Clay Minerals

Soils to Engineering Technology to Cat Litter

Clay Minerals

Clay minerals likely are the most utilized minerals … not just as the soils that grow plants for foods and garment, but a great range of applications, including oil absorbants, iron casting, animal feeds, pottery, china, pharmaceuticals, drilling fluids, waste water treatment, food preparation, paint, and … yes, cat litter!

Bentonite workings, WY

Clay Minerals

There are four main groups of clay minerals:

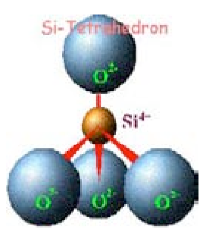
Kaolinite group - includes kaolinite, dickite, nacrite, and halloysite; formed by the decomposition of orthoclase feldspar (e.g. in granite); kaolin is the principal constituent in china clay.

Illite group- also includes hydrous micas, phengite, brammalite, celadonite, and glauconite (a green clay sand); formed by the decomposition of some micas and feldspars; predominant in marine clays and shales.

Smectite group- also includes montmorillonite, bentonite, nontronite, hectorite, saponite and sauconite; formed by the alteration of mafic igneous rocks rich in Ca and Mg; weak linkage by cations (e.g. Na+, Ca++) results in high swelling/shrinking potential

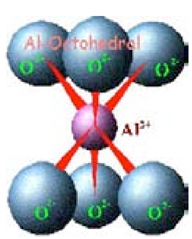
Vermiculite-

Clay Minerals are Phyllosilicates



All have layers of
Si tetrahedra

SEM view of clay



and layers of Al, Fe, Mg octahedra, similar to gibbsite or brucite

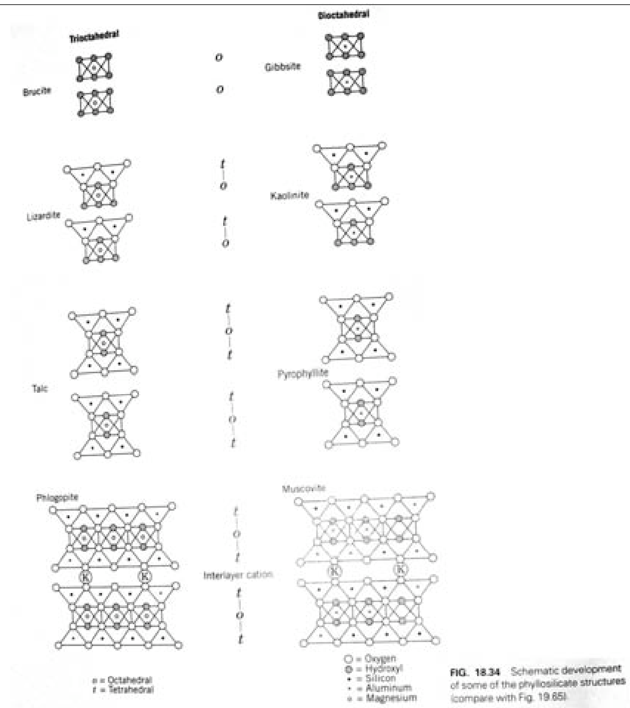
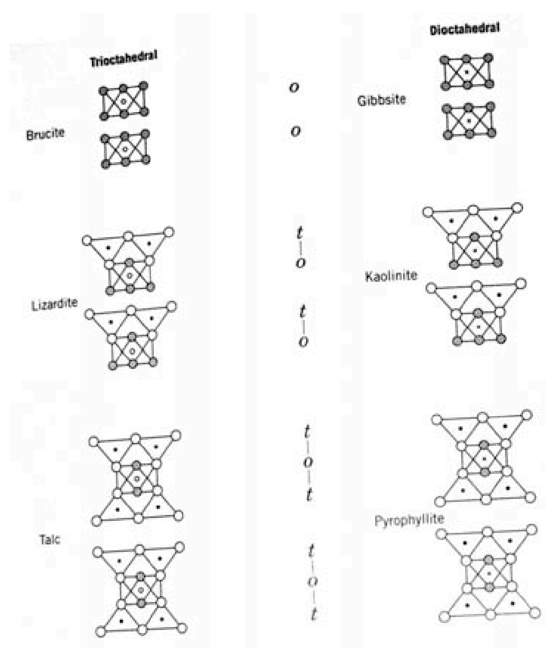
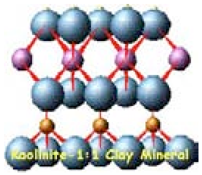


FIG. 18.34 Schematic development of some of the phyllosilicate structures (compare with Fig. 19.65)

