CERAMIC MATERIALS I

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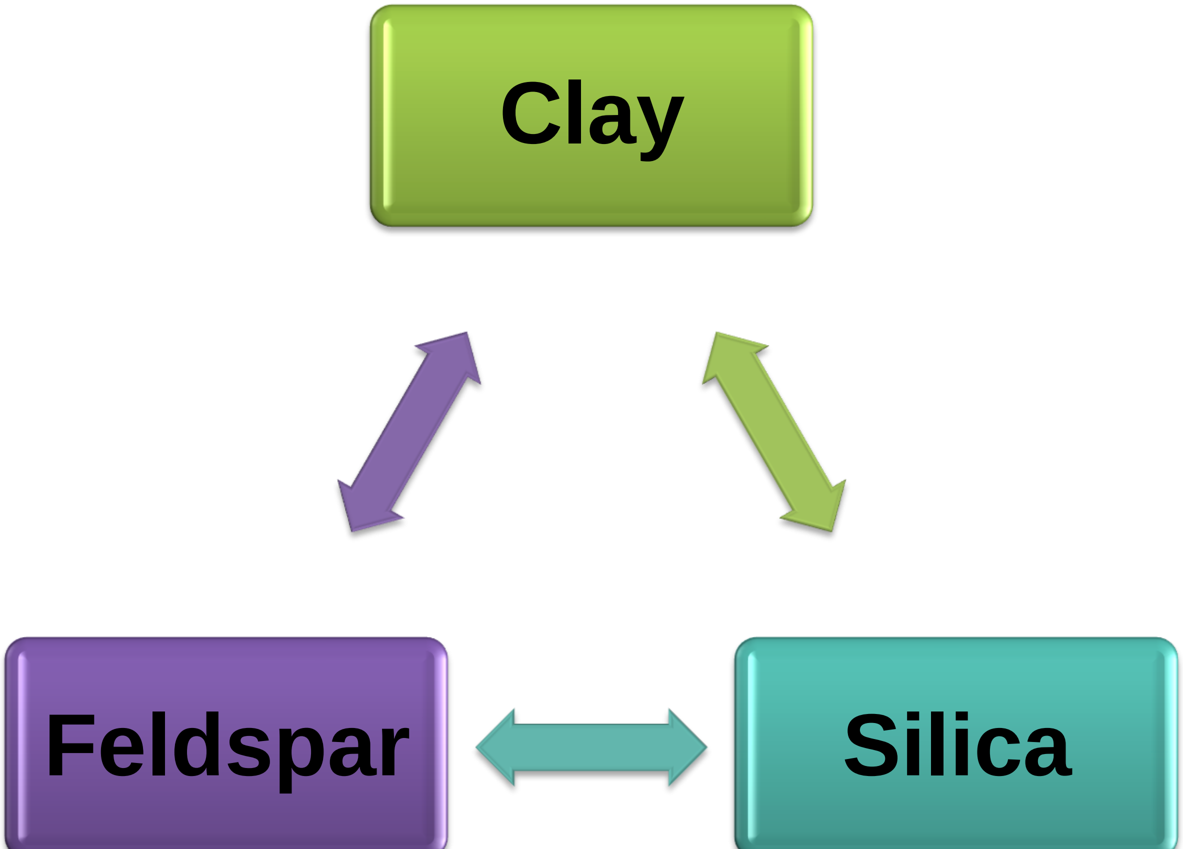
Clay products – Main Components



Traditional Ceramics

Clay products – Main Components

Clay

When mixed with water the crystals can easily slide over each other (like a pack of cards), and this phenomenon gives rise to the plasticity of clays.

Provides plasticity, when mixed with water
Hardens upon drying and firing (without losing the shape)

Adding water to clay
-- allows material to shear easily along weak van der Waals bonds
-- enables extrusion
-- enables slip casting

Silica

Silica, SiO_2, is mixed with clay to reduce shrinkage of the ware while it is being fired, and thus prevent cracking, and to **increase the rigidity of the ware so that it will not collapse at the high temperatures** required for firing. Silica is useful for this purpose becasue it is hard, chemically stable, has a high melting point and can readily be obtained in a pure state in the form of quartz.

Feldspar

Feldspars are **used as a flux in the firing of ceramic ware**. When a body is fired, the feldspar melts at a lower temperature than clay or silica, due to the presence of Na^+, K^+ or Ca^{2+} ions, and forms a molten glass which causes solid particles of clay to cling together: when the glass solidifies it gives strength and hardness to the body.

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Clay

Clay is a material having the ability to normally demonstrate marked plasticity when wet, and, in general, the properties such as adsorption, hydration, solvation, ion-exchange and hardening when dried and on firing.

Clay consists principally of fine-grained inorganic materials involving hydrous phyllossilicates usually with principal chemical components such as SiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, K_2O, Na_2O and H_2O, and/or non-crystalline materials largely composed of chemical components such as SiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, and H_2O as usual.

These materials are termed clay minerals. Indeed, based on the properties of their fine-grained particles, they represent source materials which may contribute to the properties of clays mentioned above.

Clays

CLAY: A natural material characterized by its plasticity, as taken from the claypit or after it has been ground and mixed with water.

Clay is the primary ingredient in traditional ceramics and is the general name given to the layer silicates with a grain size < 2 μm. Any of the layer silicates could qualify as a clay mineral.

The characteristic property of moist clay that permits it to be deformed without cracking and to retain its new shape when the deforming stress is removed.

Plasticity is associated with the sheet structure of the clay minerals and with the manner in which water films are held by the clay particles.

The plasticity developed when water is added provides the bond and workability so important in the fabrication of pottery, dinnerware, brick, tile and pipe.

Main Groups of Clay Minerals

Kaolinite - $Al_2Si_2O_5(OH)_4$

Also includes dickite and nacrite; formed by the decomposition of orthoclase feldspar (e.g. in granite); kaolin is the principal constituent in china clay.

Illite - $K_{1-1.5}Al_4(Si,Al)_8O_{20}(OH)_4$

Also includes glauconite (a green clay sand) and are the commonest clay minerals; formed by the decomposition of some micas and feldspars; predominant in marine clays and shales.

Smectites or montmorillonites

Also includes bentonite and vermiculite; 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.

- Montmorillonite – $(Ca, Na)_{0.2-0.4}(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2 \cdot nH_2O$
- Vermicullite - $(Ca, Mg)_{0.3-0.4}(Al,Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot nH_2O$
- Swelling clays – can take up extra water in their interlayers and are the major components of bentonite (NOT a mineral, but a mix of different clay minerals)

Characteristics of common clays

Secondary mineral	Type	Interlayer condition / Bonding	Swelling potential	Specific surface area [m^2/g]
Kaolinite	1 : 1 (non-expanding)	lack of interlayer surface, strong bonding	almost none	5 - 20
Montmorillonite	2 : 1 (expanding)	very weak bonding, great expansion	high	700 - 800
Vermiculite	2 : 1 (expanding)	weak bonding, great expansion	high	500 - 700
Hydrous Mica	2 : 1 (non-expanding)	partial loss of K, strong bonding	low	50 - 200
Chlorite	2 : 1 : 1 (non-expanding)	moderate to strong bonding, non-expanding	none	

Clays

CLAY consists of one or more clay minerals together with, in most cases, some ***free silica and other impurities***. The amount of mineral impurities, organic matter present, and particle size vary with the individual clay's evolution.

The common clay mineral is kaolinite; most clays consist of kaolinite in various degrees of atomic disorder.

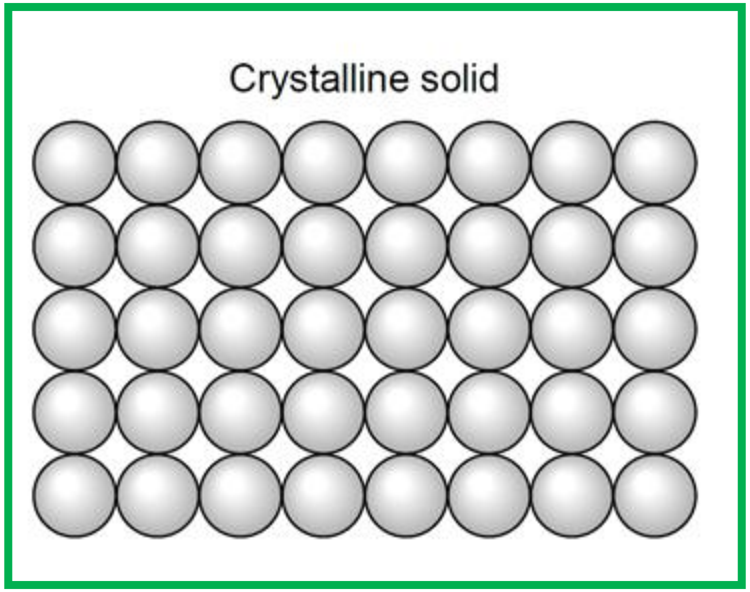
Clays are usually crystalline in nature. Some may be amorphous (e.g., allophane)

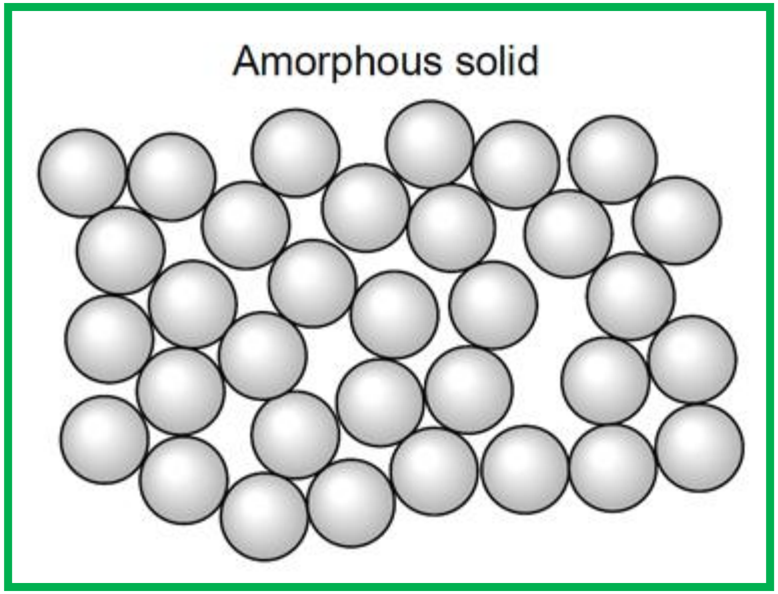
Crystalline and Amorphous

Crystalline Solid : Having the atoms in a definite long-range order.
Amorphous Solid : Phase characterised only by a short-range order and by a missing long-range order in atomic structure.

