Geology and Art, Fall 2004
Minerals and Rocks, Lecture 4
Dynamic Earth, Chapter 3

We covered the fundamentals of minerals in Lab last week so this lecture will focus on the internal structure of (silicate) minerals, specifically clay minerals.

Minerals are classified based on
- Composition: proportion of the chemical elements that make up the mineral
- Crystal Stucture: three-dimensional organization of the mineral

Chemical **Elements**

These are the most fundamental substances into which matter can be separated by chemical means (NaCl can be separated into Na^+ and Cl^-, but Na^+ can't be divided).

An atom is a single unit of a pure element (Au)

All chemical elements have one or two letter symbols (Appendix B)

Ions: atoms contain protons (positive charge) and neutrons (neutral charge) in their nucleus and electrons (negative charge) in orbits (shells) around them. A specific number of electrons are needed to fill each energy-level shell and in order to be stable, atoms tend to transfer electrons between themselves to attain filled shells. This leaves the atoms with unbalanced charges, positive or negative, these are called **ions**.

Cation: ion with a positive charge (gave up one or more electrons)
Anion: ion with a negative charge (gained one or more electrons)

Example:
Sodium (Na) has an atomic number of 11 (11 protons and 11 electrons) but the first energy-level shell holds 2 electrons and the second holds 8 so a Na ion with 10 electrons, not 11 is more stable. Na will tend to give up an electron and become a cation (Na^+)

Chlorine (Cl) has an atomic number of 17 (17 protons and 17 electrons) but the first energy-level shell holds 2 electrons, the second holds 8, and the third holds 8 so a Cl ion with 18 electrons, not 17 is more stable. Na will tend to grab an electron and become a anion (Cl^-)

Compounds: chemical compounds form when atoms of different elements combine in a specific proportion (NaCl or H_2O). A mineral is a naturally occurring compound.

Complex Ions: these are compounds that act like a single ion. Examples would be the carbonate ion (CO_3^{2-}, SO_4^{2-} or SiO_4^{4-})

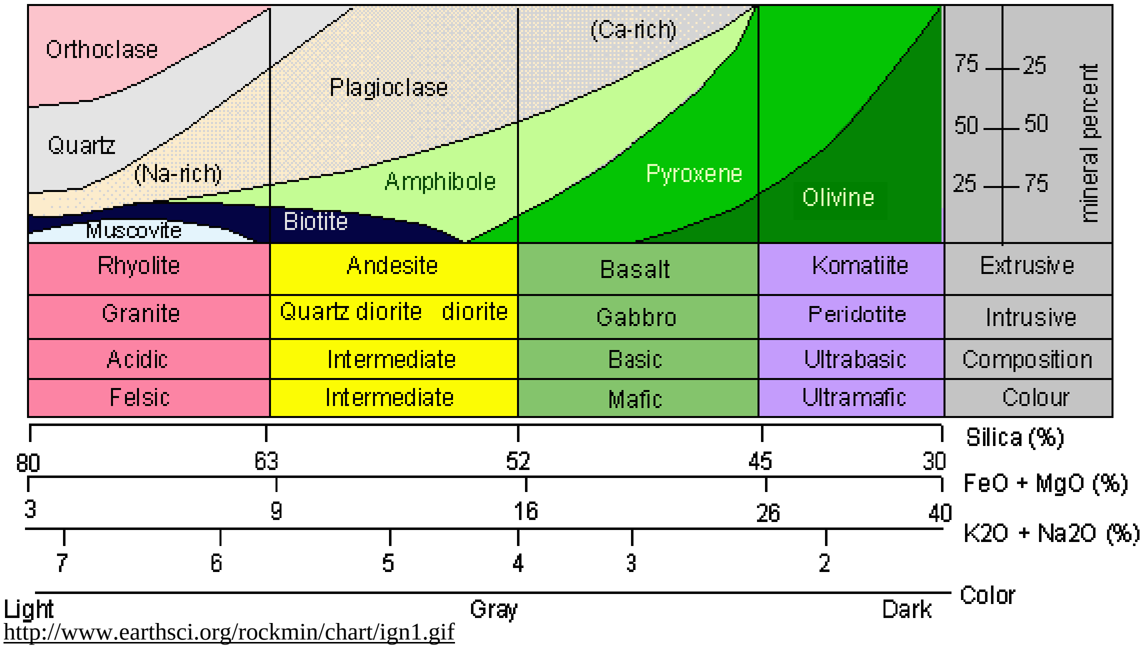
Chemical Bonds: the way which electrons are transferred (or shared) from one atom to another creates a bond that holds the two atoms together. The four different types of chemical bonds are described in more detail on page 71).
- Ionic bonds: electrostatic attraction (NaCl)
- Covalent bonds: shared electrons create very strong bonds (diamond)

