

EENS 211	Mineralogy
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<b>Weathering &amp; Clay Minerals</b>	

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Geologists recognize two categories of weathering processes

1. **Physical Weathering** - disintegration of rocks and minerals by a physical or mechanical process.
2. **Chemical Weathering** - chemical alteration or decomposition of rocks and minerals.

Although we separate these processes, both work together to break down rocks and minerals to smaller fragments or to minerals more stable near the Earth's surface.

### Physical Weathering

Physical weathering takes place by a variety of processes. Among them are:

- Development of **Joints** - Joints are regularly spaced fractures or cracks in rocks that show no offset across the fracture (fractures that show an offset are called faults).
  - Joints form as a result of expansion due to cooling or relief of pressure as overlying rocks are removed by erosion.
  - Joints form free space in rock by which other agents of chemical or physical weathering can enter.
- Crystal Growth - As water percolates through fractures and pore spaces it may contain ions that precipitate to form crystals. As these crystals grow they may exert an outward force that can expand or weaken rocks.
- Heat - Although daily heating and cooling of rocks do not seem to have an effect, sudden exposure to high temperature, such as in a forest or grass fire may cause expansion and eventual breakage of rock. Campfire example.
- Plant and Animal Activities -
  - Plant roots can extend into fractures and grow, causing expansion of the fracture. Growth of plants can break rock - look at the sidewalks of New Orleans for example.
  - Animals burrowing or moving through cracks can break rock.
- **Frost Wedging** - Upon freezing, there is an increase in the volume of the water (that's why we use antifreeze in auto engines or why the pipes break in New Orleans during the rare freeze). As the water freezes it expands and exerts a force on its surroundings. Frost wedging is more prevalent at high altitudes where there may be many freeze-thaw cycles.

## Chemical Weathering

Since many rocks and minerals are formed under conditions present deep within the Earth, when they arrive near the surface as a result of uplift and erosion, they encounter conditions very different from those under which they originally formed. Among the conditions present near the Earth's surface that are different from those deep within the Earth are:

- Lower Temperature (Near the surface  $T = -20$  to  $50^{\circ}\text{C}$ )
- Lower Pressure (Near the surface  $P = 1$  to several hundred atmospheres)
- Higher free water (there is a lot of liquid water near the surface, compared with deep in the Earth)
- Higher free oxygen (although  $\text{O}_2$  is the most abundant element in the crust, most of it is tied up in silicate and oxide minerals - at the surface there is much more free oxygen, particularly in the atmosphere).

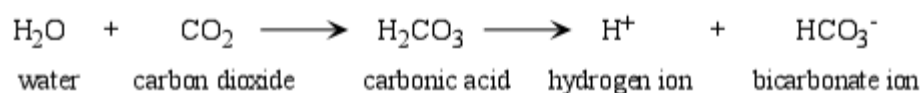
Because of these differing conditions, minerals in rocks react with their new environment to produce new minerals that are stable under conditions near the surface. Minerals that are stable under P, T,  $\text{H}_2\text{O}$ , and  $\text{O}_2$  conditions near the surface are, in order of most stable to least stable:

- Iron oxides, Aluminum oxides - such as hematite  $\text{Fe}_2\text{O}_3$ , and gibbsite  $\text{Al}(\text{OH})_3$ .
- Quartz\*
- Clay Minerals
- Muscovite\*
- Alkali Feldspar\*
- Biotite\*
- Amphiboles\*
- Pyroxenes\*
- Ca-rich plagioclase\*
- Olivine\*

Note the minerals with \*. These are igneous minerals that crystallize from a liquid. Note the minerals that occur low on this list are the minerals that crystallize at high temperature from magma. The higher the temperature of crystallization, the less stable are these minerals at the low temperature found near the Earth's surface.

The main agent responsible for chemical weathering reactions is water and weak acids formed in water.

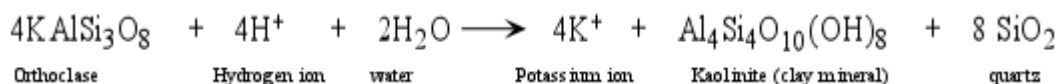
- An acid is solution that has abundant free  $\text{H}^+$  ions.
- The most common weak acid that occurs in surface waters is carbonic acid.
- Carbonic acid is produced in rainwater by reaction of the water with carbon dioxide ( $\text{CO}_2$ ) gas in the atmosphere.



$\text{H}^+$  is a small ion and can easily enter crystal structures, releasing other ions into the water.

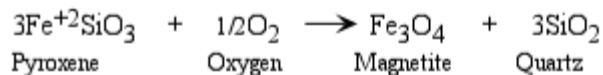
### Types of Chemical Weathering Reactions

- **Hydrolysis** -  $\text{H}^+$  or  $\text{OH}^-$  replaces an ion in the mineral. Example:

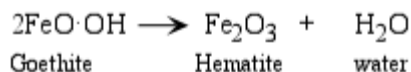


- Leaching - ions are removed by dissolution into water. In the example above we say that the  $\text{K}^+$  ion was leached.