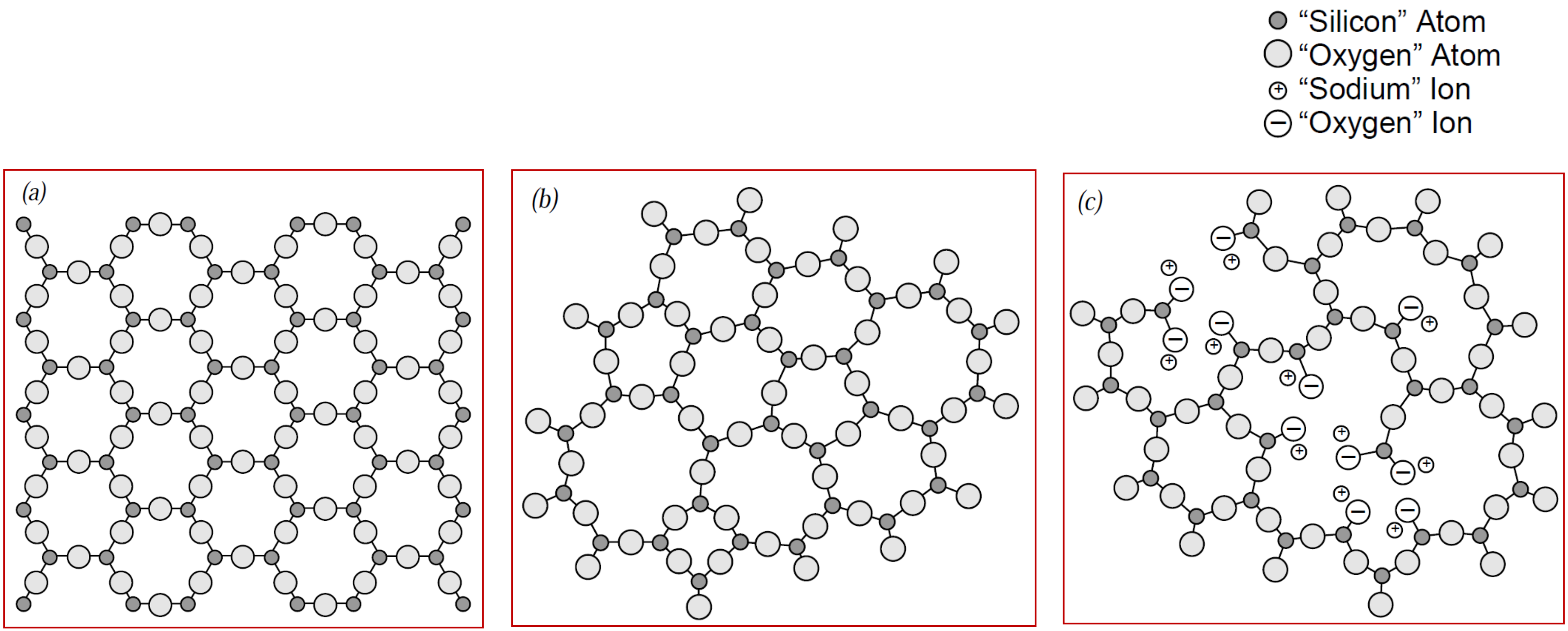
Crystalline versus Amorphous

- Glass has **amorphous** structure
- **Crystalline** materials have some periodic crystal structure that results in long term order





Crystalline versus Amorphous



Two-dimensional illustrations of the structures of *(a) crystalline silica, (b) liquid or* glassy silica and *(c) glassy or vitreous* silica containing some sodium oxide

Clays

CLAYS

Primary (Residual) Clays

They have remained at the site of their original formation.
These clays are relatively rare.

Secondary (Sedimentary) Clays

They were moved to a new location by wind, rain or ice.

Clays

- Mechanical and chemical weathering of feldspars in igneous and metamorphic rocks forms kaolin, a key ingredient in China clay. It may be disintegrated *in situ or* transported by water or wind and redeposited elsewhere.

- Primary kaolin deposits are located at the site of the original rock. These typically contain large amounts of quartz and mica, which also formed during weathering. Large, primary kaolin deposits are found in southwest England, the Ukraine, and China.

- Secondary kaolins were washed from the original weathering site, naturally beneficiated, and redeposited in large areas of pure kaolin.

PRIMARY CLAYS

Kaolin (China Clay)

- Generally 95 % pure.
- Subjected to less dramatic erosion and weathering.
- Particle size is usually coarse and not plastic.
- Secondary kaolin particles are usually finer and more plastic than primary kaolin but consist more impurities.
- When alkalies and other impurities are removed a very pure white firing clay, that matures at very high temperatures (1804°C), is achieved.
- Typical formula for kaolin is $Al_2O_3.2SiO_2.2H_2O$.

PRIMARY CLAYS

- 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.

- 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.

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

SECONDARY CLAYS

- Ball Clay
- Stoneware Clay
- Fireclay
- Volcanic Clay
- Earthenware (Red) Clay
- Slip Clay

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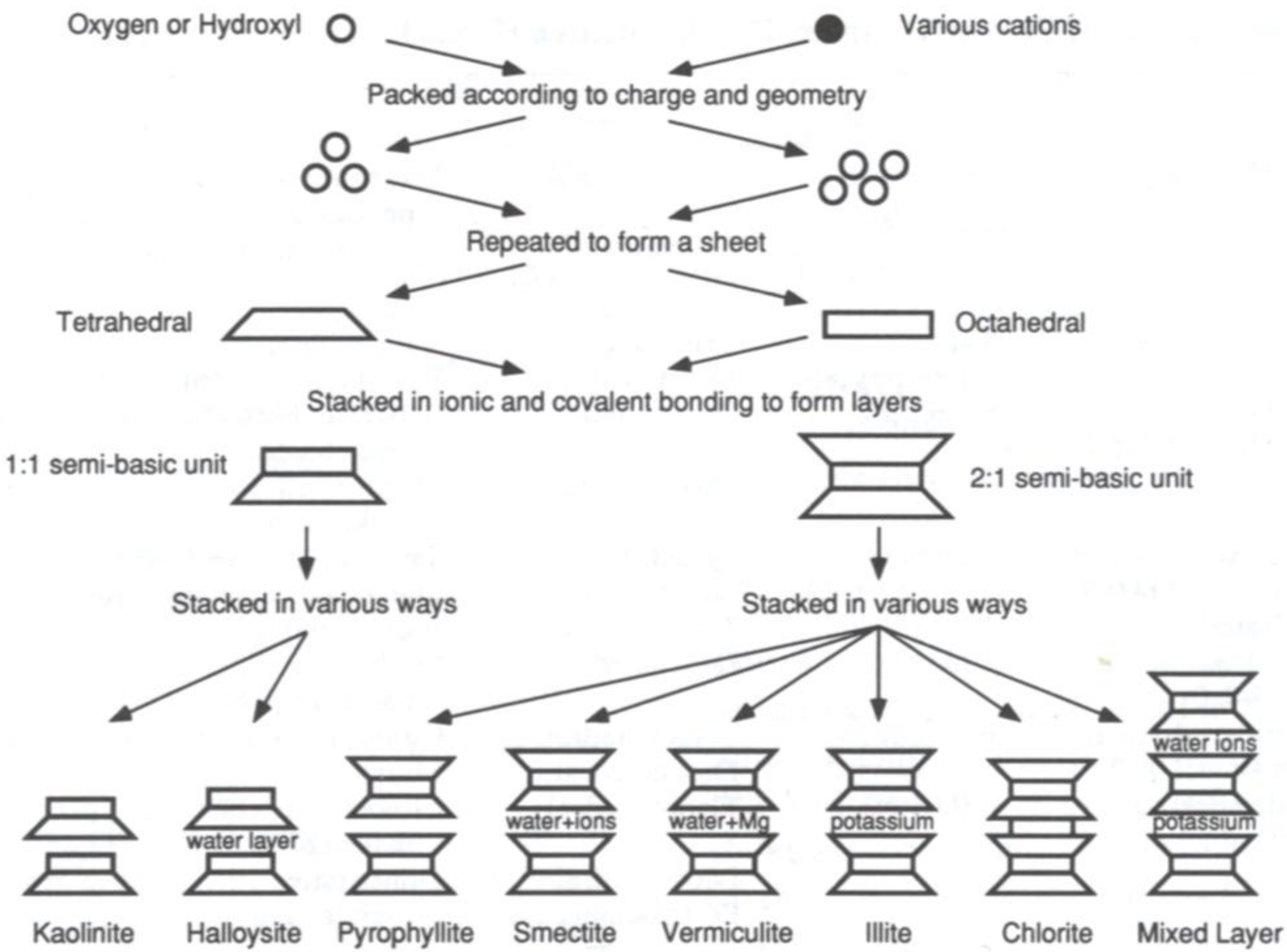
CLAY STRUCTURE