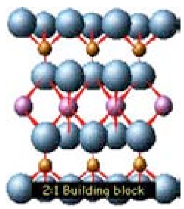


Clays

Clay Minerals



The kaolinite clays are 1:1 phyllosilicates



The montmorillonite and illite clays are 2:1 phyllosilicates

1:1 and 2:1 Clay Minerals

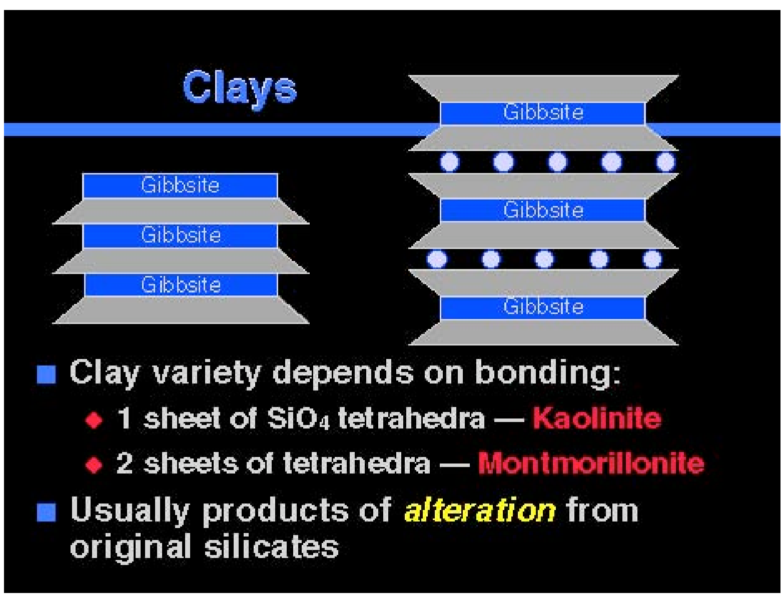
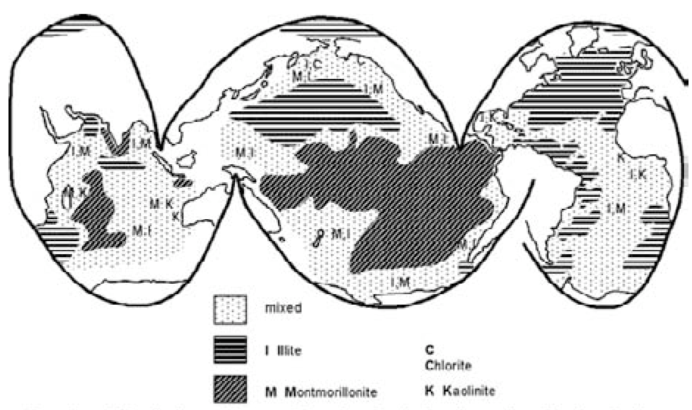


Table 32. Summary of the principal characteristics of the clay mineral groups

	Kaolinite group	Illites	Smectites	Vermiculites
Structure type:	1:1 tetrahedral and octahedral components	2:1	2:1	2:1
Octahedral component:	Di-octahedral	Mostly di-octahedral	Di- or tri-octahedral	Mostly trioctahedral
Principal interlayer cations:	Nil	K	Ca,Na	Mg
Interlayer water:	Only in halloysite (one layer water mols)	Some in hydromuscovite	Ca, two layers; Na, one layer water mols	Two layers
Basal spacing:	7.1 Å (10 Å in halloysite)	10 Å	Variable, most ~15 Å (for Ca)	Variable; 14.4 Å when fully hydrated
Glycol:	Taken up by halloysite only	No effect	Takes two layers glycol, 17 Å	Takes one layer glycol, 14 Å
Chemical formula:	$Al_4Si_4O_{10}(OH)_8$, little variation	$K_{1.0-1.5}Al_4(Si,Al)_8O_{20}(OH)_4$	$M^{+}_{0.7}(Y^{3+},Y^{2+})_{4-6}(Si,Al)_8O_{20}(OH)_4\,n\,H_2O$	$M^{2+}_{0.66}(Y^{2+},Y^{3+})_6(Si,Al)_8O_{20}(OH)_4 8H_2O$
Acids:	Kaolinite scarcely soluble in dil. acids	Readily attacked	Attacked	Readily attacked
Heating 200 °C	Halloysite collapses to approx. 7.4 Å; others unchanged	No marked change	Collapse to approx. 10 Å	Exfoliation; shrinkage of layer spacing
650 °C:	Kaolinite → metakaolinite (7 Å) Dickite → metadickite strong (14 Å)	10 Å	9.6–10 Å	Collapse to 9 Å
Optics α	1.55–1.56	1.54–1.57	1.48–1.61	1.52–1.57
γ	1.56–1.57	1.57–1.61	1.50–1.64	1.53–1.58
δ	~0.006	~0.03	0.01–0.04	0.02–0.03
$2V_\alpha$	24–50°	<10°	Variable	<18°
Paragenesis:	Alteration of acid rocks, feldspars, etc. Acidic conditions.	Alteration of micas, feldspars, etc. Alkaline conditions. High Al and K concentrations.	Alteration of basic rocks, or volcanic material. Alkaline conditions. Availability of Mg and Ca; deficiency of K.	Alteration of biotite flakes or of volcanic material, chlorites, hornblende, etc.

Marine Clays

Clays mostly form on land but are often transported to the oceans, covering vast regions.



Clay mineral distribution on the ocean floor, showing the dominant mineral in the <2 micron fraction. Mixture indicates that no one clay mineral exceeds 50% of the total.

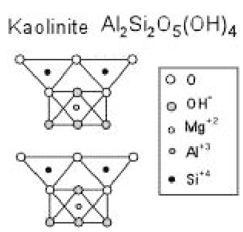
Kaolinite $Al_2Si_2O_5(OH)_2$

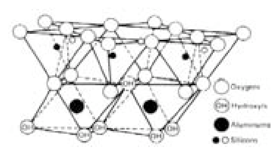
Kaolinite clays have long been used in the ceramic industry, especially in fine porcelains, because they can be easily molded, have a fine texture, and are white when fired.