- Metallic bonds: electrons are shared among several atoms and can drift (Au)
- Van der Waals bonds: weak secondary attractions between compounds (mica)

Ionic Substitution: ions of similar size and charge can substitute for one another in a mineral. In some cases you get paired substitution when two ions of similar size, but differing charge substitute for one another and a second pair of ions, again of similar size but differing charge, substitute in order to neutralize the charge difference.

Example: plagioclase feldspar

Ca-plagioclase (anorthite)	O^{2-}, Ca^{2+}, Si^{4+}, Al^{3+}	$CaAl_2Si_2O_8$
Na-plagioclase (albite)	O^{2-}, Na^{+}, Si^{4+}, Al^{3+}	$NaAlSi_3O_8$



http://www.earthsci.org/rockmin/chart/ign1.gif

Example: Olivine

Forsterite	O^{2-}, Mg^{2+}, Si^{4+}	Mg_2SiO_4
Fayalite	O^{2-}, Fe^{2+}, Si^{4+}	Fe_2SiO_4

Solid Solution: $(Mg,Fe)_2SiO_4$

Silicate Minerals

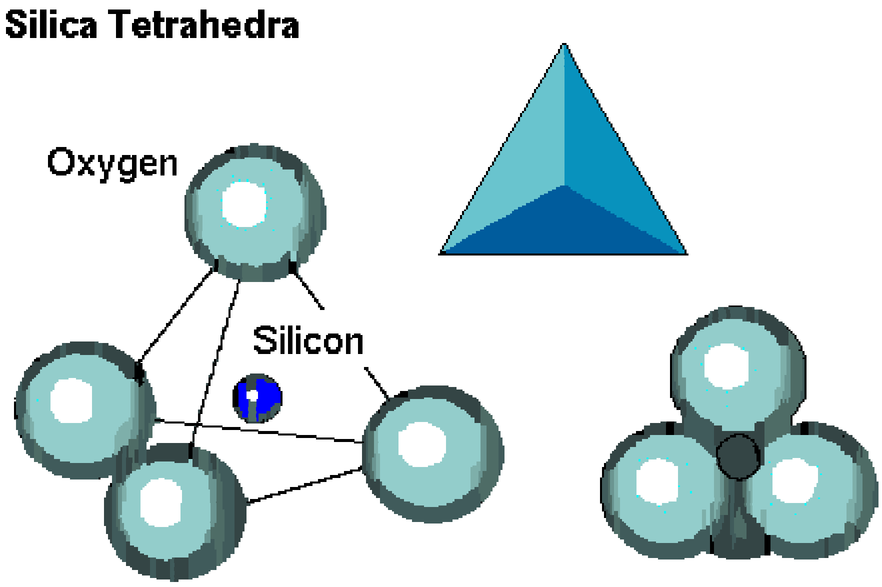
Silicate tetrahedron: the complex ion, SiO_4^{4-} is the basic building block of the silicate minerals (minerals that contain silicon). If you look at the proportion of elements that make up the Earth's crust it is clear why the family of silicate minerals is so important.