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CLAY STRUCTURE

Structure of Layer Silicate Clays

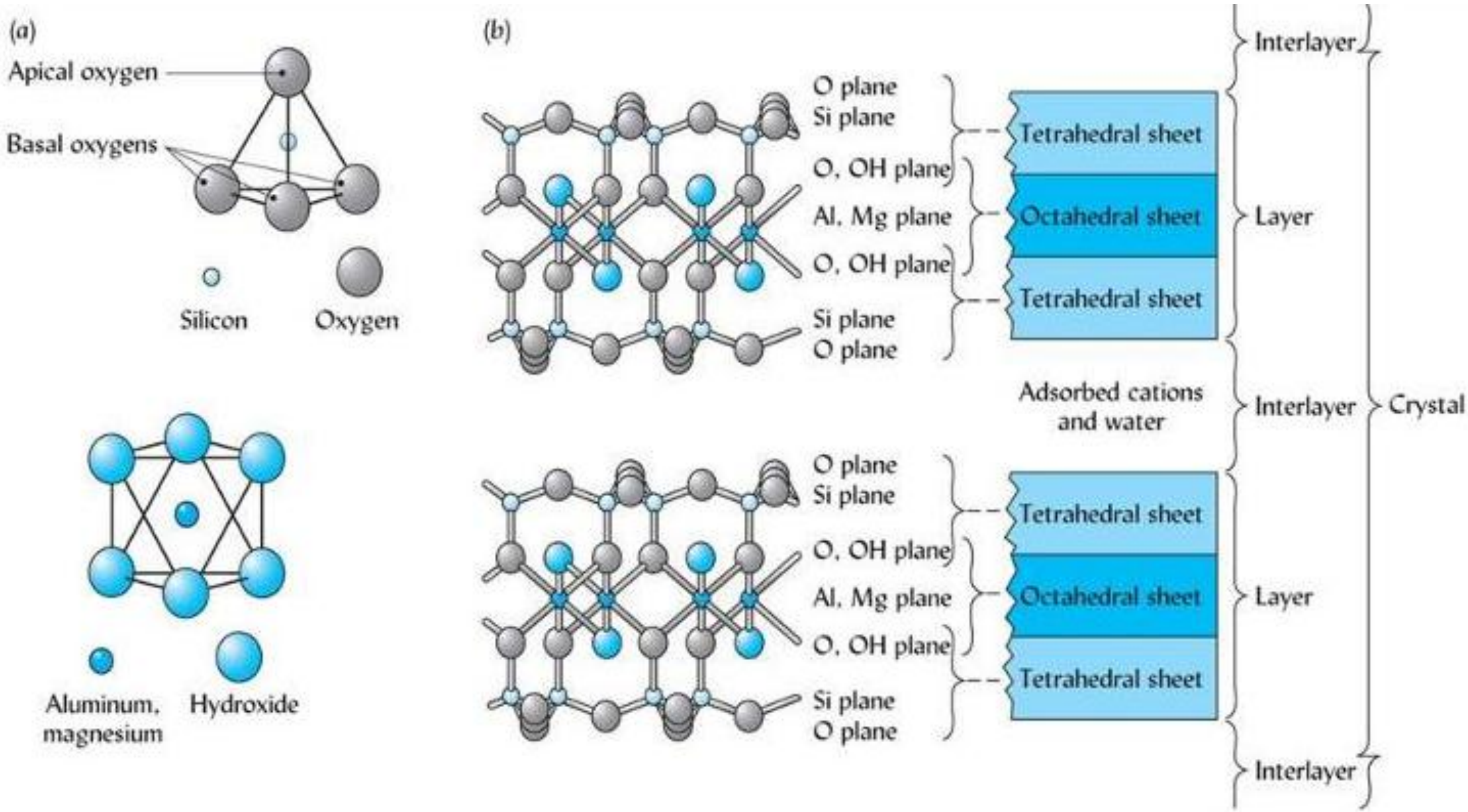
Silicate clay particles are crystalline, each particle **layer** being comprised of two basic individual **sheets**.

One of these sheets is dominated by a **plane** of silicon atoms surrounded by oxygen atoms. The oxygen atoms, in turn, act as connective links to a companion sheet dominated by an aluminum and/or magnesium plane surrounded by linkage oxygens and a few hydroxyl groups. The silica sheet is called a **tetrahedra**l sheet because of the four-sided configuration of a given silicon atom and its associated oxygen atoms.

Similarly, the aluminum/magnesium sheets are known as **octahedral** sheets because each aluminum/magnesium atom and associated oxygens and hydroxyls comprise an eight sided building block or octahedron.

CLAY STRUCTURE

Structure of Layer Silicate Clays



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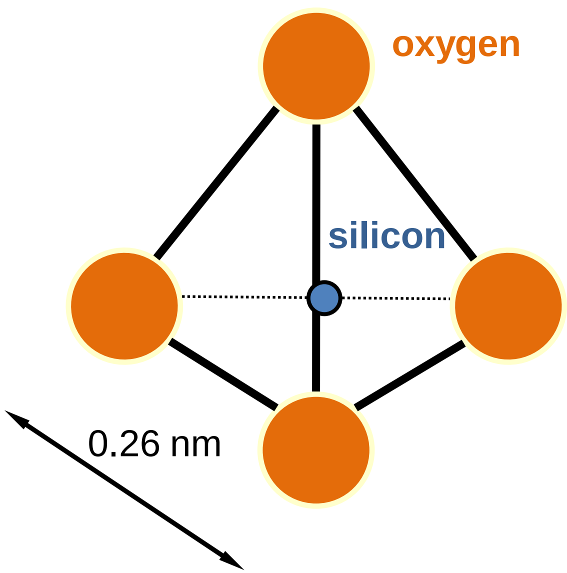
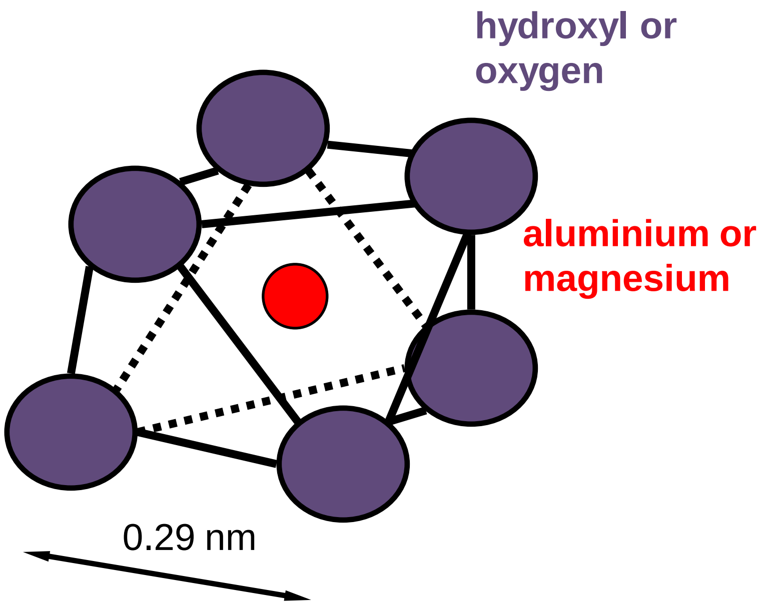
CLAY STRUCTURE

Basic Structural Units

Clay minerals are made of two distinct structural units.