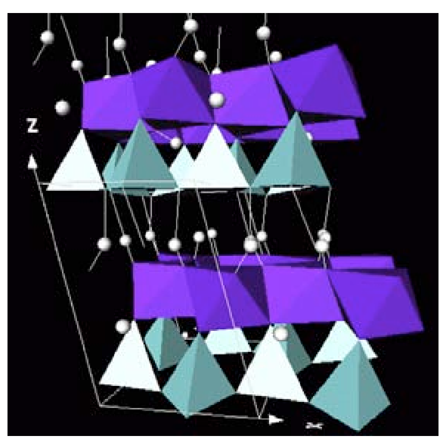
These clays are also used as a filler in making paper.

In the United States, deposits are found primarily in Georgia, North Carolina, and Pennsylvania; china clay is also mined in England (Cornwall) and France.

Kaolinite

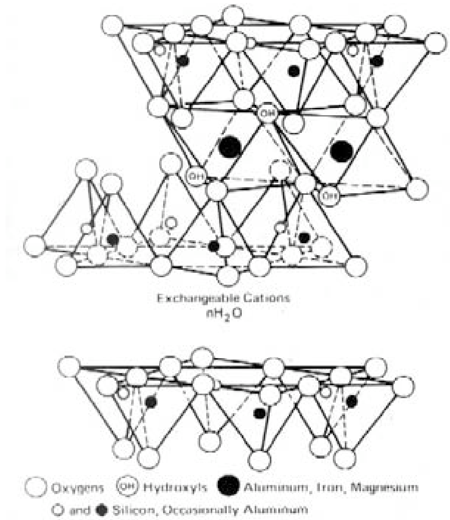






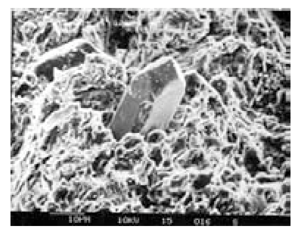
Kaolinite is the purest of clays, meaning that it varies little in composition. It also does not absorb water and does not expand when it comes in contact with water. Thus, kaolinite is the preferred type of clay for the ceramic industry.

Illite



Illite is similar to muscovite and is the most common clay mineral, often composing more than 50 percent of the clay-mineral suite in the deep sea.

They are characteristic of weathering in temperate climates or in high altitudes in the tropics, and typically reach the ocean via rivers and wind transport.



Relict zircon in illite

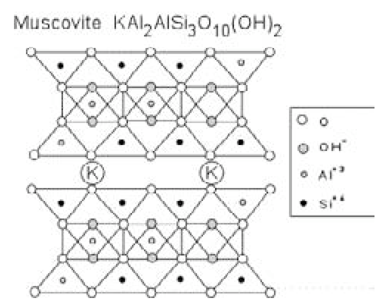
Illite

The Illite clays have a structure similar to that of muscovite, but is typically deficient in alkalies, with less Al substitution for Si. Thus, the general formula for the illites is:

$K_yAl_4(Si8_{-y},Al_y)O_{20}(OH)_4$, usually with $1 < y < 1.5$, but always with $y < 2$.

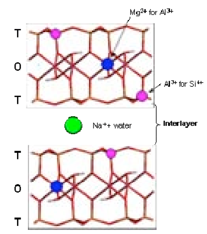
Because of possible charge imbalance, Ca and Mg can also sometimes substitute for K.

The K, Ca, or Mg interlayer cations prevent the entrance of H2O into the structure. Thus, the illite clays are **non-expanding** clays.

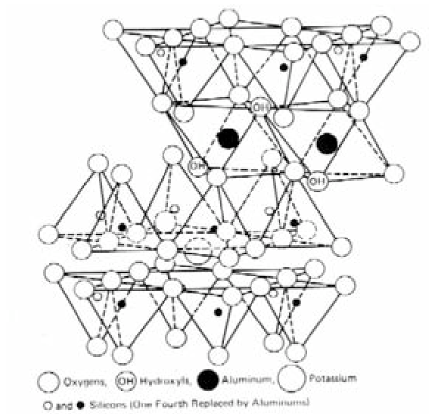


Illite type clays are formed from weathering of K and Al-rich rocks under high pH conditions. Thus, they form by alteration of minerals like muscovite and feldspar. Illite clays are the main constituent of shales.

Montmorillonite



Montmorillonite or smectite is family of expansible 2:1 phyllosilicate clays having permanent layer charge because of the isomorphous substitution in either the octahedral sheet (typically from the substitution of low charge species such as Mg^{2+}, Fe^{2+}, or Mn^{2+} for Al^{3+})



Montmorillonite

The most common smectite is Montmorillinite, with a general chemical formula :

$$(1/2Ca,Na)(Al,Mg,Fe)_4(Si,Al)_8O_{20}(OH)_4.nH2O$$

Montmorillinite is the main constituent of **bentonite**, derived by weathering of volcanic ash. Montmorillinite can expand by several times its original volume when it comes in contact with water. This makes it useful as a drilling mud (to keep drill holes open), and to plug leaks in soil, rocks, and dams.

