peaked at about 317,000 st in 1930. At that time, this was about 90% of total U.S. fuller's earth production. After 1930, the use of fuller's earth for petroleum refining decreased because of the availability of alternative oil refining methods.

After that time, U.S. oil refining use of fuller's earth declined until it reached a uniform rate of 35,000 to 40,000 st y for edible oils only. Using fuller's earth as a waste oil absorbent and floor-sweep type of clean-up agent, however, began before World War II and, by the 1950s, its use as a carrier for herbicides and pesticides had become more prominent. Cat litter production began in 1952, and it has grown rapidly since then.

In the district between Quincy, Florida, and Attapulgus, Georgia, the excellent gelling properties of palygorskite (attapulgite) fuller's earth were discovered and developed for salt water drilling mud, as a joint binder tapping compound for sealing the seams of construction wallboard, and for other applications requiring a thickened gelling clay. These uses for gelling fuller's earth products developed to replace sales lost when use for petroleum refining declined. The Florida-Georgia mining district today is the world center for gelling fuller's earth clay production.

What is now by far the most prominent American use for fuller's earth, as a pet waste absorbent product (cat litter), began to grow rapidly in the 1950s. At first, cat litter was made from oil absorbent product that had been crushed to finer than $\frac{3}{4}$ -in. size, semicalcined in countercurrent rotary kilns, milled and screened, and packaged for retail sale. Today, cat litter is typically dried to only 4% to 15% moisture, which results in improved absorption, reduced dusting, and lower energy cost.

In the early 1990s, clumping cat litter became very popular. Blending western bentonite or clumping agents with eastern fuller's earth causes liquid waste to form clumps that can easily and neatly be taken from the litter box with a perforated scoop. This leaves only unused clean granules in the litter box, minimizing waste and enabling easy handling of a formerly messy and unsanitary chore. Today, many clumping cat litter products are up to 100% western sodium bentonites.

GEOLOGY

Mineralogy

Typically, fuller's earth is a marine or semi marine sedimentary clay variably composed of the clay mineral groups smectite and hornite. Tables 4 and 5 summarize these closely similar types of clay minerals.

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Nontronite	Monoclinic	$\text{Na}_{0.33}\text{Fe}_2(\text{Si}, \text{Al})_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$
Hectorite	Monoclinic	$\text{Na}_{0.33}(\text{Mg}, \text{Li})_3\text{Si}_4\text{O}_{10}(\text{F}, \text{OH})_2$
Saponite	Monoclinic	$(\text{Ca}/2, \text{Na})_{0.33}(\text{Mg}, \text{Fe})_3(\text{Si}, \text{Al})_4\text{O}_{10} \cdot 4\text{H}_2\text{O}$

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Sepiolite	Orthorhombic	$\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$

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Le argille sbiancanti, con o senza attivazione acida, necessitano di una particolare dimensione dei pori e porosità per pulire e decolorare gli oli alimentari.

La presenza di Attapulgite in cristalli allungati aghiformi favorisce un comportamento del prodotto di tipo gelificante o tissotropico superiore quando viene disciolto in acqua o polimeri liquidi per i fanghi di perforazione petrolifera.

Forma addensata o gelificante per produrre vernici antigoccia, per addensare detergenti liquidi, per cemento per giunti di cartongesso.

CAOLINO

Il caolino è un minerale industriale ad elevate caratteristiche e particolarmente pregiato, utilizzato principalmente come:

- pigmento per migliorare l'aspetto e la funzionalità di carta e vernici
- riempitivo funzionale per gomma e plastica
- materia prima nella produzione di ceramica
- componente per prodotti refrattari, mattoni e fibra di vetro

I grandi giacimenti di caolino ad alta purezza, in grado di rifornire grandi impianti di lavorazione e accessibili alle infrastrutture di trasporto globali, sono rari. USA, Brasile, Regno Unito e Germania

Il valore di un caolino come minerale si basa sul suo grado di bianchezza, sulla granulometria (che deve essere fine) e sul contenuto di minerali del gruppo del caolino.

Due tipi di giacimenti minerali:

- Caolino primario. Il caolino deriva da una roccia ignea o metamorfica caolinizzata in situ mediante processi idrotermali o di alterazione meteorica.
- Caolino secondario. Caolino sedimentario composto da particelle minerali asportate da un giacimento primario e sedimentate.

Il caolino primario contiene quantità significative di minerali non caolinitici resistenti all'alterazione (il tasso di recupero del caolino a partire dal prodotto grezzo "di miniera" è in genere del 10-15%).

Il caolino sedimentario in genere non contiene elevate concentrazioni di minerali instabili o labili provenienti dalla roccia madre.

La caolinite è un minerale molto diffuso sulla superficie terrestre, soprattutto come componente principale dei suoli nelle zone subtropicali e tropicali umide.

Fillosilicati



Kaolinite

Coacoyula, Mexico



UNIVERSITÀ
DEGLI STUDI
DI PADOVA



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Mineralogia e Petrografia per i Beni Culturali

Kaolin

Robert J. Pruett and Sam M. Pickering, Jr.

INTRODUCTION

Kaolin is a global industrial mineral primarily used as (1) a pigment to improve the appearance and functionality of paper and paint, (2) a functional filler for rubber and plastic, (3) a ceramic raw material, and (4) a component for refractory, brick, and fiberglass products. Other lower-volume uses for kaolin include chemical manufacture, civil engineering, agricultural applications, and some pharmaceuticals. The limited availability of suitable raw material, extremely competitive market conditions, and the technological complexity of kaolin processing and kaolin product functionality creates a high barrier of entry in to kaolin production. Rock and soil containing kaolin minerals occur over wide areas on most continents, but large high-purity kaolin deposits that are capable of supplying large processing facilities and are accessible to global transportation infrastructures are rare. Therefore, the majority of the world's kaolin is mined from sedimentary kaolin deposits located in the United States and Brazil and from primary kaolin deposits in the United Kingdom and Germany. The large size of operations in these regions is driven in part by demand in the paper market for large volumes of consistent quality pigment and by the need to cover the large fixed cost base that is required to mine and process kaolin ore into marketable product.

Definitions

Kaolin is a white or nearly white clay comprising naturally occurring kaolin group minerals. It is distinguished from other industrial clays containing high levels of kaolin minerals—such as ball clay and fire clay—by its whiteness, fine particle size, and kaolin group mineral content (Table 1). The white color of kaolin can occur natu-

rally or result from extensive processing to remove color-bearing minerals and organic compounds that adsorb certain wavelengths of visible light. A second component of kaolin's white appearance is derived from its fine particle size, which causes light to scatter. In most commercial products, kaolin contains particles with an equivalent spherical diameter that is generally finer than 2 μm , though some grades of kaolin products contain particles about 10 μm in size. The term *hydrous kaolin* generally refers to processed kaolin product that contains kaolin minerals with their structural water or hydroxide component. *Calcined kaolin* refers to the thermally processed kaolin exposed to temperatures higher than 450°C to form metakaolin, or to temperatures higher than 1,000°C to form high temperature minerals such as mullite, spinel, and cristobalite.