Silicon tetrahedron

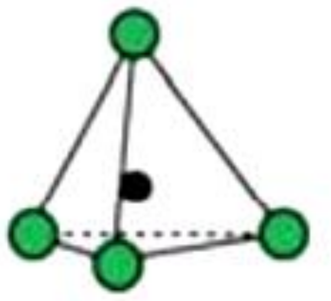


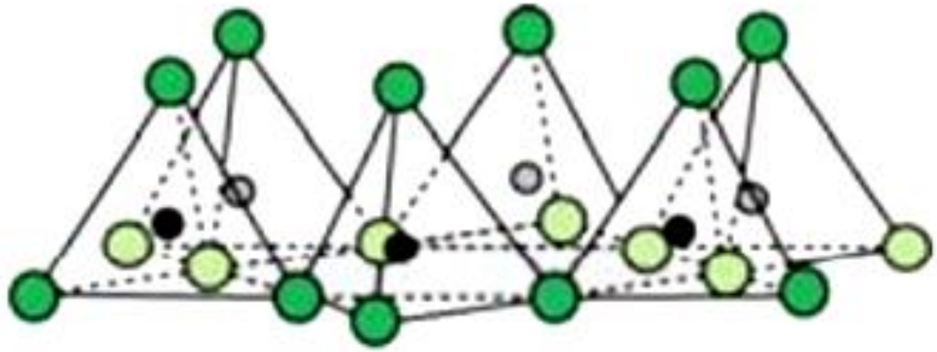
Aluminium Octahedron

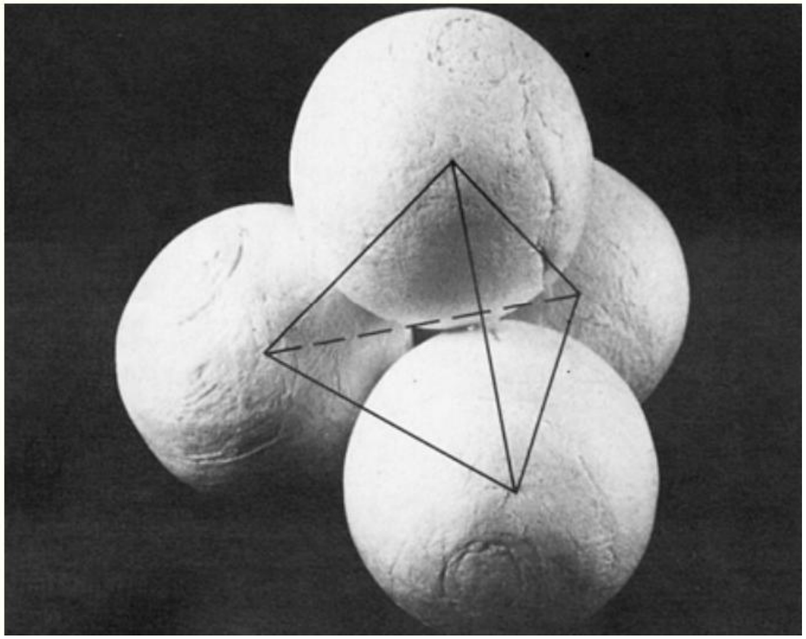
All clay minerals are made of two distinct building blocks: tetrahedrons and octahedrons. The tetrahedron on the left has oxygen atoms at the corners, and there is a silicon in the centre. Octahedron has six oxygen or hydroxyl atoms in the corners, and an aluminium or magnesium ion at the centre.

CLAY STRUCTURE

Tetrahedral Sheet



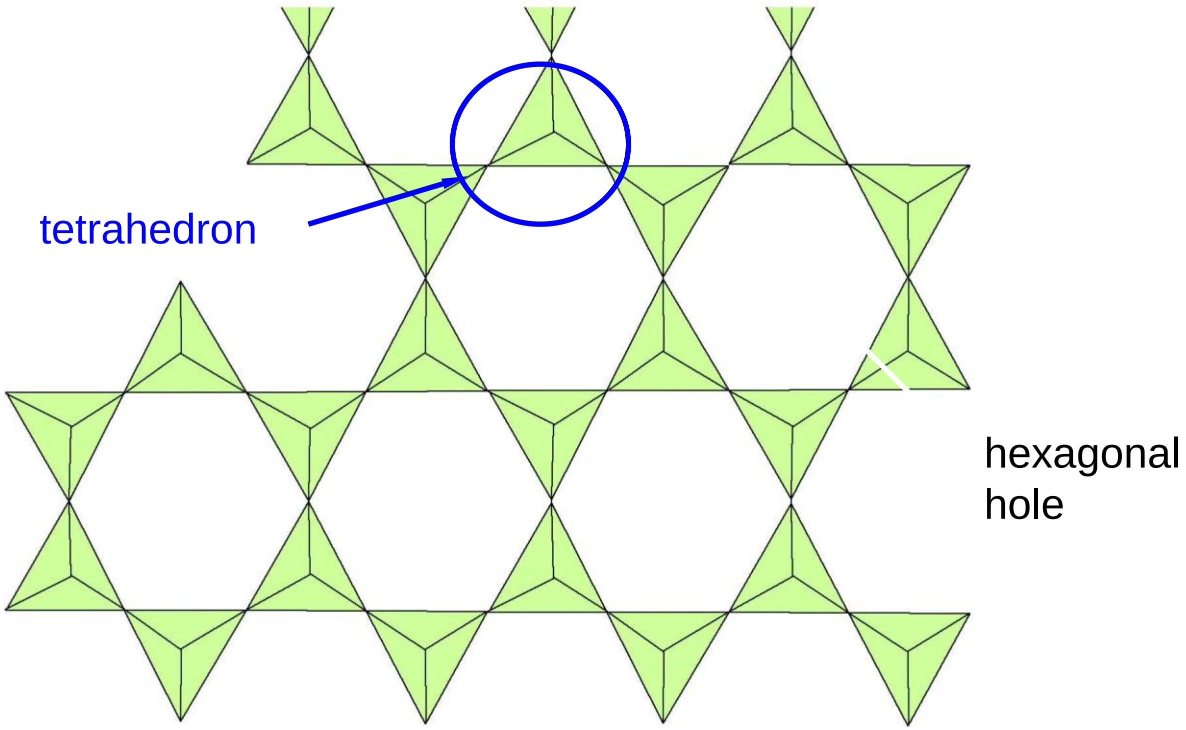




CLAY STRUCTURE

Tetrahedral Sheet

Several tetrahedrons joined together form a tetrahedral sheet.



Here is a tetrahedral sheet, formed by connecting several tetrahedons. Note the hexagonal holes in the sheets.

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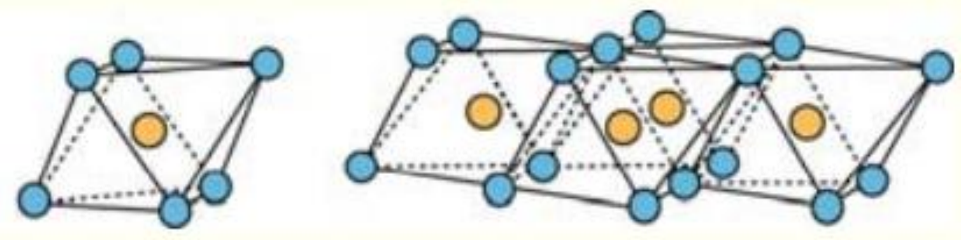
CLAY STRUCTURE

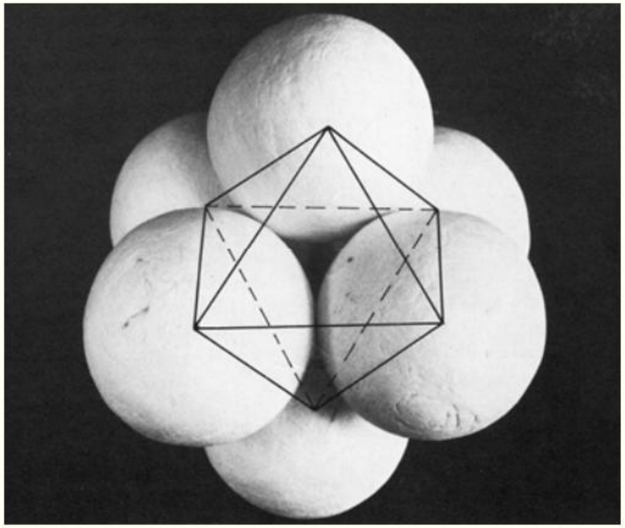
Octhaderal Sheet

In clay minerals the tetrahedral sheet is always combined with a octahedral sheet

A cation (Al^{+3}, Mg^{+2}, Fe^{+2} etc. but not Ca^{+2}, Na^{+1}, K^{+1}) is surrounded by 6 neighbors (oxygens or hydroxyls)

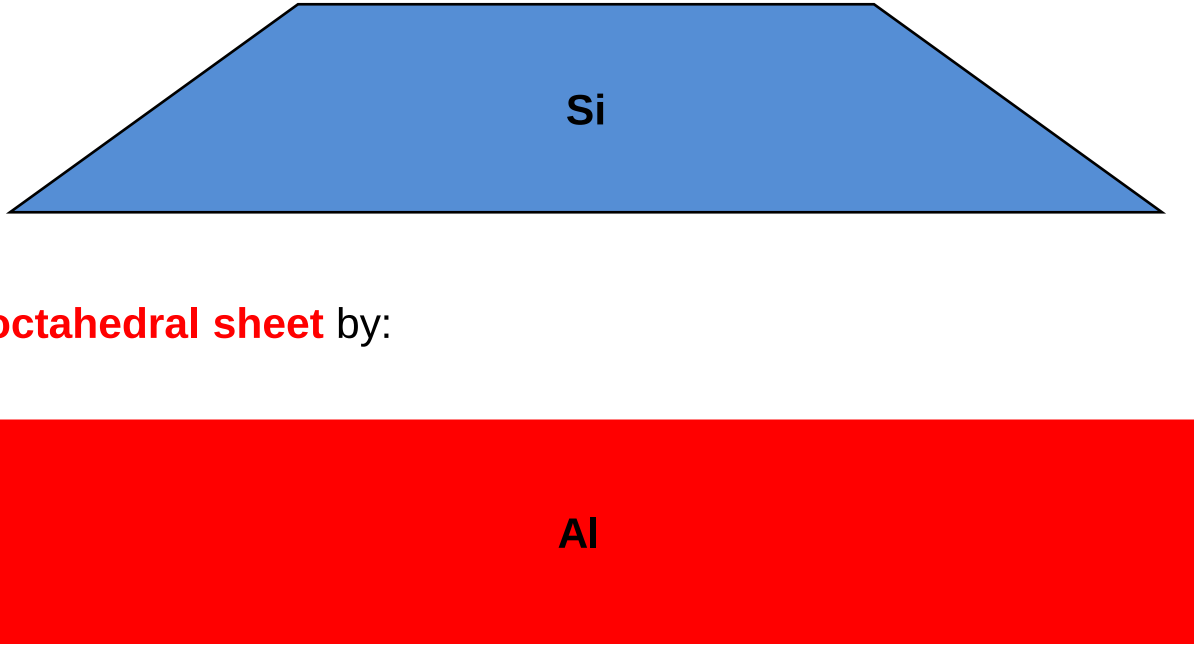
Minerals composed of octahedral sheets.
Brucit $Mg_3(OH)_6$
Gibbsite $Al_2(OH)_6$