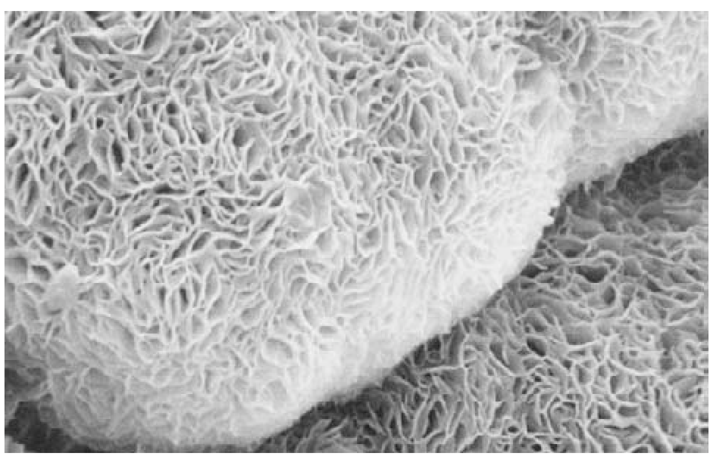
Montmorillinite, however, is a dangerous type of clay to encounter if it is found in tunnels or road cuts. Because of its expandable nature, it can lead to serious slope or wall failures.

Smectite group clays

Table 33. Smectites, pyrophyllite and talc

	Z	Y	X (exchange cations)
	Di-octahedral		
Pyrophyllite	Si_8	Al_4	—
Montmorillonite	Si_8	$Al_{3.3}Mg_{0.7}$	$(\frac{1}{2}Ca,Na)_{0.7}$
Beidellite	$Si_{7.3}Al_{0.7}$	Al_4	$(\frac{1}{2}Ca,Na)_{0.7}$
Nontronite	$Si_{7.3}Al_{0.7}$	Fe_4^{3+}	$(\frac{1}{2}Ca,Na)_{0.7}$
	Tri-octahedral		
Talc	Si_8	Mg_6	—
Saponite	$Si_{7.2}Al_{0.8}$	Mg_6	$(\frac{1}{2}Ca,Na)_{0.8}$
Hectorite	Si_8	$Mg_{5.3}Li_{0.7}$	$(\frac{1}{2}Ca,Na)_{0.7}$
Sauconite	$Si_{6.7}Al_{1.3}$	$Zn_{4-6}(Mg,Al,Fe^{3+})_{2-0}$	$(\frac{1}{2}Ca,Na)_{0.7}$

SEM View of Montmorillonite

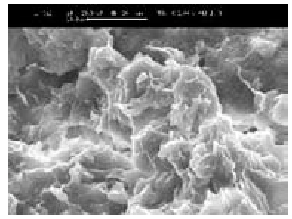


From Yucca Mountain, NV

Swelling Clays

The interlayer in montmorillonite or smectites is not only hydrated, but it is also expansible; that is, the separation between individual smectite sheets varies with the amount of water present in the soil. Because of this, they are often referred to as **"swelling clays"**.

Soils having high concentrations of smectites can undergo as much as a 30% volume change due to wetting and drying or these soils have a high shrink/swell potential and upon drying will form deep cracks.



bentonite

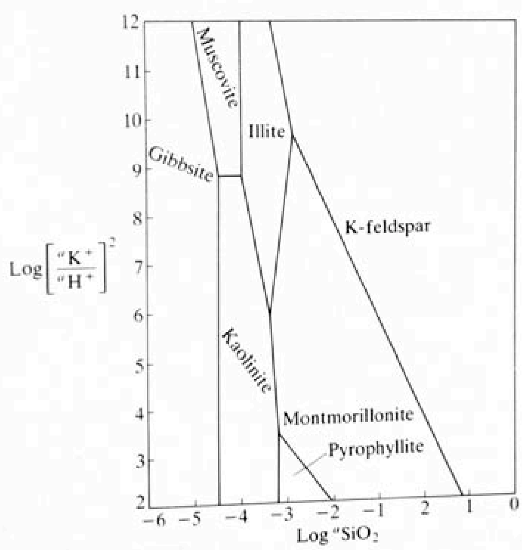


Fig. 122 Theoretical plot of ion activities showing stabilities of phases using idealized compositions and assuming that illite/smectite is a mixture rather than a solid solution (after Garrels, R. M., 1984, *Clays and Clay Minerals*, **32**, 161–6).

Clay Minerals are a product of weathering

•Reducing SiO2 and K Occurs during weathering

*These elements, along with others, are removed by fluids (mainly water)

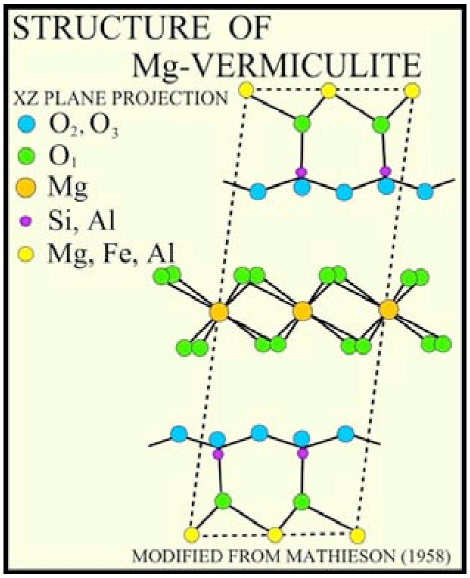
Painted Desert, NM

Bentonite-bearing shales, such as in the Painted Desert, are derived from weathering of volcanic ash. The leaching of silica is responsible for preservation of petrified wood

Vermiculite

Vermiculite is a high-charge 2:1 phyllosilicate clay mineral. It is generally regarded as a weathering product of micas. Vermiculite is also hydrated and somewhat expansible though less so than smectite because of its relatively high charge.