Crude kaolin ore deposits are contained in a variety of kaolinitic rock types. *Primary kaolin* generally describes a kaolin ore altered from an igneous or metamorphic rock that was kaolinized in situ by hydrothermal or weathering processes. Varieties of primary kaolin are China-clay rock and residual kaolin. Saprolite can be residual kaolin that forms from the weathering of felsic igneous and metamorphic rocks. *Sedimentary kaolin* is a kaolin ore formed through sedimentary depositional processes. *Secondary kaolin* is sedimentary kaolin comprising transported mineral particles. Though the term sedimentary kaolin was originally synonymous with secondary kaolin, it is clear that many kaolin ores deposited as sediments have undergone some postdepositional kaolinization of other minerals or recrystallization of kaolin minerals (Pruett 1993; Hurst and Pickering 1997). The primary or sedimentary origin of a kaolin deposit influences the exploration, mining, and processing methods used to manufacture a kaolin product (Figure 1). A variety

Table 1. Features that distinguish kaolin from ball clay and fireclay

	Kaolin	Ball Clay	Fireclay
Occurrence	Altered rock, sedimentary rock	Sedimentary rock	Sedimentary rock
Processing	Unprocessed, air-float, water-washed, delaminated, calcined	Unprocessed, air-float, some slurry	Unprocessed, calcined
Properties	White or nearly white, clay particle size	Highly plastic clay, contains some organic matter and/or swelling clay	Low in alkalis, calcium, and iron; high alumina and silica; does not deform at high temperature
Use	Pigment, filler, ceramic, refractory	Ceramic, refractory	Refractory
Synonyms	China clay, paper clay, white clay, <i>bolus alba</i>	Pipe clay	Firestone, pot clay, refractory clay, sagger

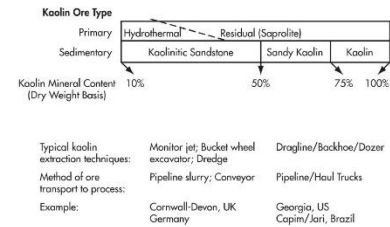


Figure 1. Relationship between kaolin mineral content and extraction method for kaolin ore types

of terms (Table 2) are used to describe rock types that contain kaolin minerals in sufficient concentration to be used or considered as kaolin ores or are associated with kaolinized rock units.

GEOLOGY

Mineralogy

Kaolin minerals are dioctahedral 1:1 phyllosilicates having a sheet of silicon atoms in tetrahedral coordination with four oxygen atoms and a sheet of aluminum atoms in octahedral coordination with two oxygen atoms and four hydroxide molecules (Figure 2). The basal oxygen atoms of the tetrahedral sheet form a crystal face, and the apical oxygen in the silica sheet are shared with aluminum. The remaining two thirds of oxygen in the octahedral sheet are shared with hydrogen (i.e., hydroxides) and form the opposing crystal face. Hydrogen bonding between the basal oxygen of the tetrahedral (T) sheet and hydrogen of the octahedral (O) sheet in an adjacent layer define a cleavage plane that enables delamination of kaolinite into flat platy particles. The difference between kaolinite, dickite, and nacrite is related to differences in the stacking order of unit layers. Kaolinite has a single tetrahedral-octahedral (TO) layer; dickite has a two TO-stacking unit layer with higher structural order than kaolinite; and nacrite has a six TO-stacking unit layer and ordered distribution of octahedral vacancies forming a crystal with rhombohedral symmetry. Halloysite has two layers of water between each TO layer in its hydrated form. Hydrated halloysite is also referred to as 10Å-halloysite, indianite, and endellite. Dehydrated halloysite is called 7Å-halloysite or metahalloysite.

Kaolinite is the most common kaolin mineral and has the greatest industrial importance. The kaolinite crystal lattice shows a range of defect concentrations and isomorphous substitution of iron for aluminum in the octahedral sheet and perhaps aluminum for silicon in the tetrahedral sheet (Schroeder and Pruett 1996). The terminology to describe kaolinite defects is confusing and discordant. Kaolinite crystal defects were initially described as well-crystallized or poorly crystallized, terms used by Grim (1953), which changed in the scientific literature to well-ordered or poorly ordered, and evolved to high-defect or low-defect, which is currently favored by mineralogists publishing in academic journals such as *Clays & Clay Minerals*. In the patent literature, industrial mineralogists and technologists typically use the terms well-crystallized or poorly crystallized, as originally used by Grim.

The Hinckley index is a method recognized by industry for measuring the relative levels of defects in kaolinite powders. The Hinckley index of kaolin is calculated using x-ray powder diffraction patterns (Figure 3). High-defect kaolinite has broad x-ray peaks,

a low Hinckley index (<0.6), and is called poorly ordered or poorly crystallized kaolinite. Low-defect kaolin has sharp x-ray diffraction peaks, a high Hinckley index (>0.7), and is called well-ordered or well-crystallized kaolinite. Hinckley index relates generally to the physical properties of kaolin, particularly to particle size. Kaolin with a high Hinckley index is typically coarse particle size (<70 wt % <2 μm), whereas kaolin with a low Hinckley index is typically fine particle size (>80 wt % <2 μm).

The accessory mineral content of kaolin is a result of its geological origin and the separation processes used for beneficiation. Primary kaolin ore from different deposits or even the same deposit generally show a wide variation in mineralogy that is controlled by the degree of alteration by weathering and hydrothermal processes. Primary kaolin contains significant amounts of nonkaolin minerals that are resistant to alteration. Common minerals that resist alteration processes are quartz, muscovite, tourmaline, and zircon. The margins of primary kaolin deposits can have sharp boundaries or can gradually change into less-altered rock that shows only partial feldspar and mica alteration. Rock that is partly kaolinized can have some host minerals from the parent rock, such as feldspar or biotite, or some minerals that are first series products of chemical alteration, such as halloysite, illite, vermiculite, or smectite.

Sedimentary kaolin typically does not contain high concentrations of unstable or labile minerals from the parent source rock (Figure 4), and the content of minerals such as quartz and mica in commercial deposits is low because coarse sand- and silt-sized particles were separated from clay during sediment transport. The fine silt- or clay-sized fractions that make up the bulk of sedimentary kaolin deposits contain impurities such as anatase, illite, smectite, hydroxyl-interlayer vermiculite, and mixed-layered clay minerals. Sedimentary kaolin that is associated with oxidized sediments contains iron oxide and iron hydroxide minerals that are common in soil environments such as hematite and goethite. Sedimentary kaolin that is associated with reducing anoxic depositional environments will generally contain organic matter and may contain iron sulfides such as pyrite, marcasite, or both.

Clay-sized titania minerals such as anatase are common in sedimentary kaolin and are uncommon in primary kaolin. Anatase and its precursor pseudorutile are weathering products of ilmenite and titanium-bearing biotite mica inherited from the parent rock (Schroeder, Pruett, and Melear 2004). The chemistry of anatase appears to reflect its precursor minerals (ilmenite, micas) by having minor levels of iron and trace levels of chromium, zirconium, and niobium substituting for titanium, thus causing the mineral to have a brown to tan color which detracts from the whiteness of kaolin products. Leuco-xene originating from ilmenite typically occurs as coarse aggregates that can be removed by standard gravity separation or magnetic separation processes, whereas anatase resulting from biotite mica alteration is typically finely disseminated in the kaolin ore and responds well to flotation or selective flocculation for removal.

OCCURRENCE

Kaolinite is a very widespread mineral across the earth's surface, especially as a major component of soils in humid subtropical and tropical areas. Kaolin deposits (Ross and Kerr 1931; Patterson and Murray 1984) of sufficient purity, brightness, whiteness, and suitable mineral-water slurry viscosity, however, are rather rare.