Tetrahedral & Octahedral Sheets

For simplicity, let’s represent silica **tetrahedral sheet** by:



and alumina **octahedral sheet** by:

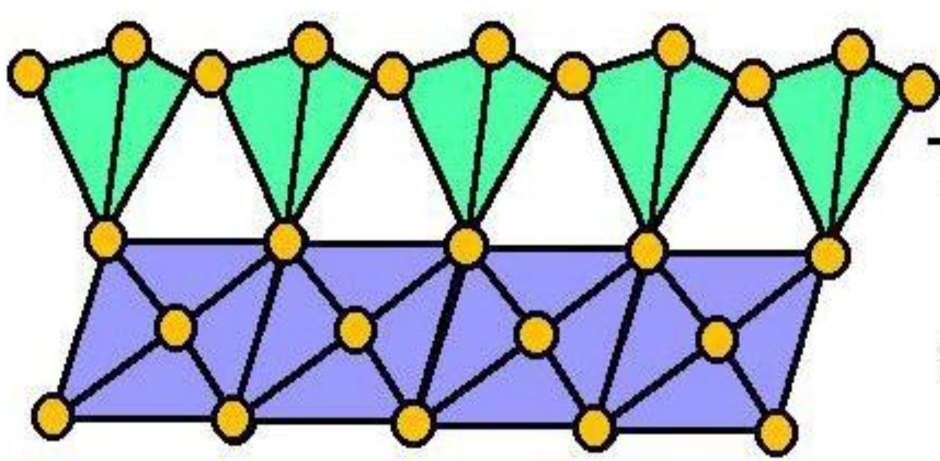
The blue and red blocks represent the tetrahedra and octahedra sheets respectively.

CLAY STRUCTURE

Different Clay Minerals

Different combinations of tetrahedral and octahedral sheets form different clay minerals:

<u>1:1 Clay Mineral</u> (e.g., kaolinite, halloysite):



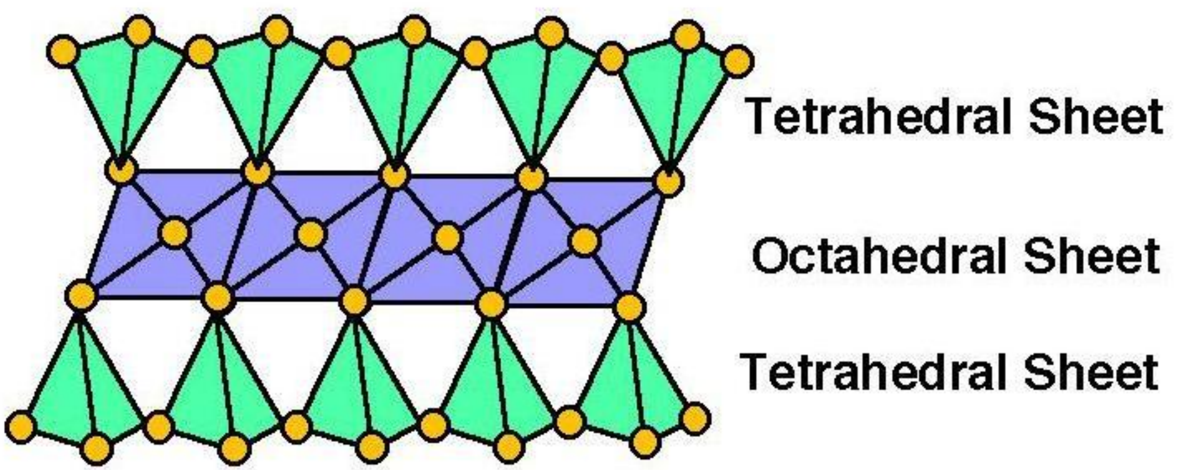
All clay mineral are made of different combinations of the above two sheets: tetrahedral sheet and octahedral sheet.

CLAY STRUCTURE

Different Clay Minerals

Different combinations of tetrahedral and octahedral sheets form different clay minerals:

2:1 Clay Mineral (e.g., montmorillonite, illite)



CLAY STRUCTURE

Kaolinite Clays

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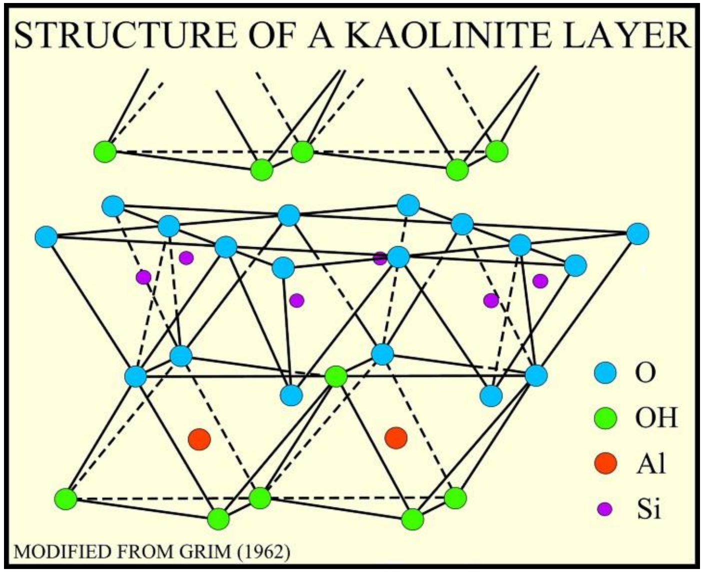
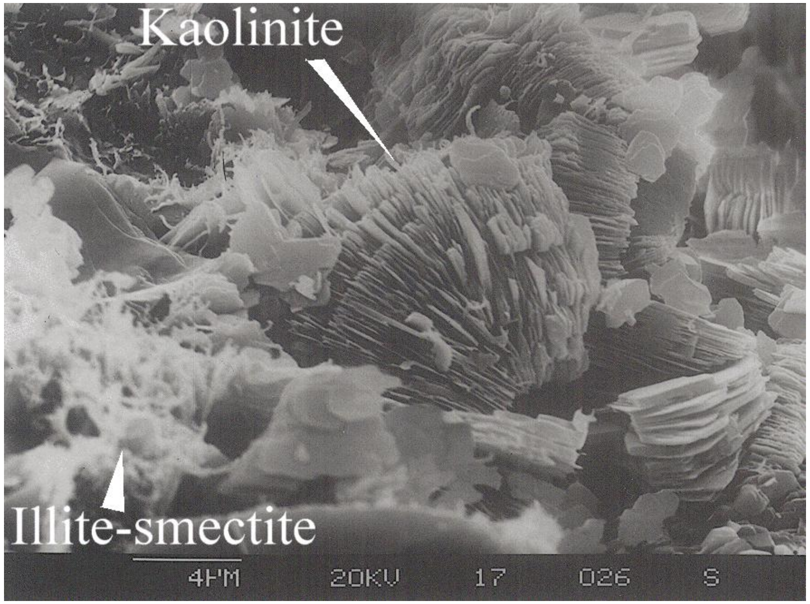
These clays are also used as a filler in making paper.