Granular clay absorbents, such as vermiculite, have been used for over 75 years to clean up minor drips, spills and over sprays in factories and garages



Vermiculite structure

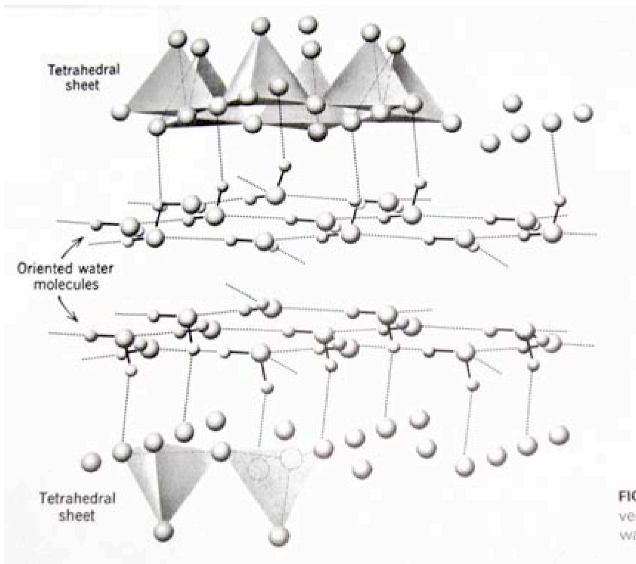
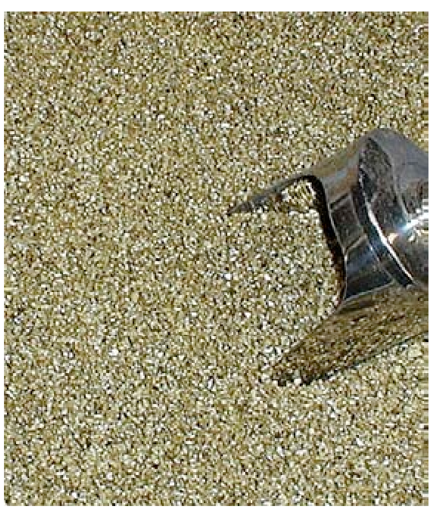
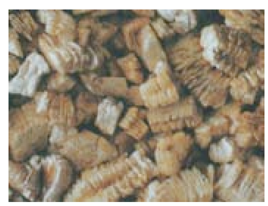


FIG. 18.36 Diagrammatic sketch of the vermiculite structure, showing layers of water (after Grim, 1968).

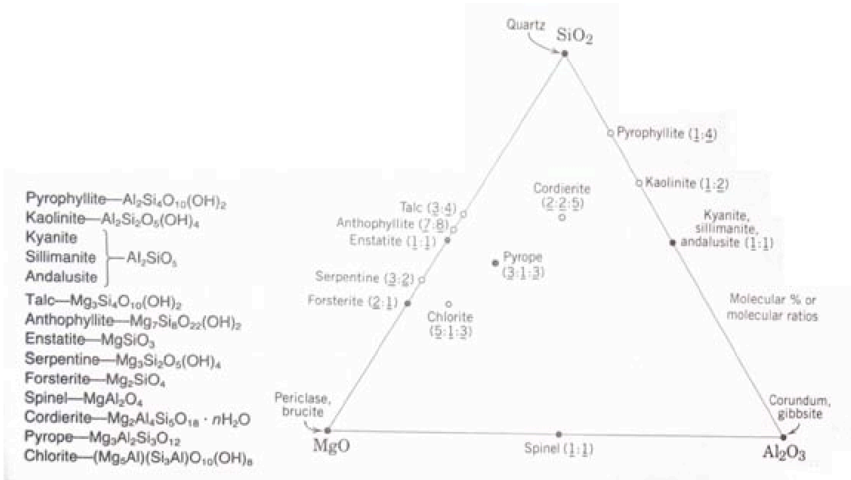
Vermiculite





Vermiculite possesses the special property of expanding to between six and twenty times its original volume when heated to approximately 1,000 degrees Celsius. This process, called exfoliation, liberates bound water from between the mica-like layers of the mineral and literally expands the layers apart at right angles to the cleavage plane.

Vermiculite is used to loosen and aerate soil mixes. Mixed with soil, it improves water retention and fertilizer release, making it ideal for starting seeds. Also used as a medium for winter storage of bulbs and flower tubers.