In general, kaolin deposits can occur as the following:

- Sedimentary bodies with fairly to extremely low "grit" content in various stages of oxidation and recrystallization
- Residual weathering blankets or funnel-shaped hydrothermal alteration zones along fracture patterns from much older aluminous rocks such as granites

I minerali della famiglia del caolino sono fillosilicati diottaedrici tipo TO, caratterizzati da uno strato di atomi di silicio in coordinazione tetraedrica con quattro atomi di ossigeno ed uno strato di atomi di alluminio in coordinazione ottaedrica con due atomi di ossigeno e quattro molecole di idrossido. Lo strato TO definisce un piano di clivaggio, che permette la delaminazione della caolinite in particelle piatte e lamellari.

Fillosilicati

Gruppo 1:1 (T-O)

Fillosilicati diottaedrici

-Kaolinite $Al_2[(OH)_4Si_2O_5]$

-Halloysite $Al_2[(OH)_4Si_2O_5] n \cdot H_2O$ ($n \approx 2$)

(Simile a kaolinite ma con nH_2O tra gli strati)

Questi minerali perdono acqua se scaldati a temperature $500 < T^\circ C < 600$.

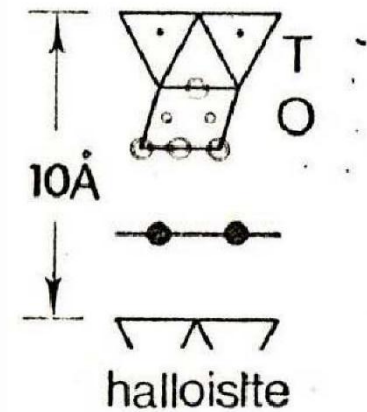
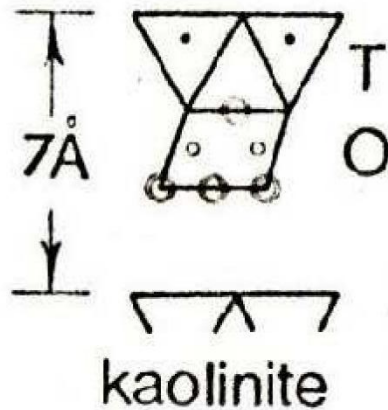
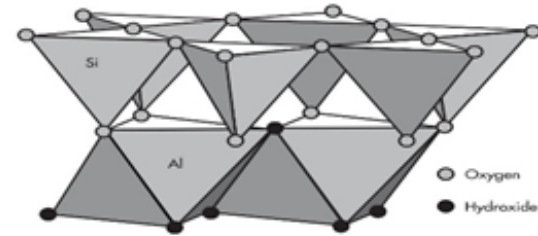
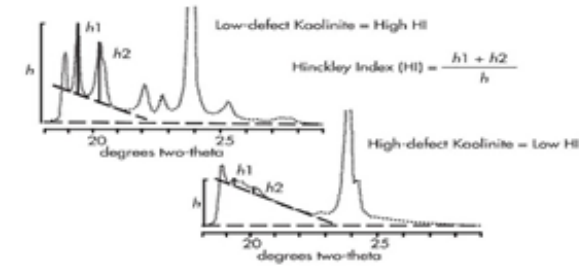


Table 2. Kaolin rock terms and definitions

Terms Generic to Kaolin	
Kaolin	A rock mass containing principally kaolinitic clays that are low in iron, and usually white or nearly white in color (Ross and Kerr 1931)
Tonstein	Kaolin composed of volcanic ash that was partly or fully altered to kaolin minerals and is commonly associated with coal deposits.
Terms Typically Related to Primary Kaolin	
China stone	Partly kaolinized granite that is harder than China-clay rock
China-clay rock	Granite showing the highest degree of kaolinization where all feldspar has altered to kaolinite and can readily be broken apart by hand
Cornish stone	China stone
Lithomarge	A smooth indurated variety of kaolin containing a mixture of kaolinite and halloysite
Saprolite	Weathered igneous or metamorphic rock showing primary relict texture that can have a high kaolin mineral content
Terms Typically Related to Sedimentary Kaolin	
Ball clay	Highly plastic secondary clay containing kaolinite and used for ceramics
Fireclay	A clay, typically containing kaolin minerals, with a high silica and alumina content; used as a refractory because it will not deform at high temperature
Flint clay	Kaolin that is smooth, tough, flintlike, and breaks with a pronounced conchoidal fracture
Hard kaolin	A term original used for kaolin used to fill hard rubber that originates from fine-particle-size kaolin deposits located in the Georgia–South Carolina kaolin district. Hard kaolin also occurs in northeastern Brazil. It has a low Hincley index and tends to break with some difficulty in a rough irregular fracture.
High-alumina kaolin	Kaolin containing minor amounts of hydrous alumina minerals such as gibbsite, boehmite, or diaspore
Kaolinitic sandstone	Sandstone containing significant and potentially separable amounts of kaolin minerals. The sand-sized particle content is >50% by volume or mass.
Sandy kaolin	Kaolinitic sediments generally containing between 5 and 50 wt % sand-sized particles
Soft kaolin	A term originally used for kaolin used to fill soft rubber that originates from coarse-particle-size kaolin deposits located in the Georgia–South Carolina kaolin district. Soft kaolin has a high Hincley index, tends to be massive, and breaks with a smooth conchoidal fracture.
Underclay	A clay that underlies a coal bed representing a soil from the coal swamp flora. Underclay is commonly kaolinitic and can be a source of ball clay or fireclay.

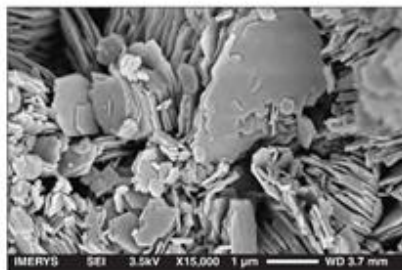


Adapted from Grim 1953.

Figure 2. Kaolinite crystal structure**Figure 3. Hincley index formula with examples of calculation for low-defect and high-defect kaolinite from x-ray powder diffraction spectra collected from random-oriented, pulverized kaolin powders**

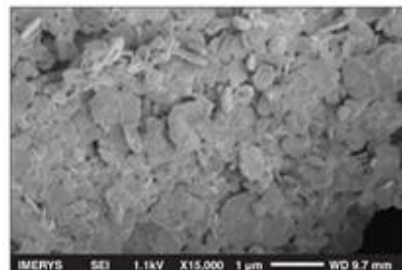
Mineralogy	Weathering	Transport/ Deposition Distance = Higher Higher Energy	Alteration	
			Early (reduction)	Late (oxidation)
Quartz	→	→		
Muscovite	→	→		
Feldspar	→	→		
Kaolinite, low-defect	→	→	→	
Halloysite	→	→	→	
Kaolinite, high-defect	→	→	→	
Biotite	→	→		
Ilmenite/Magnetite	→	→		
Pseudomorph	→	→		
Anatase	→	→		
Hematite	→	→		
Goethite	→	→		
Organic matter	→	→		
Pyrite	→	→		
Marcosite	→	→		

Figure 4. Sequence of mineral changes from a granite that are associated with (1) weathering, (2) transport and deposition, (3) early stage of postdepositional alteration, and (4) late stage postdepositional alteration for kaolin in central, middle, and eastern Georgia, United States



Courtesy of IMERYS.

Figure 7. Electron photomicrograph showing the fracture surface of coarse kaolin crude that is representative of Cretaceous kaolin deposits in Georgia



Courtesy of IMERYS.