CLAY STRUCTURE

Structure of Kaolinite

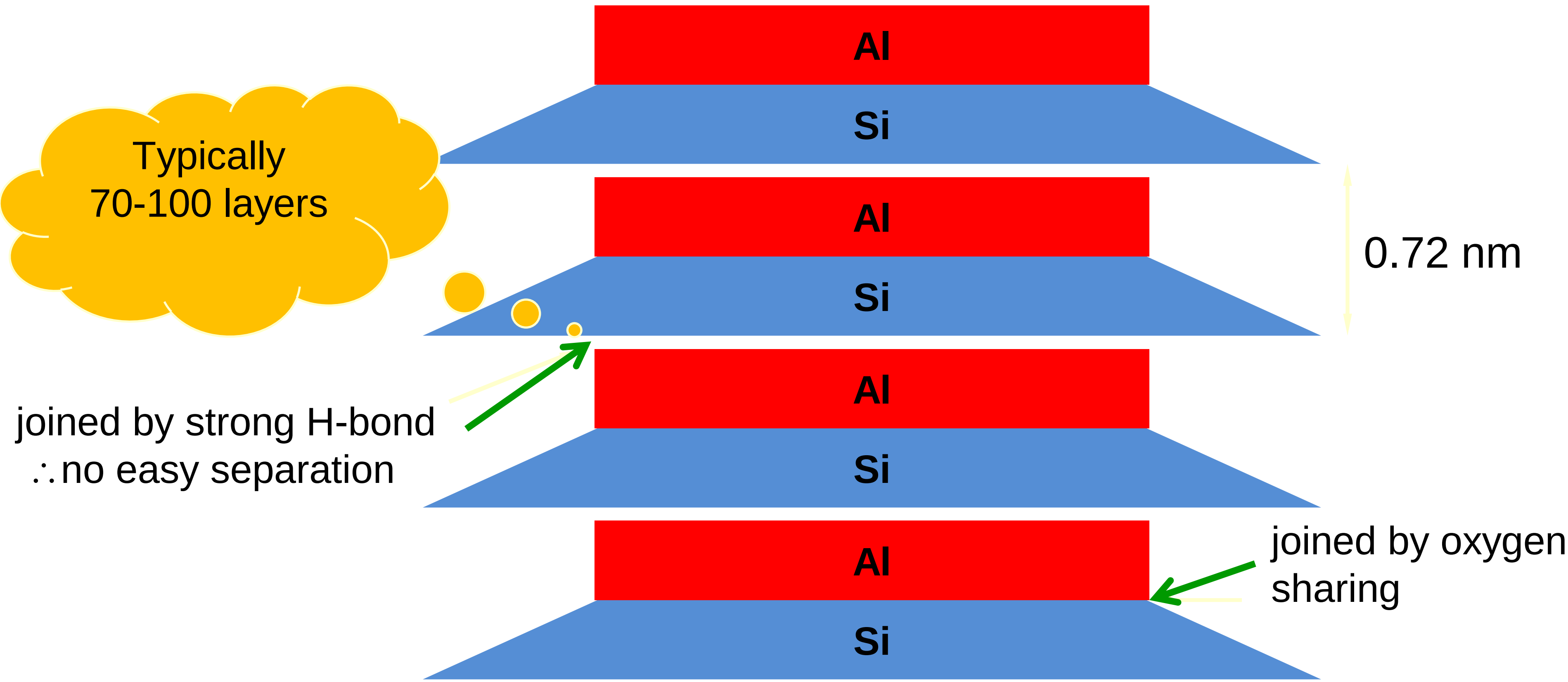
- $Si_4Al_4O_{10}(OH)_8$. Platy shape
- The bonding between layers are van der Waals forces and hydrogen bonds (strong bonding).
- There is no interlayer swelling
- Width: 0.1~ 4μm, Thickness: 0.05~2 μm





CLAY STRUCTURE

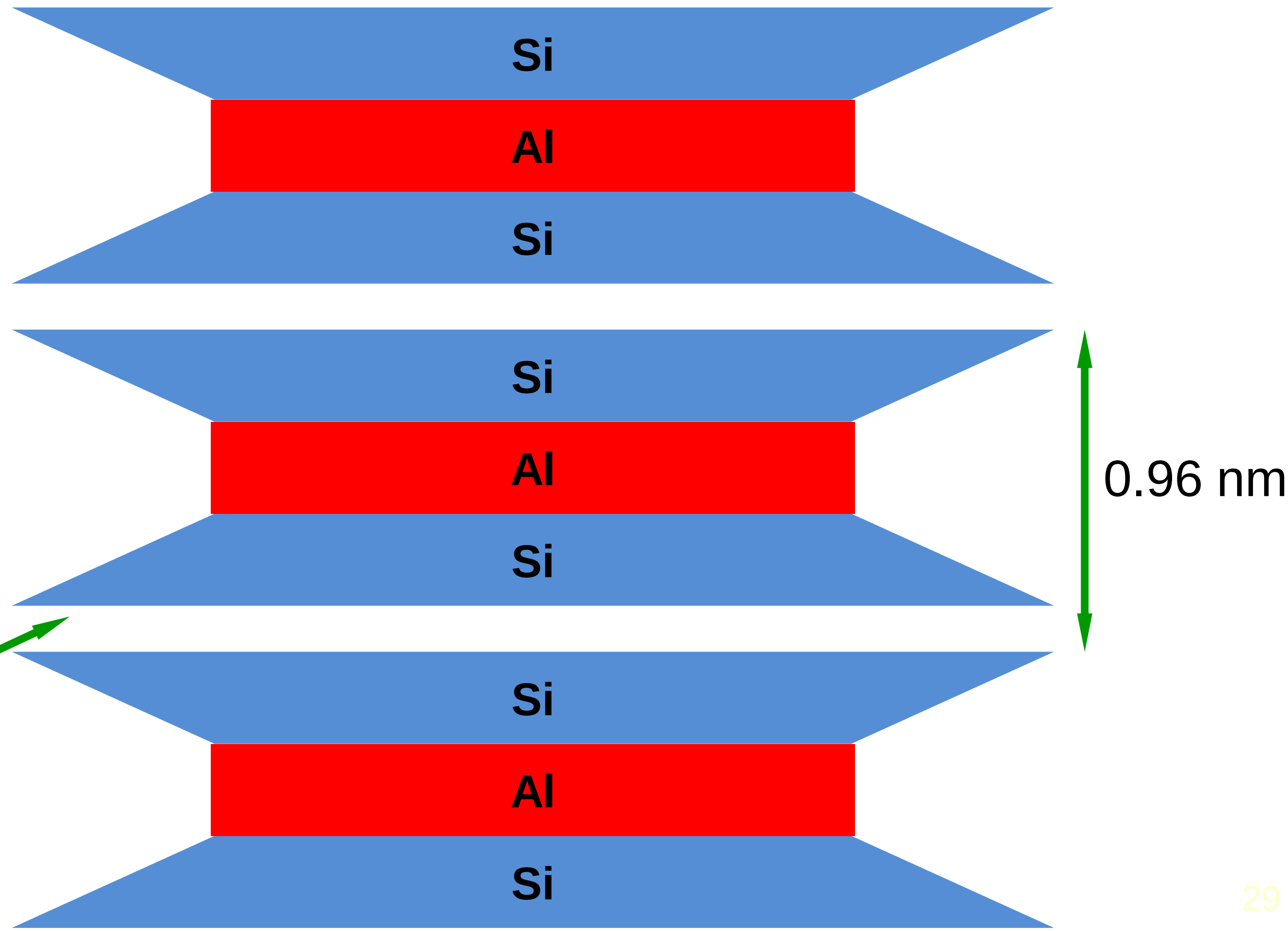
Kaolinite



CLAY STRUCTURE

Montmorillonite

also called **smectite**; expands on contact with water



∴easily separated by water

joined by weak van der Waal's bond

CLAY STRUCTURE

Montmorillonite

Montmorillonites have very high specific surface, cation exchange capacity, and affinity to water. They form reactive clays.

Montmorillonites have very high liquid limit (100+), plasticity index and activity (1-7).

Bentonite (a form of Montmorillonite) is frequently used as drilling mud.

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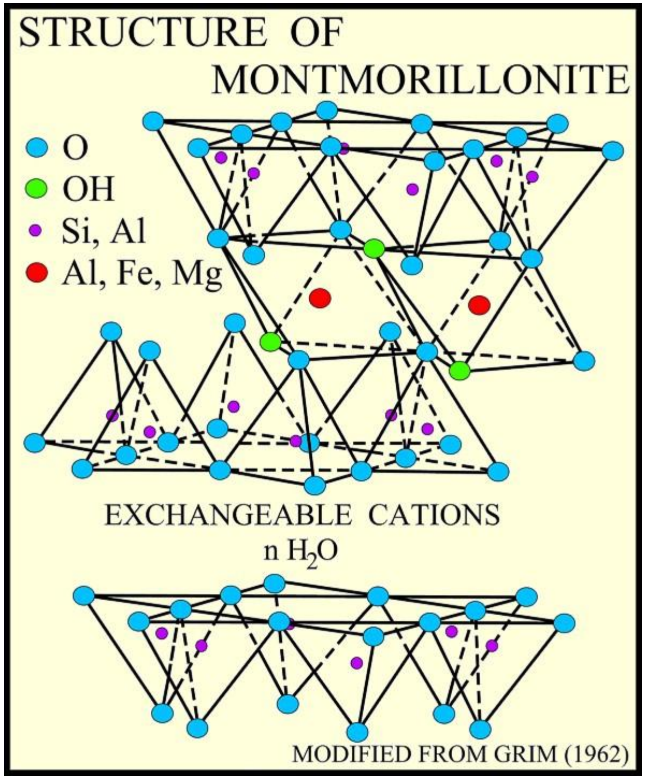
CLAY STRUCTURE

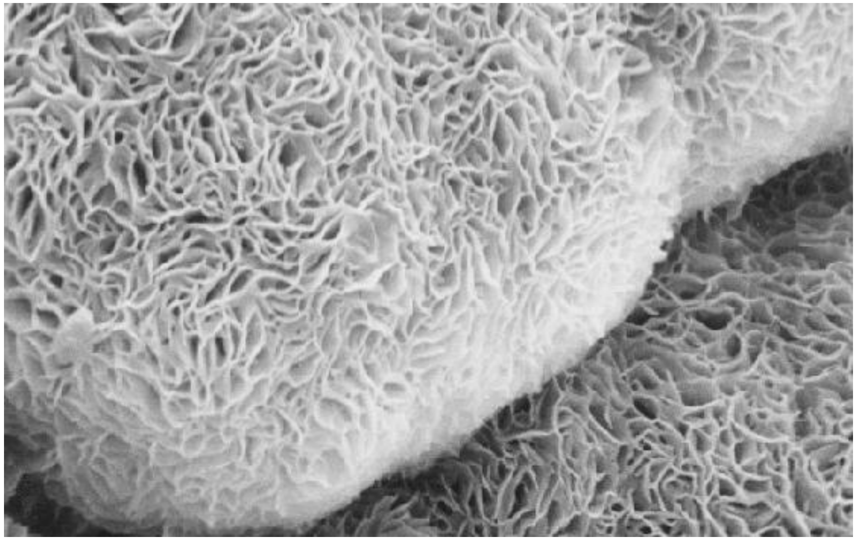
Montmorillonite

The most common smectite clay 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.