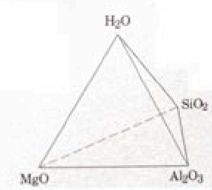
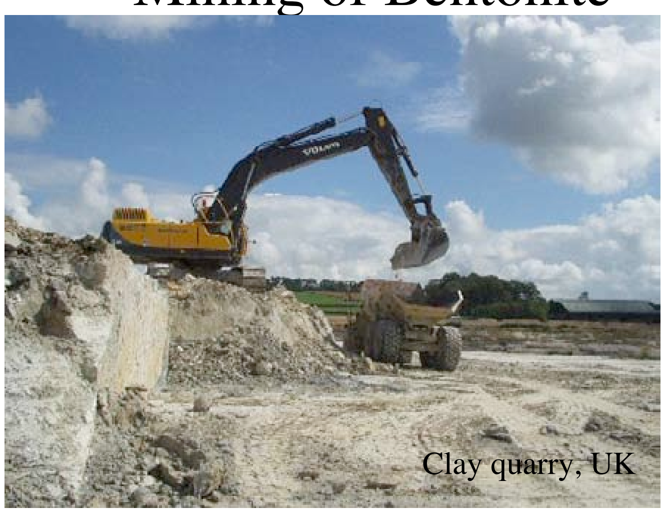


FIG. 19.66 The composition of an idealized chlorite, and those of other end-member compositions of rock-forming minerals in the system $MgO–Al_2O_3–SiO_2–H_2O$. In this diagram, which is water-free, and which may be considered as a projection from an H_2O corner (in a tetrahedron, see insert), the hydrous formulae are plotted on the basis of their molecular (MgO, Al_2O_3, and SiO_2) ratios, without reference to the OH groups or H_2O content. The opaque dots are anhydrous compositions, and the open circles hydrous compositions. The molecular ratios ($MgO:SiO_2$; $Al_2O_3:SiO_2$; $MgO:Al_2O_3:SiO_2$, and $MgO:Al_2O_3$) are noted next to the mineral names.

Mining of Bentonite

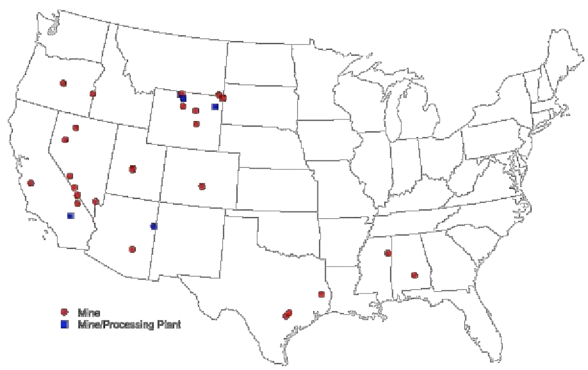


Early Americans found bentonite vital to their lives. Pioneers found moistened bentonite to be an ideal lubricant for squeaky wagon wheels. The mixture was also used as a sealant for log cabin roofing. The Indians found bentonite useful as a soap.

Bentonite Mines - USA

During the Cretaceous, volcanoes in the Yellowstone area of Wyoming were subject to long periods of eruptions. Ash falling from these eruptions dropped into seas which covered much of Wyoming, forming a sediment as much as 50 feet deep. These sediments were slowly altered into the clay known as bentonite.

In these deposits are contained 70% of the world's known supply of western or sodium type bentonite.



Main cations: Al, Si, OH | Al, Si, K, OH | Al, Ca, Na, Fe, Mg, K, Si,OH, H2O | Al, Ca, Fe, Mg, Si,OH, H2O

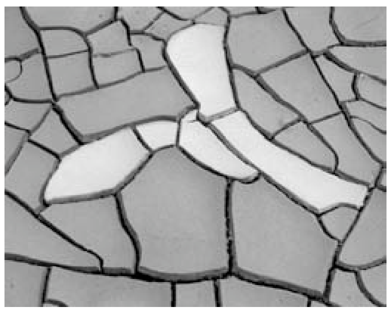
Table 32. Summary of the principal characteristics of the clay mineral groups

	Kaolinite group	Illites	Smectites	Vermiculites
Structure type:	1:1 tetrahedral and octahedral components	2:1	2:1	2:1
Octahedral component:	Di-octahedral	Mostly di-octahedral	Di- or tri-octahedral	Mostly trioctahedral
Principal interlayer cations:	Nil	K	Ca,Na	Mg
Interlayer water:	Only in halloysite (one layer water mols)	Some in hydromuscovite	Ca, two layers; Na, one layer water mols	Two layers
Basal spacing:	7.1 Å (10 Å in halloysite)	10 Å	Variable, most ~15 Å (for Ca)	Variable; 14.4 Å when fully hydrated
Glycol:	Taken up by halloysite only	No effect	Takes two layers glycol, 17 Å	Takes one layer glycol, 14 Å
Chemical formula:	$Al_4Si_4O_{10}(OH)_8$, little variation	$K_{1.0-1.5}Al_4(Si,Al)_8O_{20}(OH)_4$	$M^+_{0.7}(Y^{3+},Y^{2+})_{4-6}(Si,Al)_8O_{20}(OH)_4\,nH_2O$	$M^{2+}_{0.66}(Y^{2+},Y^{3+})_6(Si,Al)_8O_{20}(OH)_4 8H_2O$
Acids:	Kaolinite scarcely soluble in dil. acids	Readily attacked	Attacked	Readily attacked
Heating 200 °C	Halloysite collapses to approx. 7.4 Å; others unchanged	No marked change	Collapse to approx. 10 Å	Exfoliation; shrinkage of layer spacing
650 °C:	Kaolinite → metakaolinite (7 Å) Dickite → metadickite strong (14 Å)	10 Å	9.6–10 Å	Collapse to 9 Å
Optics α	1.55–1.56	1.54–1.57	1.48–1.61	1.52–1.57
γ	1.56–1.57	1.57–1.61	1.50–1.64	1.53–1.58
δ	~0.006	~0.03	0.01–0.04	0.02–0.03
$2V_\alpha$	24–50°	<10°	Variable	<18°
Paragenesis:	Alteration of acid rocks, feldspars, etc. Acidic conditions.	Alteration of micas, feldspars, etc. Alkaline conditions. High Al and K concentrations.	Alteration of basic rocks, or volcanic material. Alkaline conditions. Availability of Mg and Ca; deficiency of K.	Alteration of biotite flakes or of volcanic material, chlorites, hornblende, etc.