Element	**Weight %**
Oxygen	45.2
Silicon	27.2
Aluminum	8
Iron	5.8
Calcium	5.1
Magnesium	2.8
Sodium	2.3
Potassium	1.7

Titanium	0.9
Hydrogen	0.1
Manganese	0.1
Phophorous	0.1
Total	*99.23*

The silicate tetrahedral contains oxygen (O) and silicon (Si). Oxygen has the atomic number 8 that means there are 6 electrons in its outer energy-level shell. This means to be stable oxygen becomes the anion, O^{2-}. Silicon has the atomic number 14 that means there are 4 electrons in its outer energy-level shell. This means to become stable silicon becomes the cation Si^{4-}.

When four oxygen atoms are stacked together in a tetrahedron (four-sided) the silicon cation just fits in the center of the tetrahedron. The silicon cation creates covalent bonds with the four oxygen anions, creating a complex ion with a residual charge of 4+.

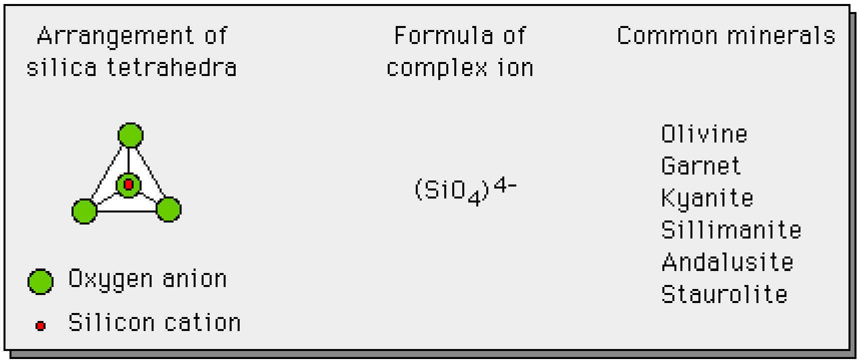


This complex ion can obtain stability by bonding with other cations or by bonding linking tetrahedral so that two or more silicate tetrahedral are joined at an apex, this process is called **polymerization**.

Silicate minerals are classified based on the degree of polymerization that the silicate tetrahedral have undergone.

Silicate Classification (Figure 3.23 on page 87)

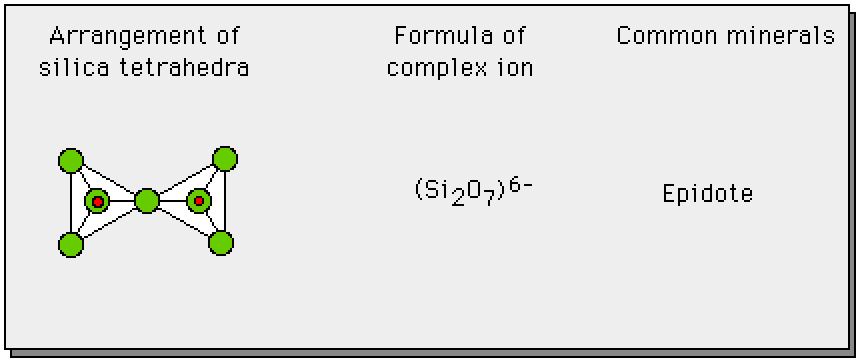
Nesosilicates: these are isolated silicate tetrahedral. There is no polymerization.



Arrangement of silica tetrahedra	Formula of complex ion	Common minerals
● Oxygen anion • Silicon cation	$(SiO_4)^{4-}$	Olivine Garnet Kyanite Sillimanite Andalusite Staurolite