Figure 8. Electron photomicrograph showing the fracture surface of fine kaolin crude that is representative of fine Tertiary kaolin deposits in Georgia

Table 3. Comparison of typical sedimentary characteristics for soft, coarse-particle-size kaolin deposits with those for hard, finer-particle-size kaolin deposits

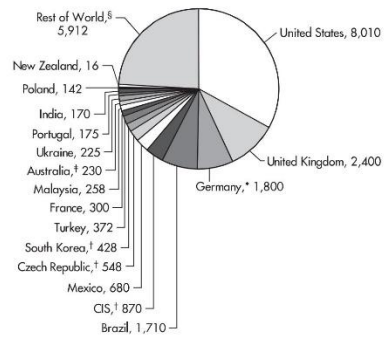
Typical Characteristics of Sedimentary Kaolins	Soft Kaolin	Hard Kaolin
Texture of crude clay fracture surfaces	Breaks easily into smooth, conchoidal surfaces	Tough, breaks less easily, rough, earthy, blocky surfaces
Larger trace fossils	Burrows and trace fossils very scarce to absent	Common, mainly intertidal trace fossil burrows
Microscopic fossil types of dominant plant pollen and spores	Mainly pollen of upland, back-deltaic, and continental aspect	Trace bacteria, more marine pollen, dinoflagellates, and hystrichospherids
Typical degritt crude clay particle size	Coarser than about 65% to 70% finer than 2 µm	Finer than about 80% to 90% finer than 2 µm
Clay particle crystal habit or morphology	Coarse books, stacks, and vermiculites in a matrix of euhedral thin crystallites, more recrystallized	Vermiculites, books, and stacks very rare or absent, only thin submicron single crystal plates, less recrystallized
Crystallite particle packing relationship	Open, porous, interlocking face to edge packing	Tight, little pore space, face to face packing
Crystal cleavage, ability to produce delaminated products	Coarse vermiculites and books cleave and delaminate well for high aspect ratio products	Hardly delaminates at all, crystal plates are too fine and thin
X-ray diffraction patterns	Well-resolved peaks in the 020, 1T0, 11T, 02T, and 021 bands, low crystal defect kaolinite	Poorly resolved peaks in the 020, 1T0, 11T, 02T, and 021 bands, diffuse patterns, high crystal defect kaolinite
Hinckley index	High Hinckley index, two phase mixture	Low Hinckley index, single phase
Clay chemistry after degritt removal of detrital minerals	Fe and Ti low, increase with decreasing crude particle size, lower alkali metals	Fe and Ti higher, often same, or increase with decreasing crude particle size, slightly higher alkalis
Accessory detrital mineral suites	Altered muscovite abundant, detrital heavy minerals more mature but less abundant	Muscovite scarce, coarser anatase more abundant, immature heavy minerals
Moist crude clay bulk density and specific gravity	1.2–1.3 st/yd ³ , specific gravity 1.3–1.6	1.3–1.4 st/cu yd, specific gravity 1.6–1.7
Aqueous slurry viscosity at highest-solids concentration	Generally Hercules higher and Brookfield lower	Generally Hercules lower and Brookfield higher
Georgia, geological age, and stratigraphic occurrence	Older, in Georgia in Cretaceous Buffalo Creek Formation or early Paleocene Marion Member	Younger, in Georgia from Early to Middle Eocene Jeffersonville Member of the Huber Formation
Northern Brazil occurrence	Rio Capim District, Para State	Rio Jari District, Amapa State
Depositional environment	Fluvial upland back-deltaic, mostly fresh water	Coastal, marginal marine, often brackish or saline

Adapted from Fickering and Hunt 1989.

front and also in the less saline back-delta areas. These lens-shaped clay units were deposited during several worldwide episodes of marine transgression and highstand along the fall line in Georgia and South Carolina. This process of deposition and the role of weathering and bacterial alteration are more thoroughly described in Elzea Kogel et al. (2000) and Elzea Kogel et al. (2002). Dombrowski (1992) suggested that the older Cretaceous coarse kaolin (Figure 7) was derived from weathered granitic and gneissic source

rocks, and the Early Tertiary fine-particle-size kaolin (Figure 8) from phylitic meta-volcanic source rocks. In general, Table 3 describes soft and hard kaolin and holds true for kaolins in both Georgia and the eastern Amazon region of Brazil.

Because the river deltas were heavily overgrown with thick plant cover, the clays were laid down with a considerable organic content of decaying vegetation. The resulting clay deposits were originally rather dark organic, pyritic mud, and usually cap distinct,



Modifications from the USGS numbers including the following:
 * German kaolin production taken from *Minerals Yearbook 2002*.
 † Assumed 15% beneficiated, dry product recovered from crude kaolin.
 ‡ Includes ball clay.
 § Modified to reflect adjusted volumes for CIS, Czech Republic, and South Korea; and deletion of volume from Colombia.

Figure 5. World production, kt (as compiled by the U.S. Geological Survey [USGS], 2002)

• Weathering alteration deposits of feldspar-rich (arkosic) sedimentary rock

The most prominent world kaolin mining districts are in the United States (southeastern), Brazil (northern), the United Kingdom (Cornwall-Devon), and Germany (Bavaria and Saxony). The volume of beneficiated kaolin produced from these four districts is shown in Figure 5. Kaolin production from some other countries is reported using different metrics such as crude tons mined (Commonwealth of Independent States [CIS], Czech Republic, and the Republic of Korea), or includes ball clay (Australia) or common clays (Colombia). The prominence of U.S., Brazilian, U. K., and German kaolin production is both in terms of volume and quality of beneficiated product that reaches global pigment and filler markets as opposed to local commodity markets where kaolin is sold as inexpensive mineral filler or as a structural component in brick.

United States

In the southeastern United States, kaolin has been mined since colonial times in the upper Coastal Plain areas of Georgia and South Carolina. These deposits are composed of deltaic sediments of Late Cretaceous to Early Tertiary age that represent the Oconee Group (Figure 6).

The major sedimentary units here are cross-bedded, fining-upward coarse- to fine-grained quartz sands which originated as outwash from weathered Paleozoic to Precambrian granitic rock bodies contained in the Piedmont and Blue Ridge provinces of the Appalachian Mountains. Lens-shaped clay accumulations were formed by sediments deposited in low, swampy areas on the advancing delta



LEGEND: rk = Finer particle size hard kaolin (both unoxidized and oxidized).
 ck = Coarser particle size soft kaolin (both unoxidized and oxidized).
 kl = Gray kaolins and lignites.
 U = Profound unconformity.
 U - = Subtle unconformity.

*Stratigraphic unit that produces important tonnages of commercial grade kaolins.

Adapted from Pickering and Avant 1999.

Figure 6. Stratigraphy of the Georgia kaolin district

I distretti minerari per la produzione di caolino più importanti al mondo si trovano negli Stati Uniti (Sud-est), in Brasile (parte settentrionale), nel Regno Unito (Cornovaglia e Devon) e in Germania (Baviera e Sassonia).

Il caolino per essere trasformato in prodotto commerciale richiede una complessa lavorazione con numerosi passaggi.

La lavorazione del caolino è tecnicamente complessa e rappresenta una barriera costosa per l'ingresso di potenziali produttori in molti mercati in cui purezza, uniformità, caratteristiche di manipolazione e aspetto sono proprietà apprezzate.

- I giacimenti primari di caolino, con le loro tipiche elevate percentuali di materiale granulare grossolano, presentano comunemente una consistenza morbida e farinosa. Questo tipo di caolino primario viene spesso estratto con un "cannone ad acqua", mediante il quale l'argilla viene lavata via dalla parete rocciosa da un getto d'acqua ad alta pressione. La sospensione argillosa risultante scorre verso la parte più bassa della miniera, dove la maggior parte delle particelle granulari grossolane si deposita, separandosi dalla sospensione contenente il caolino, che viene pompata attraverso una condotta fino alla raffineria.