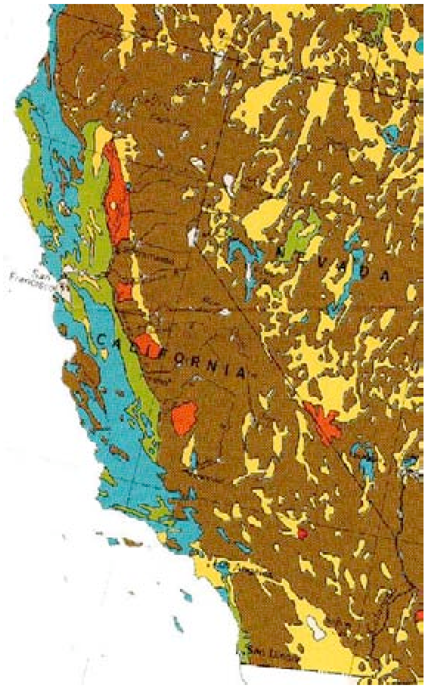
Swelling Clay Mapping - USGS

Smectite group- montmorillonite and others

Red = High swelling clay content
Blue = Next high
Brown = Minimum



mud cracks of clay



Swelling Clay Mapping - USGS

Red = High swelling clay content
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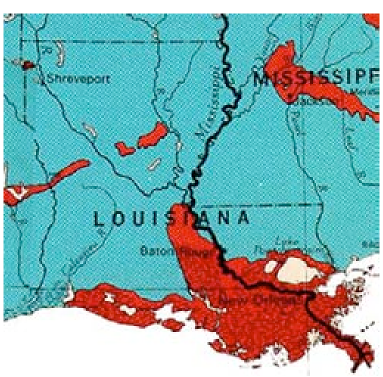
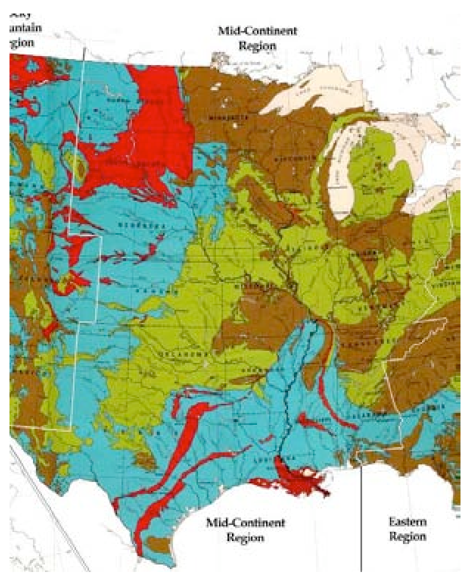




Uses of Clay

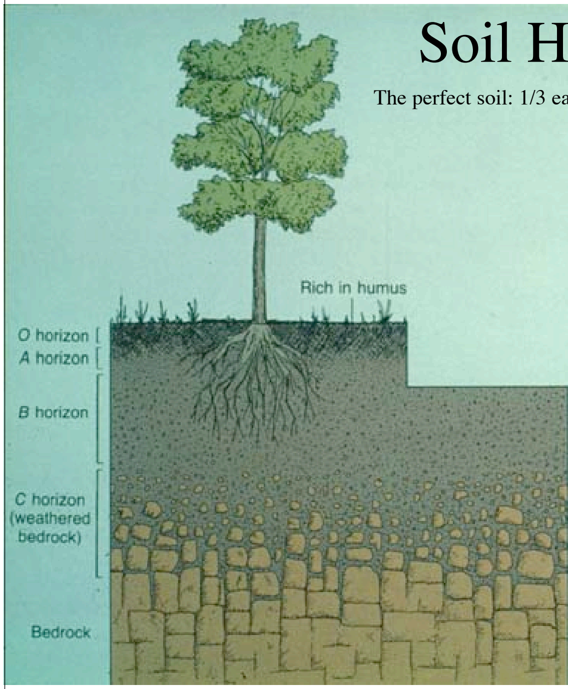
Of course, soils…flowers don't easily grow out of rocks!

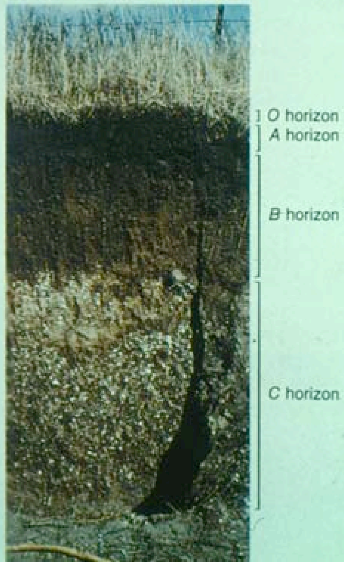
Uses of Clay - Soils

… or do our many grain foods, such as wheat

Soil Horizons

The perfect soil: 1/3 each of sand, silt, and clay





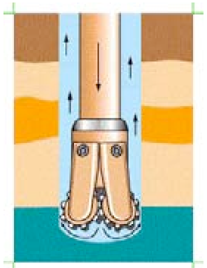
Spheriodal Weathering, San Diego Co.