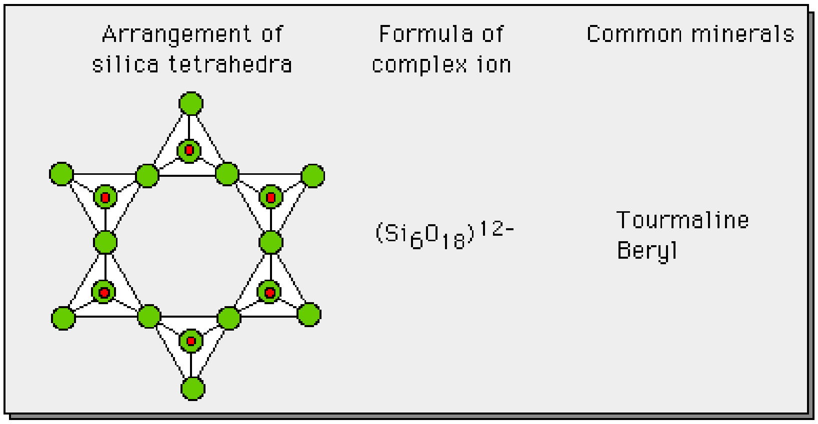
http://tesla.jcu.edu.au/Schools/Earth/EA1001/Mineralogy/Silicates.html

Sorosilicates: these are pairs of silicate tetrahedral that are joined at an apex.



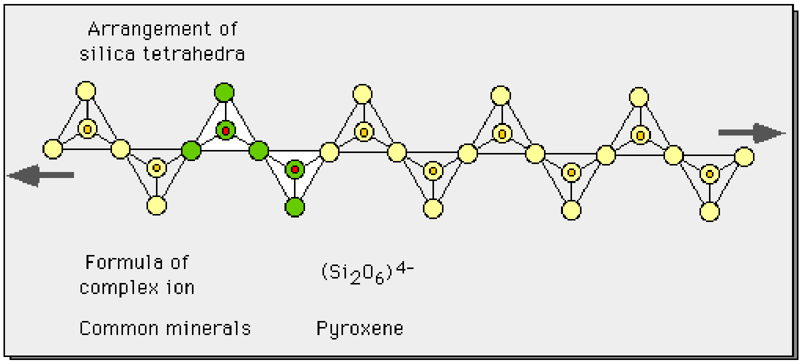
Arrangement of silica tetrahedra	Formula of complex ion	Common minerals
	$(Si_2O_7)^{6-}$	Epidote

Cyclosilicates: these are rings of three, four or six tetrahedral. The large whole in the center of the ring allows large cations to be incorporated (Be).

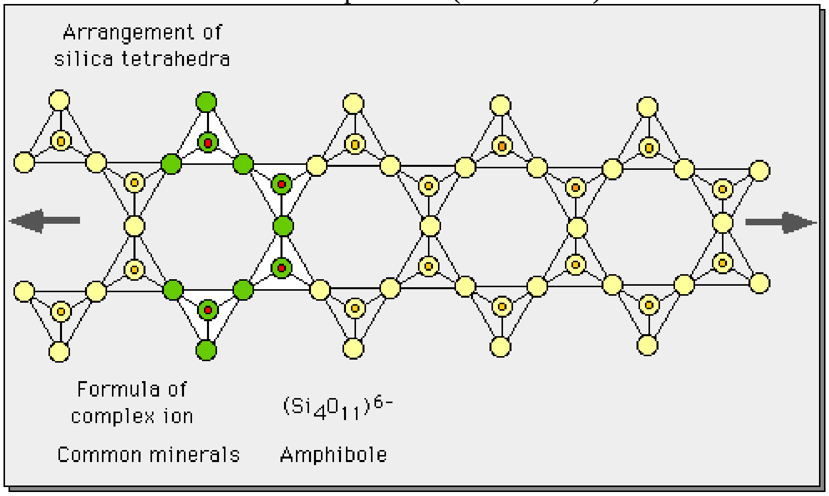


Arrangement of silica tetrahedra	Formula of complex ion	Common minerals
	$(Si_6O_{18})^{12-}$	Tourmaline Beryl