- Preparazione del materiale. La frantumazione è un processo in cui il minerale di caolino estratto viene trasformato in una sospensione di acqua e minerale con una percentuale di solidi compresa tra il 35% e il 70%. Molti impianti di frantumazione si trovano all'inizio delle condotte che trasportano la miscela di acqua ed argilla all'impianto di lavorazione. Lo scopo della frantumazione è la disaggregazione meccanica della roccia per separare le particelle e l'aggiunta di sostanze chimiche per impedirne la flocculazione.

- Pulitura, dessabbiatura e rimozione della sabbia. La pulitura ha lo scopo di rimuovere la sabbia e le particelle grossolane di dimensioni pari a quelle del limo. Di solito si usa un classificatore a spirale (vite continua) che consente alle particelle di sabbia grossolana di depositarsi in un concentrato che può essere rimosso meccanicamente e permette alla sospensione di caolino contenente particelle fini di traboccare e procedere verso lo

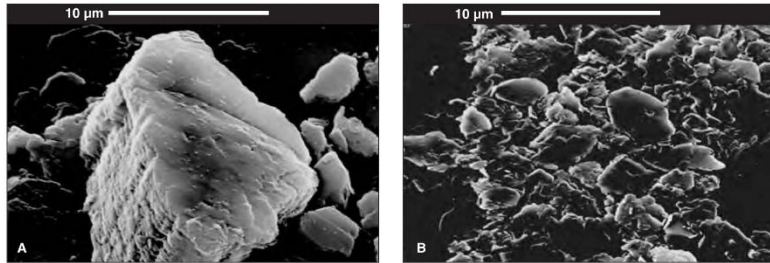
- Aumento del grado di bianco. Separazione magnetica, flocculazione selettiva, flottazione, lisciviazione acida e sbiancamento ossidativo. Permettono la rimozione delle particelle non caolinitiche, la maggior parte delle quali sono impurità coloranti (come ossidi di ferro, idrossidi di ferro, minerali di biossido di titanio come anatasio, tormalina e miche) o abrasive (come quarzo e feldspato). La flottazione selettiva richiede che la sospensione di caolino sia condizionata a circa pH 6,5 con aggiunta di esametafosfato di sodio, silicato di sodio, e cloruro di sodio, lasciata riposare per consentire l'aggregazione delle particelle di anatasio e floccolata utilizzando un polimero (ad es. poliacrilammide) ad alto peso molecolare, fortemente anionico e solubile in acqua per formare "fiocchi" di anatasio (ossido di titanio) che si depositeranno in un addensatore. La lisciviazione acida e lo sbiancamento ossidativo sono trattamenti chimici applicati alle sospensioni di caolino per migliorarne la brillantezza e la tonalità di bianco, dato che permettono la rimozione di ossidi di ferro solubili come ematite e goethite.

- Macinazione a umido e delaminazione. La macinazione viene utilizzata per ridurre la granulometria del prodotto e favorire la liberazione dei minerali nei successivi processi di separazione. La delaminazione è la scissione o la separazione di "blocchi" (lump) di caolinite in particelle lamellari più fini. I prodotti delaminati sono utilizzati in particolare per il rivestimento della carta patinata perché offrono una buona copertura del foglio ed una buona stampabilità.

- - Disidratazione. La maggior parte delle tecnologie di disidratazione richiede l'ottenimento di una sospensione di caolino flocculato da sottoporre a lisciviazione acida

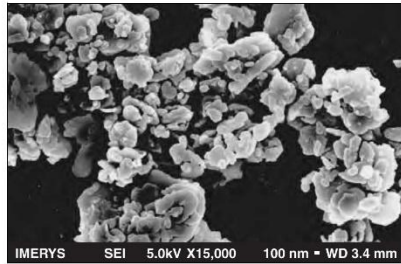
- Essiccazione. Il caolino può essere essiccato utilizzando diversi tipi di essiccatori

- Calcinazione. La calcinazione è un processo termico che provoca la trasformazione dei minerali di caolino in altre fasi amorfe o cristalline. La calcinazione può aumentare la brillantezza del caolino bruciando la materia organica.



Courtesy of IMERYS.

Figure 14. Electron photomicrographs showing (A) kaolinite stacks prior to grinding and (B) kaolinite plates after delamination and classification to a delaminated kaolin product



Courtesy of IMERYS.

Figure 15. Electron photomicrograph showing calcined agglomerates composed of sintered kaolin particles. Porosity of the calcined kaolin agglomerate imparts opacity and light-scattering properties.

clay slurries using sand or other media to delaminate and separate fine kaolinite platy particles (Feld et al., 1960). Delaminated products show value in paper coating because they have good sheet coverage and printability.

Dewatering

Dispersed kaolin clay slurries are typically shipped by tanker truck, rail, or ship at about 60% to 70% solids, depending on product type. Kaolin slip solids in the processing operation can range from 5% to 70%, depending on mining and blending technology. Kaolin slip solids are typically between 15% and 35% at the leaching stage, which occurs after physical separation of impurities, particle classification, and grinding. Most dewatering technologies require obtaining a flocculated kaolin slip in preparation for reduced-acid leaching. Kaolin particles are flocculated when pH is adjusted to <5 and chemicals such as alum and high molecular weight polymers are added to aid dewatering. Thickeners, centrifuges, rotary vacuum filters, and pressure filters are then used to dewater flocculated slip (Murray 1980; Leung 1988). Dewatering a dispersed kaolin slip is possible with use of centrifuges, membrane filters, evapora-

tors, and back mixing with dried clay. The limitations of filtration technologies and the need to add water to redispersed flocculated slip typically allow only evaporating and back mixing with dry clay to increase slurry solids to 65% to 70%. The spray-dry back-mix process involves addition of spray-dried clay to slurry in a mixing tank in a proportion required to raise slip solids to the appropriate amount for shipping.

Drying

Kaolin can be dried using several types of dryers: spray, rotary, tray, fluid bed, and apron. The spray dryer is the most common dryer technology used by U.S. and Brazilian kaolin producers. Spray drying involves feeding slip to a nozzle atomizer located at the top of a heated chamber. Atomized droplets of slip quickly dry into beads about 0.25 to 1 mm in diameter with a moisture content between 1 and 3 wt%. The other dryer technologies previously mentioned are fed undispersed filter cake. The apron dryer is a common process for making acid-lump type products that contain low levels of dispersant. A band conveys a 2.5 to 15 cm (1 to 6 in.) bed of shredded or extruded filter cake on a perforated apron through a tunnel-like chamber containing hot gases. Dried product can be loaded bulk into road, rail, or sea containers or packaged into 50-lb or 1-t bags. Dried product can be milled or pulverized to a powder form to help further reduce moisture content and improve ease of product makedown into slurry for intended applications.

Calcination

Calcination is a thermal process that causes kaolin minerals to transform to other amorphous or crystalline phases. The phase transformations that occur during calcination are the dehydroxylation of kaolinite to metakaolinite at about 500°C and crystallization of metakaolinite into mullite above 1,000°C. Calcination can increase the brightness of kaolin by burning off organic matter and structures the clay into aggregates (Figure 15). Calciners used by the kaolin industry include the horizontal rotary kiln and vertical Herreshoff. Milling is typically used on the calcined product to break up coarse agglomerates and residue.