Corn, Cactus, and Flowers

all need proper soils

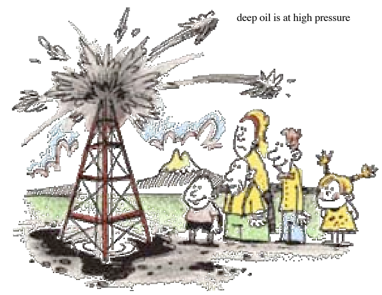
Uses of Clay - Oil & Water Drilling

Uses of Clay - Drilling Mud



Cooling and cleaning the drill

Drilling mud slurry

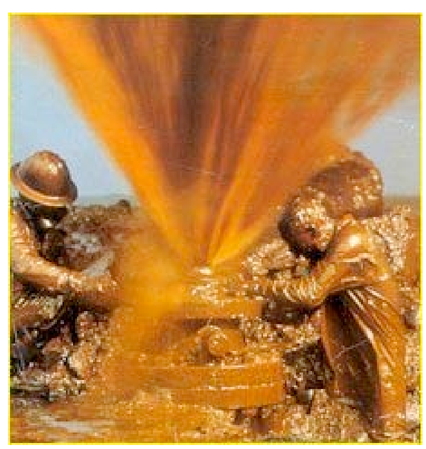


“Gushers” used to be common until the use of drilling mud was implemented

Bentonite and other clays are used in the drilling of oil and water wells. The clays are turned into mud, which seals the walls of the boreholes, lubricates the drill head and removes drill cuttings.

Drilling Fluid: Lifeblood of the Well

In 1900, while drilling an oil well in Spindletop, Texas, workers ran a herd of cattle through a pit filled with water. The mud that resulted, a viscous, muddy slurry of water and clay, was pumped into the borehole. Drilling fluids are still called mud, but engineers no longer rely only on water and clay. Instead, they carefully design compounds and mixtures to meet specific needs under various drilling conditions. <u>Modern drilling fluids are truly the lifeblood of the well</u>. Today's deep wells could not exist without them.



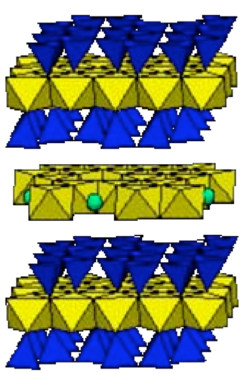
Oil Wells

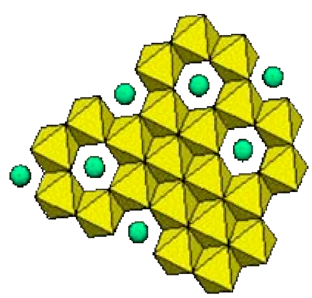
Central Texas

These wells could never have been drilled without the role of clays as drilling mud, now augmented with such compounds as barite

Uses of Clay - Contaminant Removal

Clay slurrys have effectively been used to remove a range of comtaminants, including P and heavy metals, and overall water clarification.

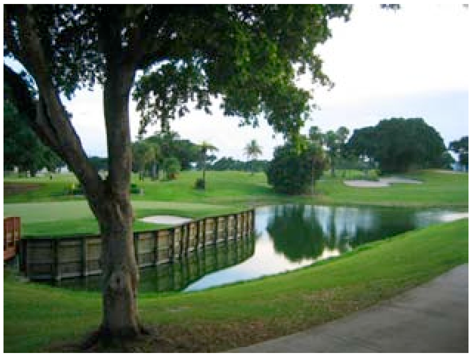




Schematic of montmorillonite absorbing Zn

Uses of Clay

Filtering: Clays are used to decolorize, filter, and purify animal, mineral, and vegetable oils and greases due to their high absorbing properties.



Environmental Sealants: Bentonite is used to establish low permeability liners in landfills, sewage lagoons, water retention ponds, golf course ponds, and hazardous waste sites.

Uses of Clay

Pharmaceuticals/ Cosmetics:
Bentonite is used as a binder in tablet manufacturing and in diarrhea medications. Clays are used as thickeners in a wide variety of cosmetics including facial creams, lipsticks, shampoos and calamine lotion.

Pelletizing: Bentonite is used to bind tiny particles of iron ore, which are then formed into pellets for use as feed material for blast furnaces.

Paints: Finely ground clays are used in the paint industry to disperse pigment evenly throughout the paint. Without clays, it would be extremely difficult to evenly mix the paint base and color pigment.

Other Uses of Clay

clay pipes

marbles, ca. 1800

clay pots

ceramic vase

Uses of Clay - Cat Litter

How a Simple Idea Improved the Quality of Life for Millions

In 1947, an enterprising young man named Edward Lowe assisted his neighbor with a problem she was having. The woman was using ashes in her cat box and the cat was tracking the ashes throughout the house. Mr. Lowe suggested she try the all-natural granular absorbent clay that he was selling to garage and machine shop owners for use in cleaning up minor oil spills and drips.

Both the owner and her pet loved the absorbent clay granules. The rest, as they say, is history. From these modest beginnings, the $1.3 billion cat litter industry was born and pet ownership was changed forever.

Kitty Litter