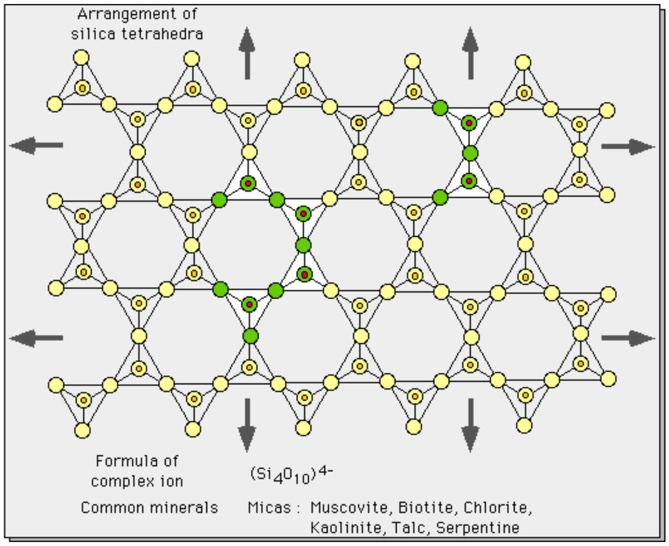
Inosilicates: chains of polymerized silicate tetrahedral, either single chains or double chains. Single chains include the pyroxenes (see igneous mineralogy diagram).



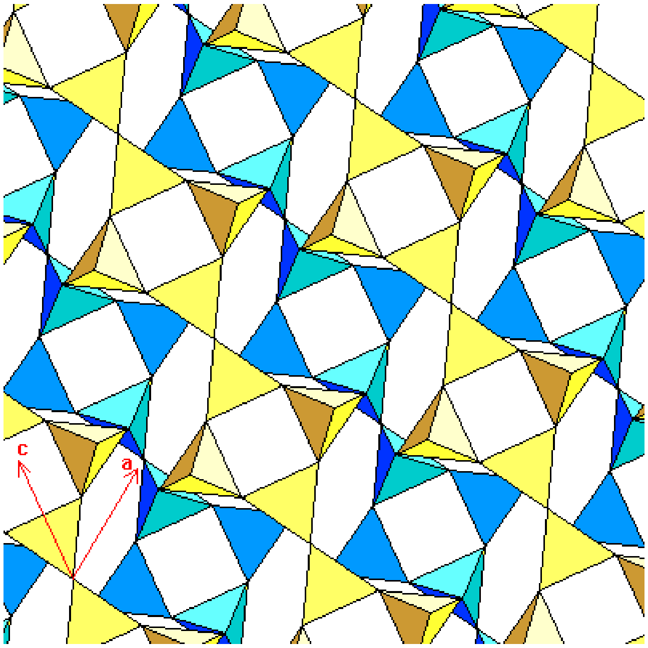
Double chains include the amphiboles (hornblende).



Phyllosilicates: these are sheets of polymerized silicate tetrahedral. The layers are bonded to each other with weak van der Waals bonds, making them easy to split from one another. This includes the micas (biotite, muscovite) and the clay minerals.



Tectosilicates: the tetrahedral are bound together in a three-dimensional network with a ratio of two oxygens for each silicon atom. Quartz (SiO_2) and feldspar are examples of these silicates.



http://www.uwgb.edu/dutchs/PETROLGY/FeldsparStruct.HTM

Clay Minerals: the clay minerals are hydrous aluminum silicates and are classified as phyllosilicates (or layer silicates). There is considerable variation in chemical and physical properties within this family of minerals, but most have a common platy morphology and perfect cleavage.

Clay minerals contain tetrahedral and octahedral sheets.

Tetrahedral Sheets: dominated by Si^{4+} but Al^{3+} substitutes frequently (and Fe^{3+} occasionally).

Octahedral Sheets: this can be thought of as two planes of closest-packed oxygen atoms with cations occupying the wholes. The cations are generally Al^{3+}, Mg^{2+}, Fe^{2+}, or Fe^{3+}.

1:1 layer structure: one tetrahedral layer bonds to one octahedral layer
2:1 layer structure: an octahedral layer is sandwiched between two tetrahedral layers.