Georgia Kaolin Processing

Georgia kaolin is most commonly processed in the slurry form by a variety of advanced beneficiation methods (Pruett 2000). Typically, the wet-process plant first blends kaolin from several mines to

enable production of a specific range of products. The kaolin is blended into slurry that is then centrifuged to make products having a range of particle sizes, which then may be whitened and brightened by chemical reduction leaching, oxidation bleaching, HIMS, selective flocculation, froth flotation, thermal calcination, and other proprietary methods. The refined kaolin products may be shipped to North American customers as high-solids slurry in tank cars or dried for worldwide export. In typical years, approximately two thirds of Georgia kaolin production is used in North America, and one third is exported, mostly to customers in Western Europe and southeastern Asia (Figure 16). About two thirds of the kaolin produced in the Georgia district by wet slurry processing is used as a pigment for coating fine printing papers (Figure 17) for use in magazines, catalogs, and annual reports. These slurry-processed products may also be used as a pigment extender in paints, plastics, adhesives, and sealants; for various ceramic, refractory, and catalyst raw materials; and as an inorganic binder in pharmaceuticals. Export kaolin products may be shipped in bulk, in polypropylene big-bags, or by large metal shipping containers.

A rather small percentage of Georgia kaolin production (Figure 13), and most of South Carolina's production (374 kt, USGS 2002), is processed by dry air-float methods. Dry processing is less costly than wet processing but is not capable of improving kaolin quality other than by limited removal of grit material. The typical dry-process plant hauls the kaolin from the mines by highway truck and sorts it at the plant into various different crude grades in several separate bins. The different grades of clay are blended as they are loaded into a slicer, which breaks the lumps down to feed a dryer. The dried clay is then transported on a column of rapidly moving air into a roller mill or other dry mill where the clay is pulverized to a powder form. The air column sweeps the powdered clay from the mill through a whizzer or cyclone classifier where coarse sand-size particles can be removed as gangue or returned to the mill for further size reduction. Air float processed Georgia and South Carolina kaolins are used for ceramic sanitaryware, dinnerware, and decorative tile; as a pigment extender in floor coverings, paints, insecticide, and herbicide carriers; and as aluminum raw material for fiberglass and Portland cement manufacture.

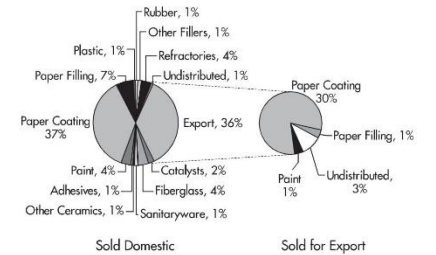
EXPLORATION

Strategy

The most effective exploration for new deposits of commercial grade kaolin is begun by considering how the mineral was originally concentrated, altered, or deposited. The history of a kaolin deposit's formation is a useful indicator of the topography, elevation, structural attitude, degree of alteration, and stratigraphic sequence in which favorable deposits of kaolin are most likely to be discovered.

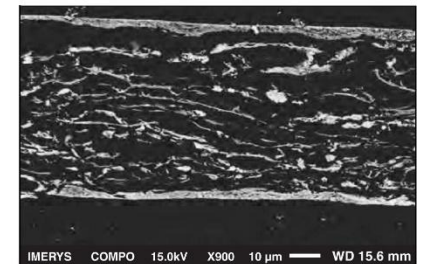
As examples, the Devon and Cornwall-type hydrothermally altered primary kaolins are typically discovered as alteration deposits along high-angle shear zones or joints in the parent granite and therefore are commonly found in near-vertical funnel-shaped concentrations. Exploration for this type of kaolin takes into consideration the preferred orientation of joint systems that were used by hydrothermal kaolinizing fluids, which cut the types of granitic rocks that tend to be altered to commercial grade kaolin. Knowing that kaolinization occurs in the district to a depth of several hundred meters, a drilling program needs to be prepared to drill to at least that depth.

By contrast, Sparta-type primary kaolin from middle Georgia formed by surficial weathering of the muscovite-biotite granite and therefore occurs as a near-surface pallid saprolite blanketed beneath upland divides where the weathering zone has been seasonally wet-



Source: USGS 2002.

Figure 16. Georgia kaolin production for 2002 compiled by the USGS. Total kaolin volume sold by Georgia producers in 2002 was 6,830 kt with a value of \$893 million.



Courtesy of IMERYS.

Figure 17. Electron photomicrograph showing a cross-section of coated paper. The very bright lines at the top and base of the paper are kaolinite coatings. The bright regions between the coating and darker-colored wood fibers are mineral filler.

ted and dried. By this model, Sparta-type primary kaolins are not expected to occur beneath stream valleys which have been continually water saturated. A drilling strategy for this type of primary kaolin concentrates on shallow exploration and stops coring when the saprolite begins to contain unaltered feldspars from the parent rock.

As a further example, the very productive central Georgia kaolins and eastern Amazon region Brazilian kaolins were deposited in low-energy water bodies associated with a fluvial deltaic sedimentary environment. These kaolin deposits therefore occur as clay lenses scattered in fining-upward sedimentary sequences. The common presence in Georgia of a thick overlying smectitic marine clay unit suggests that exploration needs to be concentrated along elevations where the marine clay cover has been breached by later erosion, allowing fresh groundwater to access the kaolin lenses and to oxidize sulfide minerals and organic matter.

Necessity for Continuous New Exploration

Because most kaolin mining operations require a very large capital investment for processing plant construction and for periodic

La tecnica più efficace per l'individuazione di nuovi giacimenti di caolinite di qualità commerciale inizia studiando come il minerale si sia originariamente concentrato, alterato o depositato. La genesi di un giacimento di caolino è legata alla topografia, all'altitudine, all'assetto strutturale, al grado di alterazione ed alla sequenza stratigrafica in cui è più probabile scoprire giacimenti di caolino economicamente sfruttabili.

Tendenze di mercato

- Il mercato della carta condiziona fortemente la domanda di produzione mondiale di caolino arricchito
- La domanda di caolino per la produzione di carta è diminuita progressivamente dagli anni '80, quando il carbonato di calcio precipitato (PCC) ha sostituito il caolino come carica preferenziale nelle carte non patinate "senza legno" (Wood free)

PALYGORSKITE E SEPIOLITE (HORMITI)

La Palygorskite e la Sepiolite sono silicati idrati di magnesio, ferro e alluminio. Termine alternativo: Attapulgitite

Sia la Palygorskite che la Sepiolite sono definite “argille assorbenti” a causa del loro alto rapporto superficie/volume e dell'elevata capacità di assorbimento.

Nel 1862 Savchenov usò per la prima volta il termine Palygorskite. Montmorillon (montmorillonite) in Francia e Attapulgitite (attapulgitite) negli Stati Uniti ospitano giacimenti dello stesso minerale, che inizialmente si credeva fossero diversi da quello russo.

Palygorskite (termine ufficiale), Montmorillonite, Attapulgitite, Sepiolite, Meerschaum, Ecume de mer: molti termini per indicare lo stesso minerale.

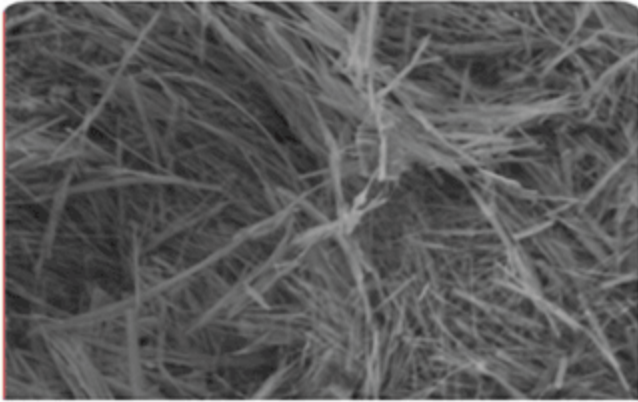
Sia la Palygorskite che la Sepiolite sono silicati a strati TOT, il che significa che lo strato ottaedrico è delimitato sia sopra che sotto da uno strato tetraedrico di silice. Gli strati tetraedrici sono suddivisi in “nastri”, da un'inversione periodica delle file di tetraedri. La morfologia allungata e la presenza di canali sono gli attributi fisici più importanti ai fini commerciali.