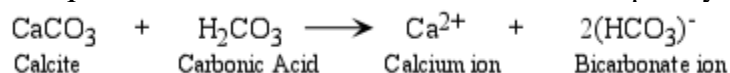
- **Oxidation** - Since free oxygen ( $\text{O}_2$ ) is more common near the Earth's surface, it may react with minerals to change the oxidation state of an ion. This is more common in Fe (iron) bearing minerals, since Fe can have several oxidation states, Fe,  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$ . Deep in the Earth the most common oxidation state of Fe is  $\text{Fe}^{+2}$ .



- **Dehydration** - removal of  $\text{H}_2\text{O}$  or  $\text{OH}^-$  ion from a mineral.



- **Complete Dissolution** - all of the mineral is completely dissolved by the water.



### Weathering of Common Rocks

Rock	Primary Minerals	Residual Minerals*	Leached Ions
Granite	Feldspars	Clay Minerals	$\text{Na}^+$ , $\text{K}^+$
	Micas	Clay Minerals	$\text{K}^+$
	Quartz	Quartz	---
	Fe-Mg Minerals	Clay Minerals + Hematite + Goethite	$\text{Mg}^{+2}$
Basalt	Feldspars	Clay Minerals	$\text{Na}^+$ , $\text{Ca}^{+2}$
	Fe-Mg Minerals	Clay Minerals	$\text{Mg}^{+2}$
	Magnetite	Hematite, Goethite	---
Limestone	Calcite	None	$\text{Ca}^{+2}$ , $\text{CO}_3^{-2}$

\*Residual Minerals = Minerals stable at the Earth's surface and left in the rock after weathering.

As you can see from the above, clay minerals and oxide minerals (including quartz) are the most common byproducts of chemical weathering. Thus clay minerals and quartz are the most abundant contributors to clastic sediment and soil. We here discuss the structure, properties, occurrence, and identification of clay minerals, but first we need to discuss the phyllosilicates in general.

## Clay Minerals

Clay minerals are an important group of minerals because they are among the most common products of chemical weathering, and thus are the main constituents of the fine-grained sedimentary rocks called mudrocks (including mudstones, claystones, and shales). In fact clay minerals make up about 40% of the minerals in sedimentary rocks. In addition, clay minerals are the main constituent of soils. Understanding of clay minerals is also important from an engineering point of view, as some minerals expand significantly when exposed to water. Clay minerals are used extensively in the ceramics industry and are thus important economic minerals.

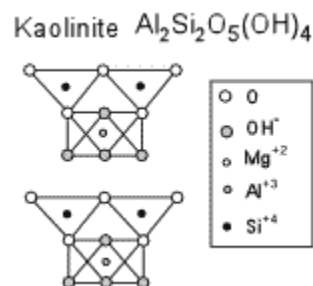
Based on their structures and chemical compositions, the clay minerals can be divided in to three main classes:

1. The kandites based on a structure similar to Kaolinite
2. The smectites based on a structure similar to Pyrophyllite
3. The illites based on a structure similar to Muscovite

Each of these are formed under different environmental and chemical conditions.

### Kandites

The kandites are clays that show a T-O structure, with the octahedral layer similar to the gibbsite structure. Since the layers are electronically neutral, the bonding between layers is by weak van de Waals bonds. Kaolinite is the most common of this group and has the chemical formula  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . Other kandites with similar structures are Anauxite, Dickite, and Nacrite.



Kaolinite is formed by weathering or hydrothermal alteration of aluminosilicate minerals. Thus, rocks rich in feldspar commonly weather to kaolinite. In order to form, ions like Na, K, Ca, Mg, and Fe must first be leached away by the weathering or alteration process. This leaching is favored by acidic conditions (low pH). Granitic rocks, because they are rich in feldspar, are a common source for kaolinite.

Halloysite, is also a kandite clay, with a structure similar to Kaolinite. However, it has water molecules occurring between the T-O sheets, and has the chemical formula -  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ .

Kaolinite, because it does not absorb water, does not expand when it comes in contact with

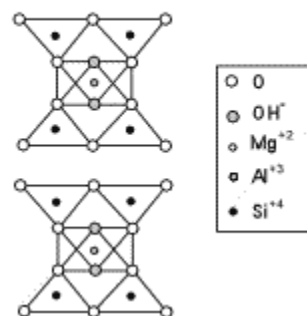
water. Thus, kaolinite is the preferred type of clay for the ceramic industry.

## Smectites

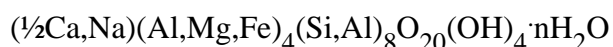
The smectite group of clays has a T-O-T structure that is similar to that of Pyrophyllite, but can also have significant amounts of Mg and Fe substituting into the octahedral layers. Thus, the smectites can be both dioctahedral and trioctahedral.

The most important aspect of the smectite group is the ability for  $\text{H}_2\text{O}$  molecules to be absorbed between the T-O-T sheets, causing the volume of the minerals to increase when they come in contact with water. Thus, the smectites are expanding clays.