1:1 Layer Structure

Kaolin (Serpentine) Group: they have a ratio of 1T:1O

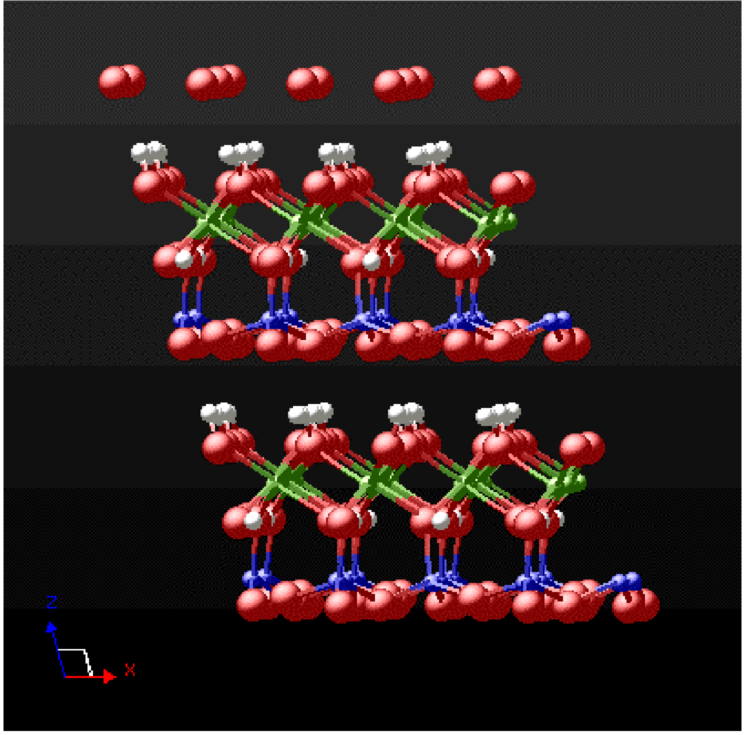
$Al_4Si_4O_{10}(OH)_8$

No substitution (no fluxes)

Kaolin is found nearly everywhere. It is produced within soils in warm moist regions. Also a weathering product (hydrothermal alteration) of feldspars.

Ballclays: yield a white product when fired
Fireclays: similar ballclays but found directly beneath coals

Flintclays: clay that is hard, smooth, and breaks with conchoidal fracture but are not plastic when wet

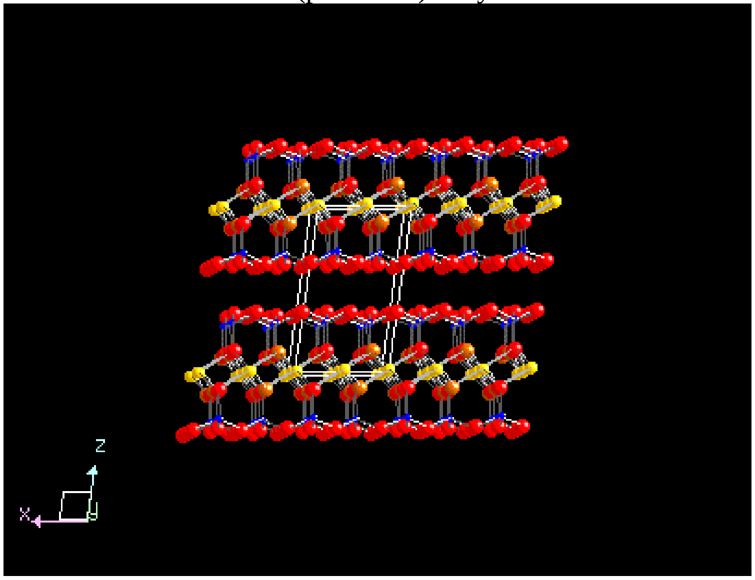


http://www.gly.uga.edu/schroeder/geol6550/CM07.html
(Bish, D., 1993)