I due minerali si formano principalmente in lagune marine poco profonde o piane di marea ed in laghi ipersalini. Il magnesio necessario per la formazione di Palygorskite, Sepiolite e Dolomite è stato apparentemente introdotto dalla reazione di materiale detritico con salamoie e sali ricchi di magnesio, derivanti dall'evaporazione dell'acqua marina intrappolata.

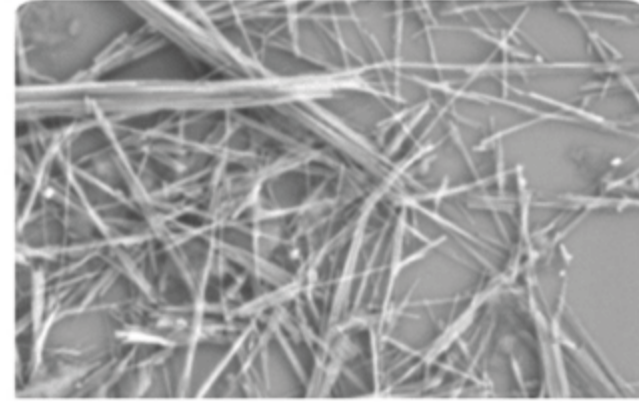
In Somalia, un giacimento di Sepiolite viene utilizzato principalmente per produrre sculture decorative che vengono vendute ai turisti.

Viene anche usata per la produzione di pipe pregiate (“Schiuma di Mare”)

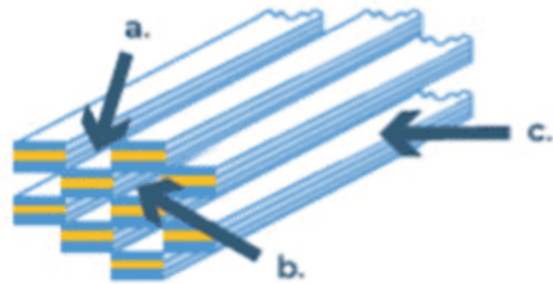
SEPIOLITE



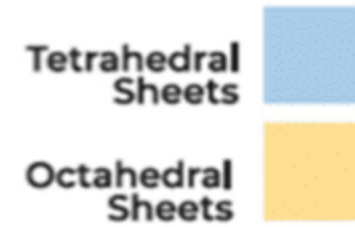
ATTAPULGITE



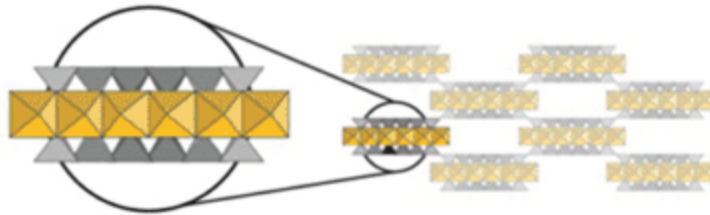
FIBER Structure



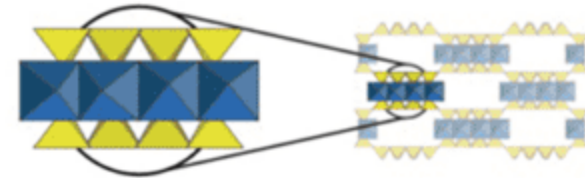
- a. Open Channels.
- b. Zeolitic Channels.
- c. Si-OH Groups at the external surface.



Structure SEPIOLITE CLAY



Structure ATTAPULGITE CLAY





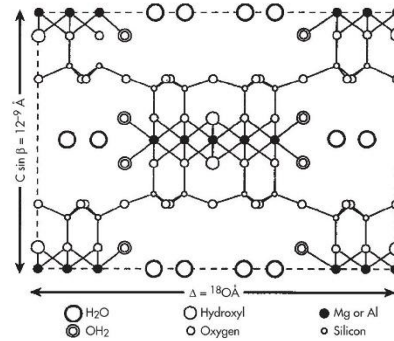


Figure 1. Structure of palygorskite

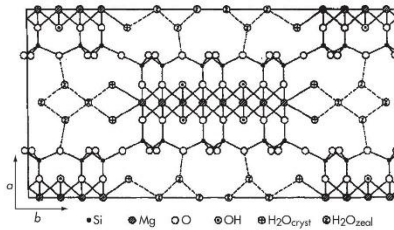


Figure 2. Structure of sepiolite

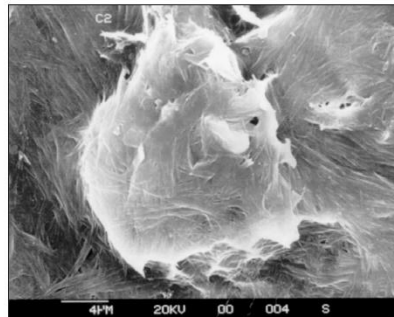


Figure 3. SEM of palygorskite

general most formed in shallow marine lagoons or tidal flats and in supersaline lakes. The magnesium needed to form the palygorskite, sepiolite, and dolomite was apparently introduced by the reaction of detrital material with magnesium-rich brines and salts resulting from the evaporation of the entrapped sea water (Patterson 1974). The palygorskite and sepiolite precipitated in these hypersaline restricted lagoons or lakes. The dolomite formed under conditions in which the amount of aluminum and silicon was less available from the clastic materials that entered the basin (Weaver and Beck 1972).

United States

The palygorskite-rich deposits in south Georgia and north Florida dominate the world's production. The deposits extend from Quincy, Florida, on the south to the Meigs, Georgia, area on the north (Figure 5), about 80 km. The deposition of the palygorskite took place in a shallow water trough that connected the Gulf of Mexico with the Southeast Georgia Embayment on the Atlantic Ocean (Merkel 1989). The seawater in this trough was characterized by fluctuating salinities, and at times the lagoons were closed off from normal circulation. There was sufficient magnesium present to precipitate palygorskite. The mineralogical content changes from dominantly palygorskite in the Quincy-Atapulgus District to a mixture of smectite and palygorskite in the northern area around Ochlocknee and Meigs. Millot (1970) believes that smectite is transformed to palygorskite and sepiolite in a saline, alkaline water environment. These Georgia-Florida deposits are early to middle Miocene in age.

The palygorskite-type fuller's earth occurs in two distinct stratigraphic intervals. The younger Meigs Member of early middle Miocene age unconformably overlies the Dogtown Clay Member of late Lower Miocene age (Figure 6). Both of these members are part of the Hawthorne Group. The Meigs Member contains about equal proportions of smectite and short-length palygorskite along with quartz and a small amount of sepiolite, Opal-A, and sporadic amounts of clinoptilolite. In some sections of the deposit, diatoms comprise up to 50% or more of the fabric. The Dogtown Member has longer length palygorskite and minor amounts of quartz, smectite, and dolomite along with trace amounts of pyrite (Merkel 1989). The deposits in the Dogtown Clay Member in the southern district range from 2 m to slightly more than 3 m in thickness. The deposits in the Meigs Member in the northern district near Ochlocknee and Meigs range from 9 to 14 m in thickness.