Pyrophyllite  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$



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



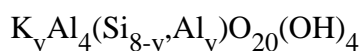
Montmorillinite is the main constituent of Bentonite, derived by weathering of volcanic ash. Montmorillinite can expand by several times its original volume when it comes in contact with water. This makes it useful as a drilling mud (to keep drill holes open), and to plug leaks in soil, rocks, and dams.

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.

Other, less common, members of the smectite group include Beidellite, Hectorite, Nontronite, Sauconite, and Saponite.

## Illites

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

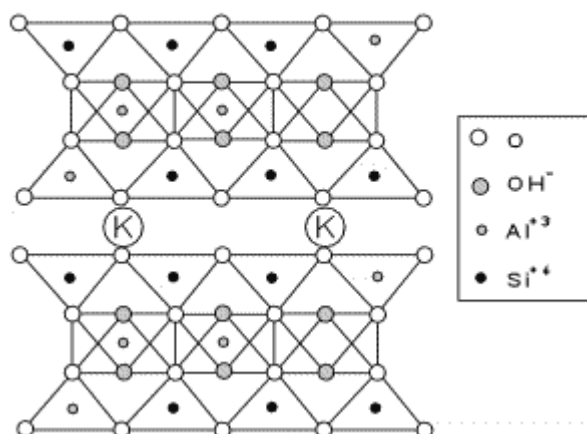


usually with  $1 < y < 1.5$ , but always with  $y < 2$ .

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  $\text{H}_2\text{O}$  into the structure. Thus, the illite clays are non-expanding clays.

Muscovite  $\text{KAl}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2$



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 ancient mudrocks and shales.

### Mixed Layer Clay

Mixed layer clays are common, and consist of clays that change from one type to another through a stacking sequence. The sequences can be ordered and regular, or high unordered and irregular. For example montmorillinite layers can alternate with illite layers in an ordered way, or there can be several layers of montmorillinite with random layers of illite.

### Distinguishing Clay Minerals

Generally, the clay minerals occur as such small mineral grains that they cannot be easily distinguished in either hand specimen or thin section. However, the smectites can be distinguished from the other clays in the field by the "eating test" - place some clay in your mouth. If you can feel it expand as it becomes moistened, then it is one of the smectite clays, and is not a kandite or illite clay.

X-ray techniques, are thus usually required to identify the clay minerals. First, however, the clays have to be separated from other constituents. To do this, we first disaggregate the sample and place it in a settling tube filled with water. Particles will settle in the water according to Stokes Law:

$$V = 2/9(\rho_g - \rho_w) g r^2/\eta$$

where

$V$  = the settling velocity

$\rho_g$  = density of the mineral grain (2.6 - 2.8 g/cm<sup>3</sup> for clay minerals)

$\rho_w$  = density of water (1g/cm<sup>3</sup>)

$g$  = acceleration due to gravity (980 cm/sec<sup>2</sup>)

$r$  = radius of the mineral particle (10<sup>-4</sup> cm for clays)

$\eta$  = viscosity of water (10<sup>-2</sup> gcm/sec<sup>2</sup>)

Usually a disaggregating agent (Calgon) is added to the water to keep the individual particles from adhering to one another. The particles are placed in a large glass cylinder filled with water and the disaggregating agent, and the mixture is stirred.

One then must use Stokes law to figure out how far particles of clay size will settle in a given time. That distance is measured on the cylinder, and that amount of water is then poured off and collected. It is then poured through a filter to separate the clay minerals from the water. The filter is then dried and the clay minerals are placed on a glass slide ready for X-ray diffraction analysis.

Recall that Bragg's Law:

$$n\lambda = 2d \sin \theta$$

allows one to calculate the "d" spacing between lattice planes if the wavelength,  $\lambda$ , of the X-rays is known, and the diffraction angle  $\theta$  is known.

Normally in powder X-ray diffraction studies we would want the mineral grains to be oriented randomly on the glass slide. But for clay minerals, the most diagnostic "d" spacing is between the {001} planes. So, when the grains are placed on the glass slide they are usually placed in a few drops of water so that they will settle onto the slide with their {001} planes parallel to the slide. Thus, when we X-ray them, we get diffraction predominantly off of the {001} planes and can measure the "d" spacing between these planes.

The table below shows the d spacing for the {001} plane as measured for various clay-type minerals. Untreated is for the minerals in their natural state, Ethylene Glycol values are obtained after treating the minerals in a solution of Ethylene Glycol (the principal ingredient in anti-freeze), and the last column show the effect if the mineral is heated to 550°C after the Ethylene Glycol treatment.

<b>d Spacing on {001} for Clay-Type Minerals (Å)</b>			
<b>Mineral</b>	<b>Untreated</b>	<b>Ethylene Glycol</b>	<b>Heated to 550°C</b>
Kaolinite	7.1	No Change	Destroyed
Montmorillinite	14 - 15	17	9.5
Illite	10	No Change	Little Change
Chlorite	7	No Change	13.2
Mixed Layer	11	12	10

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