2:1 Layer Structure

Talc (pyrophillite) Group: they have a ratio of 2T:1O

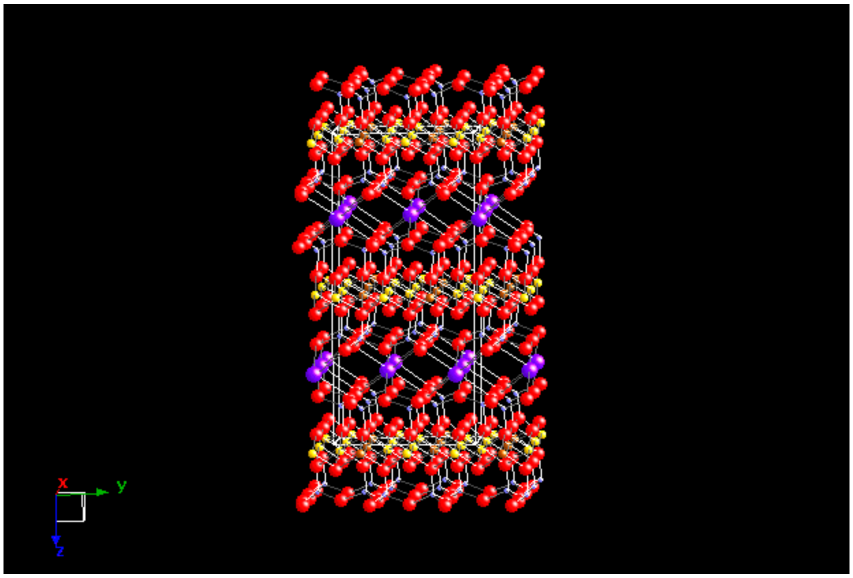
$Mg_3Si_4O_{10}(OH)_2$
Little or no ionic substitution
Forms when ultramafics (peridotite) is hydrated



Biotite: they have a ratio of 2T:1O also

$KMg_2FeAlSi_3O_{10}(OH)_2$

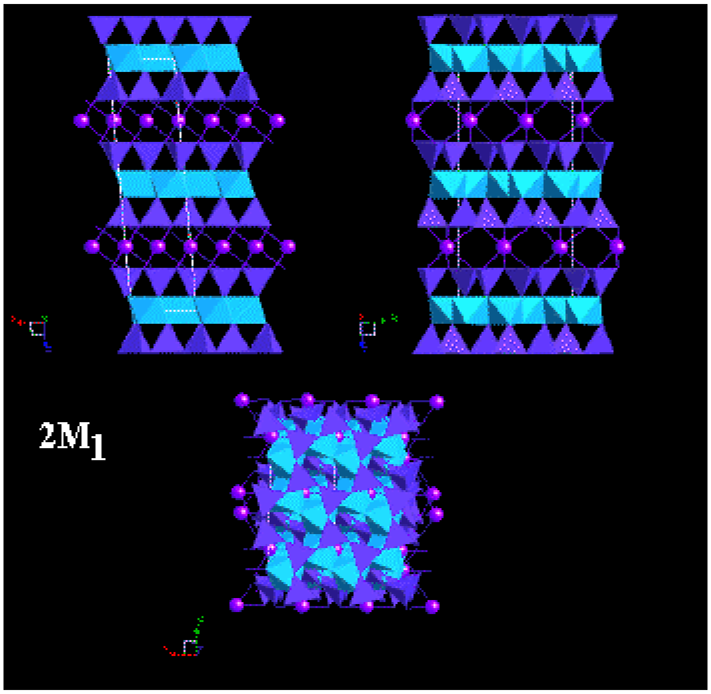
This mica is commonly found in igneous (see igneous mineralogy) and metamorphic rocks.



Illite: also has a 2T:1O structure and is similar to muscovite. This is a very common clay mineral

$K_{0.75}Al_{1.3}Mg_{0.25}Fe^{+3}_{0.25}Si_{3.7}Al_{0.3\;10}(OH)_2$

Illite forms in weathering, hydrothermal alteration, diagenic, and metamorphic environments.



Montmorillonite:

$Na_{0.3}Al_{1.7}Mg_{0.3}Si_4O_{10}(OH)_2$
Bentonite is a genetic rock term that contains significant quantities of montmorillonite. Bentonites are usually found as distinctive beds formed by the deposition and alteration of volcanic ash. Typically, they are composed of montmorillonite, but also can contain glass, mixed-layer clays, illite, kaolinite, quartz, zeolites, carbonates....