Sepiolite is mined in small quantities near Lathrop Wells, Nevada, about 160 km north west of Las Vegas in the Amargosa Valley. The sepiolite occurs in thin beds less than 1 m thick interbedded with deposits of saponite. These deposits are Pleistocene in age (Papke 1969).

China

Palygorskite is mined and processed in an area located near the provincial boundary of Anhui and Jiangsu near Guanshan and Xuyi, respectively (Figure 7). At the Guanshan deposit, the palygorskite occurs directly beneath a thick basalt. The palygorskite ranges between 3 and 6 m in thickness (Zhou and Murray 2003). The palygorskite in the Guanshan deposit was precipitated in a lacustrine environment as the alteration product of a basaltic ash (Zhou 1996). The deposits are in the upper member of the Huaguoshan Formation, which is Middle Miocene in age (Figure 7). Within the last 20 years, more than 20 high-quality palygorskite deposits have been discovered in the area shown in Figure 7. The Geological Survey of China estimated that there are more than 200 Mt of palygorskite reserves in this area. The mineralogy of these deposits is dominantly



Figure 4. Location of major palygorskite and sepiolite deposits



Figure 5. Location of the south Georgia-north Florida fuller's earth deposits

palygorskite with minor amounts of smectite, quartz, and dolomite. In the Guanshan deposit, the smectite content increases significantly below the palygorskite layer.

Senegal

Palygorskite is mined near the town of Theis, Senegal, which is approximately 100 km east of Dakar. In this area, the palygorskite directly overlies an aluminum phosphate deposit that is also mined.

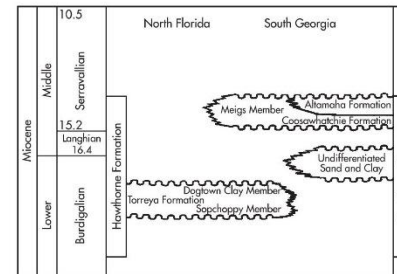


Figure 6. Stratigraphic relationship of the Meigs Clay and Dogtown Clay members

The age of the palygorskite is Early Eocene, and the beds range from 2 to 6 m in thickness (Wirth 1968). The palygorskite is transported by truck to Dakar, and the majority is shipped to Europe. It is estimated that about 400 kt are processed and shipped annually. The palygorskite is used for industrial absorbents, pet litter, and drilling mud mainly in the North Sea. The deposits are palygorskite along with minor amounts of sepiolite, quartz, and dolomite. The palygorskite beds extend south-southwest from Theis to the southern border of Senegal, a distance of about 100 km. The overburden is very thin, usually less than 2 m.

Spain

The world's major commercial sepiolite deposit is located at Vicalvaro near Madrid. The sepiolite was precipitated in Tertiary lakes in an evaporitic sequence (Huertas, Limares, and Martin-Vivaldi 1971). The thickness ranges from 1 to 5 m. The major uses for this

Applicazioni industriali

Adesivi, “vettori agricoli” per antiparassitari e fertilizzanti, leganti per mangimi animali, agenti antiagglomeranti, supporti per catalizzatori, oli decoloranti, fluidi di perforazione, rivestimenti ambientali, fonderie e leganti, vettori di prodotti chimici granulari, assorbenti per pavimenti industriali, detersivi in polvere, lubrificanti per la trafilatura dei metalli, vernici e rivestimenti, carta, lettiere per animali domestici, prodotti farmaceutici, lucidanti, riempitivi di rinforzo (“carica”), fertilizzanti in sospensione, emulsioni di cera

I fanghi di perforazione a base di Palygorskite e Sepiolite possono essere utilizzati in presenza di acque salate al posto delle bentoniti classiche quando le salamoie presenti nelle formazioni rocciose rappresentano un problema serio all'avanzamento dei lavori.

Agenti sospensivanti e addensanti in vernici, medicinali, prodotti farmaceutici e cosmetici.

Composti per la pulizia dei pavimenti che assorbono le fuoriuscite di olio e grasso sui pavimenti di fabbriche, stazioni di servizio per carburanti e in altre lavorazioni in cui le fuoriuscite di olio e grasso rappresentano un problema per la sicurezza ambientale.

Assorbenti e per veicolare prodotti chimici e pesticidi. Il pesticida o il fertilizzante chimico viene rilasciato lentamente per fornire la protezione o la fertilizzazione necessaria alla pianta in

ARGILLE REFRATTARIE

Le argille refrattarie sono utilizzate principalmente nella produzione di mattoni e blocchi refrattari di varie forme, mattoni refrattari, malte refrattarie e materiali monolitici.

Le argille refrattarie si suddividono in diverse categorie commerciali:

- plastiche
- semiplastiche
- semi-flint
- flint. L'argilla flint ha proprietà uniche per un'argilla: è priva di plasticità, si rompe con una superficie concoidale in particelle simili a schegge ed è fragile come il calcare.

Applicazioni

Le argille refrattarie vengono utilizzate per rivestire forni, fornaci, fonderie, reattori chimici e gassificatori.

L'industria siderurgica consuma il 70% dei materiali refrattari utilizzati, l'industria del cemento e della calce ne consuma il 7%, l'industria ceramica il 6%, l'industria del vetro il 4% e l'industria petrolifera circa il 4%.

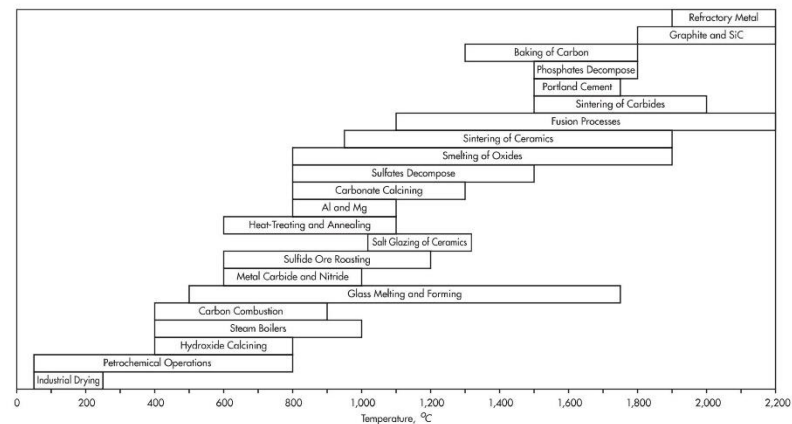


Figure 2. Temperature regimes for industrial applications of refractories

Table 1. Types of furnaces used in U.S. industry

Furnace Type	Industrial Furnace Applications								
	Aluminum	Cement and Lime	Chemical and Petrochemical	Forest Products	Glass	Heat-Treatment	Iron and Steel	Metal Casting	Other
Blast							X		X*
Basic oxygen	X						X		
Reverberatory						X	X	X	X†
Multiple hearth									X†
Ladles/hundishes/troughs/runners	X				X			X	X†X
Electrolytic smelters	X								X§
Kilns and calciners	X	X	X	X	X		X		X***††
Electric arc							X		X‡‡
Cupolas						X	X		
Heat-treatment/annealing furnaces and drying ovens	X						X	X	X**§§
Stills and retorts									X***
Reactors/reformers/refiners									
Steam boilers/incinerators	X	X	X	X		X			X†††
Gasifiers			X	X					
Heat exchangers	X	X	X	X	X	X	X	X	

* Lead.

† Copper.

‡ Molten metal handling.

§ Magnesium.

** Ceramics.

†† Mining.

‡‡ Oxide melting.

§§ Various metal products.

*** Organic and inorganic products.

††† Virtually all industries.