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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

İllite

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:

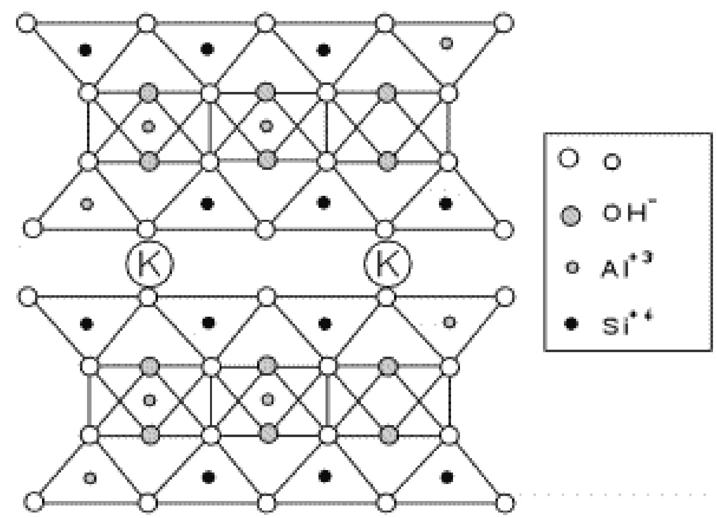
$K_yAl_4(Si_{8-y},Al_y)O_{20}(OH)_4$, usually with $1 < y < 1.5$, but always with $y < 2$.

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.

Muscovite $KAl_2AlSi_3O_{10}(OH)_2$



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.

Commercial Clays

Commercial Clays and Their Main Uses

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

* : *Ceramic Materials: Science and Engineering,* by C. Barry Carter and M. Grant Norton, Springer, 2007, 349.

Chemical Composition of Clays

Oxide	Kaolinite	Illite	Smectite	Vermiculite	Al-Chlorite	Mg-Chlorite	Palygorskite	Sepiolite
SiO_2	45.44	49.78	59.49	43.21	39.85	30.89	55.86	52.5
Al_2O_3	38.52	26.35	21.93	17.21	33.52	18.55	10.54	0.6
Fe_2O_3	0.8	4.3	3.77	8.03	4.56	1.69	3.23	2.9
FeO		0.61	0.2	0.6		1.42		0.7
MnO				0.21				
MgO	0.08	2.75	3.55	25.71	4.58	33.74	9.2	21.31
CaO	0.08	0.32	1.18	5.1	0.15		1.56	0.47
K_2O	0.14	7.02	0.34	0.32	1.61		0.05	
Na_2O	0.66	0.25	0.82	0.05			0.68	
TiO_2	0.16	0.42	0.25	0.06	1.03	0.05	0.47	
H_2O^-	0.6	1.48				1.08	8.71	12.06
H_2O^+	13.6	7.12	8.38		13.18	12.97	9.13	9.21
Total	100.08			100.5		100.38	99.58	
Molar SiO_2/Al_2O_3	2.02	3.22	4.61	4.26	2.02	2.83	9.04	148.31

From Weaver and Pollard (1973): Kaolinite from a weathered pegmatite, Virginia (Table LIX). Mean of 24 illites from several countries (Table III). Mean of 101 montmorillonites–beidellites (Table XXV). Al-chlorite from a soil, B.C., Canada (Table XLII). Palygorskite from Attapulgus, Georgia (Table LII). Sepiolite from Madagasgar (Table LVI). Mg-chlorite from Foster (1962), sample no. 50. Ca-saturated vermiculite from Australia (Newman and Brown, 1987, Table 1.18).

Plasticity

The characteristic property of moist clay that permits it to be deformed without cracking and to retain its new shape when the deforming stress is removed.

Plasticity is associated with the sheet structure of the clay minerals and with the manner in which water films are held by the clay particles.

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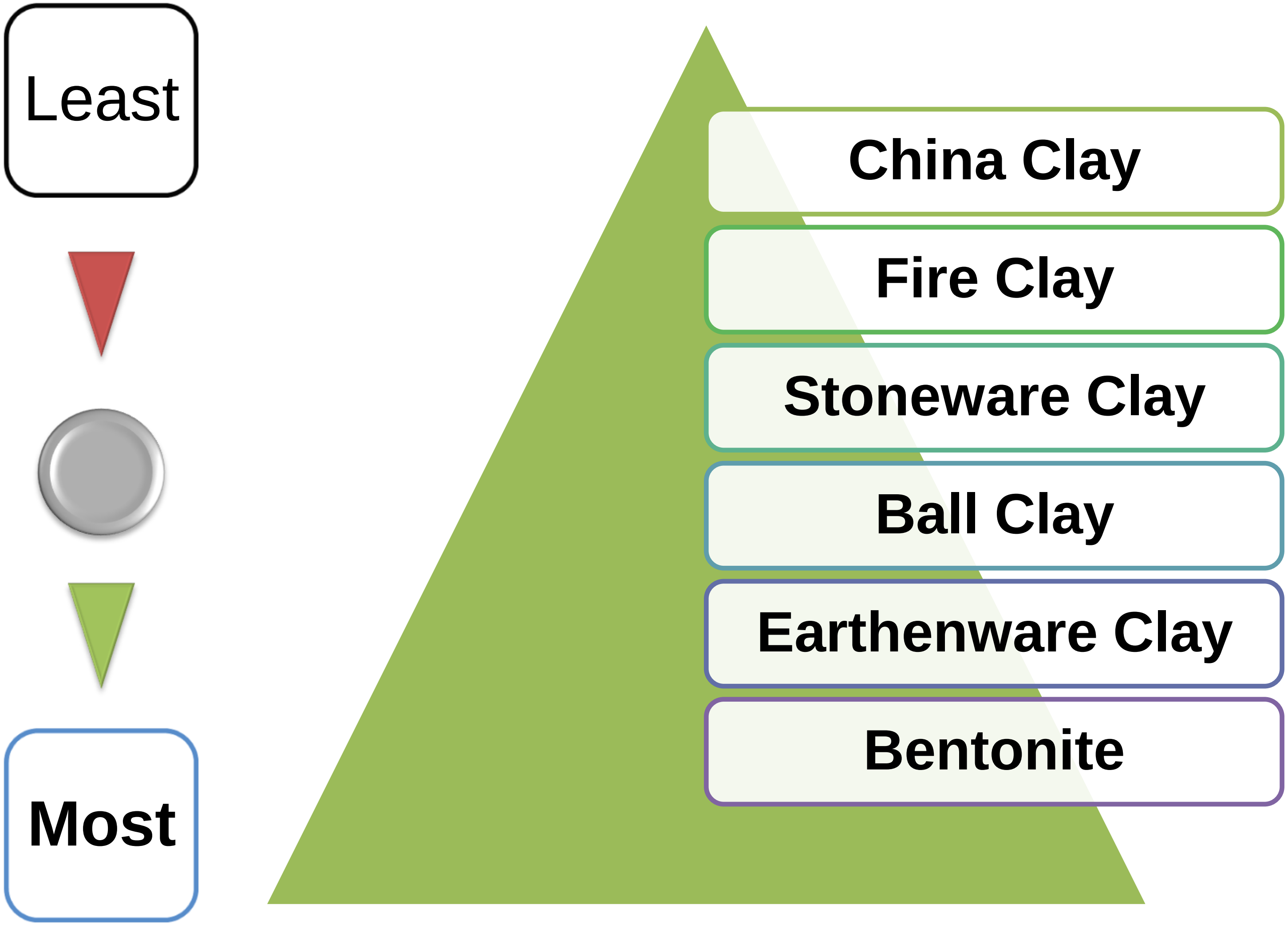
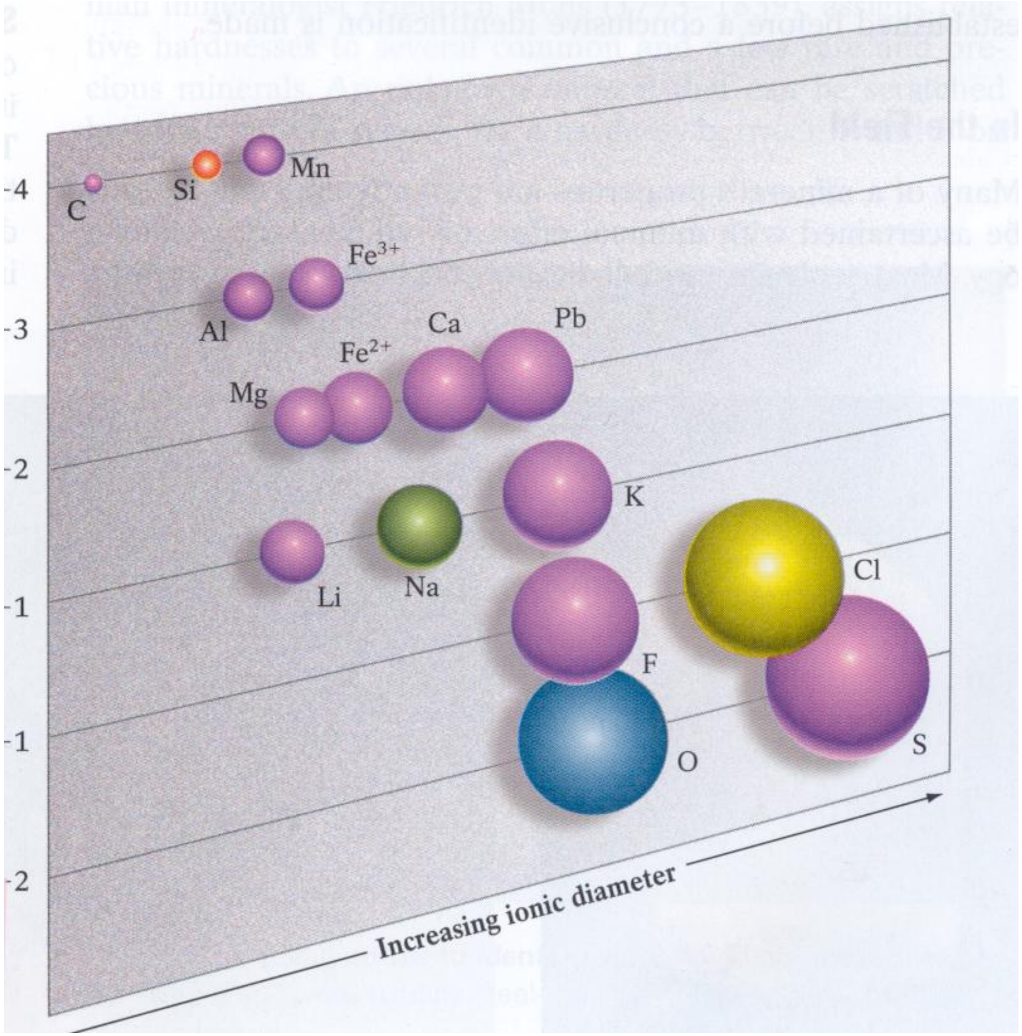
CLAYS Ranked by Plasticity