Firing Clay and Phase Changes

Traditional triaxial whitewares consist of clay, feldspar, and quartz (SiO_2). The phrase "triaxial whiteware" refers to a three component composition consisting of clay, silica (or quartz) and feldspar (traditional formulation). Clay by itself is very fine grained, and shrinks too much to be used alone. We add a filler to limit shrinkage. Clay is also a very refractory material. We add a flux to reduce the firing temperature.

Quartz is a filler in a traditional triaxial whiteware. In the formulation (recipe) used in our laboratory, we substitute alumina (Al_20_3) for the silica because quartz undergoes shrinkage during cooling that results in microcracks, thus reducing the strength of the fired product. Filler is added to a triaxial whiteware to limit firing and drying shrinkage.

Feldspar is a flux. A flux reduces the firing temperature required to create a ceramic object from its constituent raw materials.

During firing, complicated chemical and structural changes occur to the raw materials. These changes can best be summarized schematically on the firing reactions diagram below. Refer to the diagram and not the following points.

- On a volume basis, constituents of the ware at room temperature are:
    - Clay- about 35%
    - feldspar- about 15%
    - quartz- about 20%
    - open porosity- about 30%
- As temperature increases from room temperature to 100 degrees C, adsorbed water is lost from the surface of the clay particles (endothermic reaction).
- As the temperature climbs from 100 degrees C to about 700 degrees C, organic materials burn out of the clay (exothermic).
- From about 450 degrees C to 700 degrees C, dehydroxylation (loss of lattice water) of the kaolinite transforms it to metakaolin. A slight volume reduction occurs due to the collapse of the kaolinite crystal structure with the loss of water.
- At 573 degrees C, low quartz transforms (on heating) to high quartz.
- At 980 degrees C, metakaolin transforms to the so-called spinel phase.
- Somewhere above 1000 degrees C, feldspar melts, porosity begins to disappear, and the silica exsolved in the metakaolin to spinel transformation begins to form glass.
- Glass flows to fill more porosity, the the product shrinks.
- At 1050 degrees C and above, mullite forms from the spinel form of clay. Mullite continues to increase (grow from the melt) as temperature increases. Mullite is stable until 1540 degrees C, at which temperature it melts.
- As the feldspar melts, a soda-rich (Na_2O) glass results. This glass attacks the quartz and incorporates the silica exsolved from spinel during mullite formation into even more glass.
- Porosity continues to decrease. As gas is trapped by the flow of glass, closed bubbles are formed. finally, only closed porosity remains, and firing shrinkage is complete.
- On a volume basis, the constituents of the ware after firing are:
    - mullite- about 25%
    - glass- about 55%

  - quartz- about 15%
  - closed porosity- about 5%

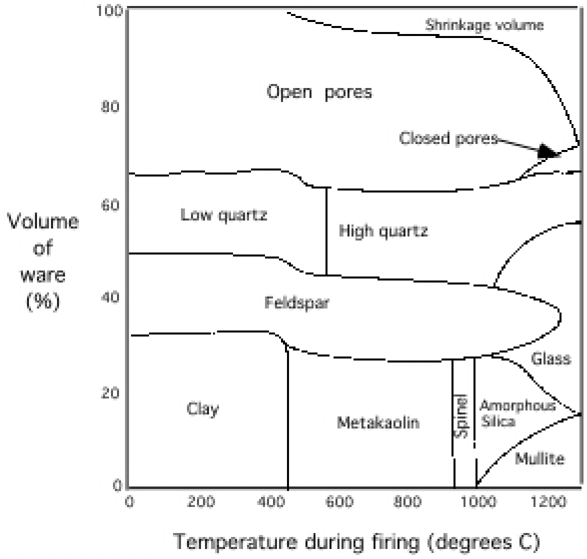


Illustration of Firing Reactions in a Traditional Triaxial Whiteware

Homework: make a model of a kaolin mineral (TO)