Impurities

Ions of Similar Charge & Size Can Easily Substitute for Each Other



Important Properites of Clays

- **Particle size:** is a very important property because it influence many other properties such as plasticity, dry strength and base exchange capacity.
- **Particle shape:** thickness affect surface area.
- **Base exchange capacity:** when a balance structure have some ions replaced by others of different valence (Al^{3+} by Mg^{2+} , there will be a charge deficiency in the structure, this deficiency is balanced by ions adsorbed on the surface of the crystal.
- The maximum capacity to adsorb ions is called the **base exchange capacity**.
- **Organic matter:** we have to remove organic matter when studying the properties of clay minerals.
- **Color**
- **Chemical composition:** for specific uses
- **Plastic properties:** Montmorilonite, the finest grained clays are highly plastic.
- **Dried properties:** drying shrinkage, dried strength , volume changes when clay is dried
- **Firing properties:** like shrinkage and porosity.

Clay products – Main Components

Clay

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Provides plasticity, when mixed with water
Hardens upon drying and firing (without losing the shape)

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Silica

Silica, SiO_2, is mixed with clay to reduce shrinkage of the ware while it is being fired, and thus prevent cracking, and to **increase the rigidity of the ware so that it will not collapse at the high temperatures** required for firing. Silica is useful for this purpose becasue it is hard, chemically stable, has a high melting point and can readily be obtained in a pure state in the form of quartz.

Feldspar

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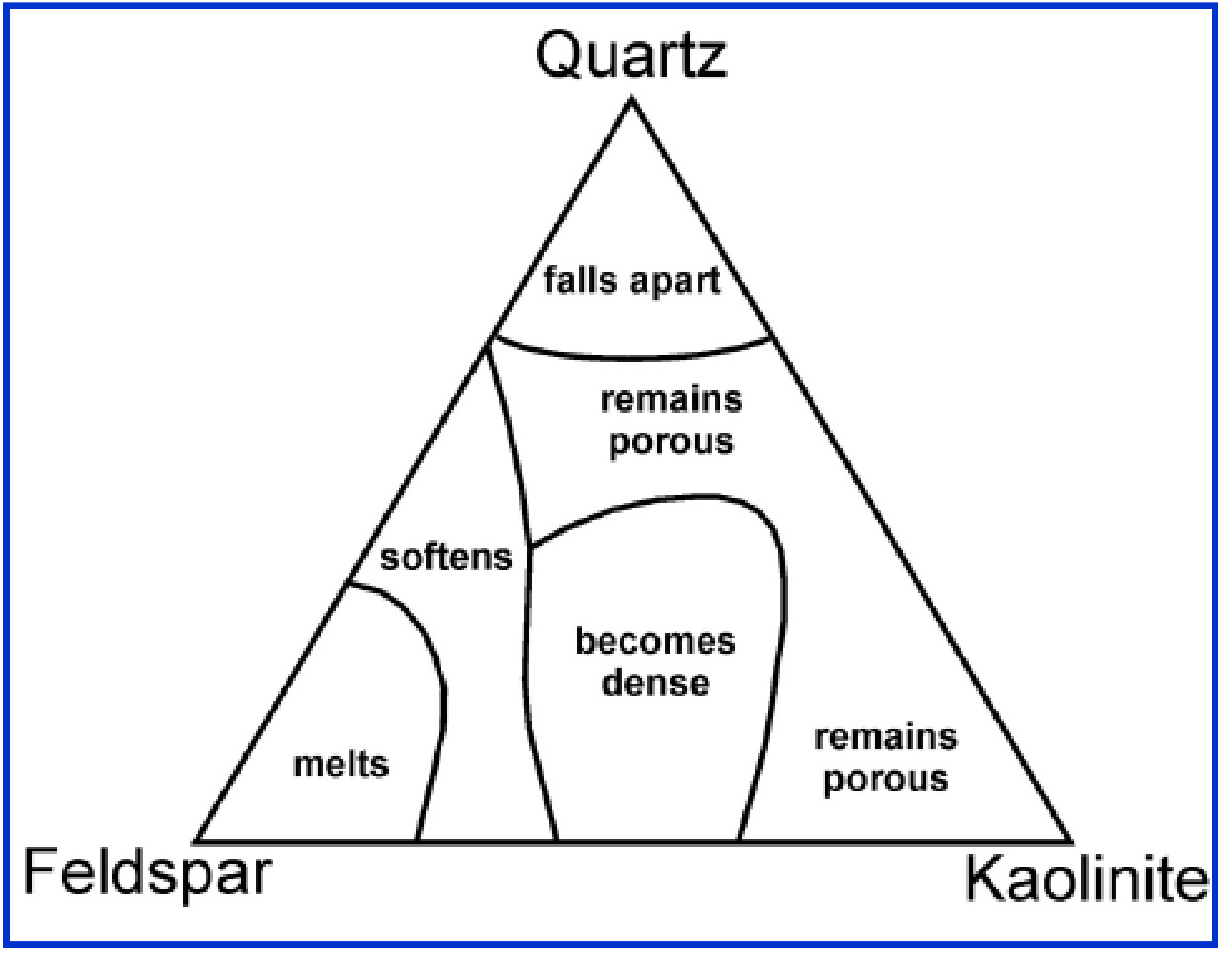


Mineral Processing

Mineral processing steps

1.Comminution: size reduction by crushing and milling

2. Screening: size separation by sieves

3. Classification: size separation by differential gravitational settling

4. Concentration, separation: separation of different phases in the feed

- Gravity separation
- Dense medium separation
- Froth flotation
- Magnetic separation

Depending on the ore, the number and sequence of the processes will be different

SUMMARY

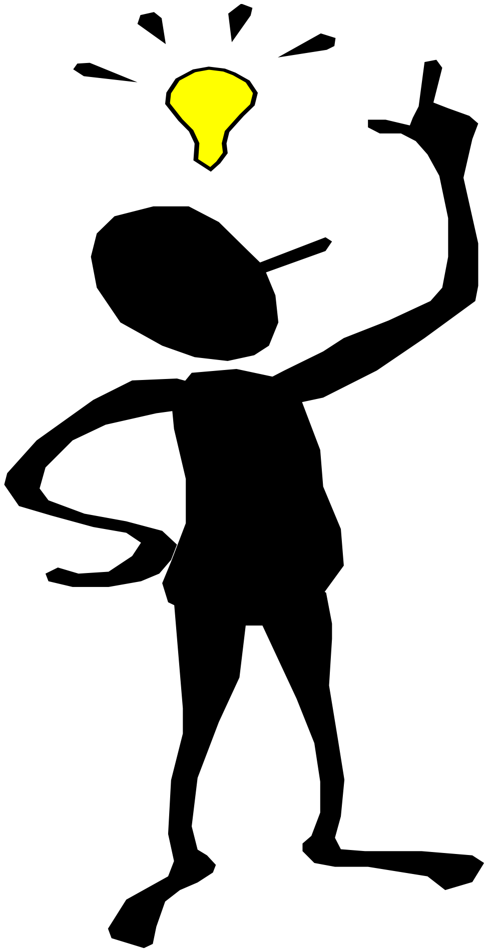
- Where and how we get the raw materials will determine impurity concentrations in the final powder.

- The abundance of a mineral may affect the cost of the final ceramic component (e.g., SiO_2 comes from sand; it is abundant and inexpensive. Glass bottles are cheap; the cost of an Si wafer is not related to the cost of sand).

- If the raw materials are not oxides then they have almost certainly been synthesized.

THE END

Thanks for your kind attention



Any Questions