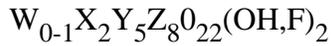


## **Inosilicates (Double Chain Silicates) - The Amphiboles**

The amphibole group of minerals is based on the double-chain silicate structure as shown here.

The basic structural unit is  $(\text{Si}_4\text{O}_{11})^{-6}$ . The structural formula can be written as:



where  $W = Na^{+1}$  or  $K^{+1}$  in the A site with 10 to 12 fold coordination.

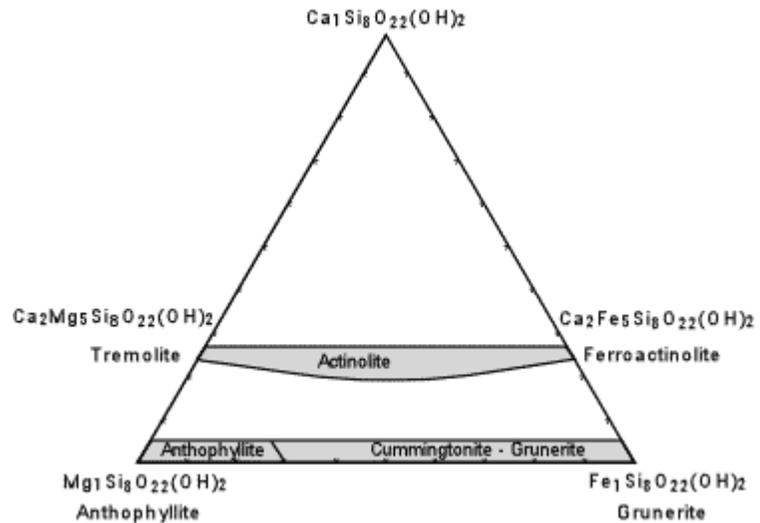
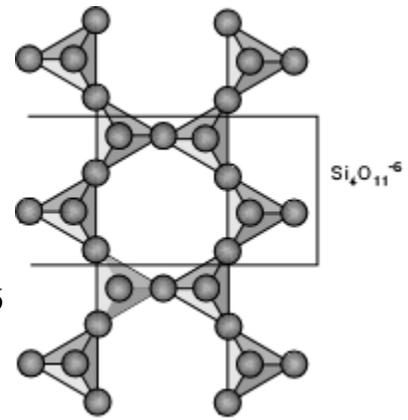
$X = Ca^{+2}, Na^{+1}, Mn^{+2}, Fe^{+2}, Mg^{+2}, Fe^{+3}$ , in an M4 site with 6 to 8 fold coordination.

$Y = Mn^{+2}, Fe^{+2}, Mg^{+2}, Fe^{+3}, Al^{+3}$ . or  $Ti^{+4}$  in an M1 octahedral coordination site.

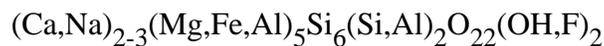
$Z = Si^{+4}$  and  $Al^{+3}$  in the tetrahedral site.

There is complete solid solution between Na and Ca end members and among Mg and Fe end members, with partial substitution of  $Al^{+3}$  for  $Si^{+4}$  in the tetrahedral site, and partial substitution of F for OH in the hydroxyl site.

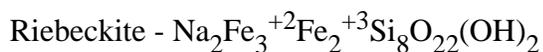
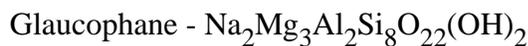
The composition of the common (non-sodic) amphiboles are shown in the diagram here. Note the similarity to the pyroxene compositional diagram, above. Actinolite is the solid solution between Tremolite [ $Ca_2Mg_5Si_8O_{22}(OH)_2$ ] and Ferroactinolite [ $Ca_2Fe_5Si_8O_{22}(OH)_2$ ]. Cummingtonite - Grunerite is a solid solution between Anthophyllite [ $Mg_7Si_8O_{22}(OH)_2$ ] and Grunerite [ $Fe_7Si_8O_{22}(OH)_2$ ].



Hornblende is the most common amphibole and has more in common with the Tremolite - Ferroactinolite series, with Al substituting into the Y sites and the tetrahedral site. It thus has the complicated formula:

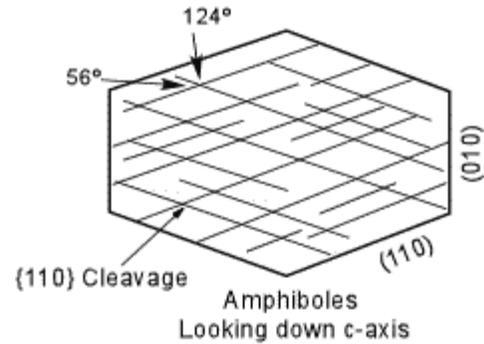


The sodic amphiboles have the following formulae:



Arfvedsonite -  $\text{NaNa}_2\text{Fe}_4^{+2}\text{Fe}^{+3}\text{Si}_8\text{O}_{22}(\text{OH})_2$

All of the amphiboles except Anthophyllite are monoclinic, and all show the excellent prismatic cleavage on {110}. The angles between the cleavages, however are  $56^\circ$  and  $124^\circ$  making all amphiboles easy to distinguish from the pyroxenes. Looking at faces that show only a single cleavage trace would show inclined extinction, except in Anthophyllite.



### Occurrence and Distinction of the Amphiboles

**Tremolite** - Occurs almost exclusively in low grade metamorphic rocks, particularly those with a high Ca concentration, such as meta-dolomites, meta-ultrabasic rocks. Tremolite in hand specimen is white in color and shows a fibrous habit and the characteristic amphibole cleavage. In thin section it is distinguished from wollastonite and diopside by its amphibole cleavage. In thin section it is clear with no pleochroism, which distinguishes it from other amphiboles. It shows high relief, inclined extinction, and is optically negative with a 2V of about  $85^\circ$ .

**Actinolite** - Also occurs almost exclusively in low grade metamorphic rocks, particularly in meta-basalts and meta-gabbros where it is commonly associated with chlorite. It is green in hand specimen and shows the characteristic amphibole cleavage, usually showing an elongated habit. In thin section it shows a characteristic pale yellow to green pleochroism, has high relief, and is optically negative with a 2V of  $60$  to  $85^\circ$ .

**Hornblende** - is a common mineral in both igneous and metamorphic rocks. In igneous rocks it is found in andesites, dacites, and rhyolites, as well as in gabbros, diorites, and granites. In metamorphic rocks it is a common constituent of meta-basalts that have been metamorphosed to intermediate grades of regional metamorphism (amphibolites). It is also found in some ultrabasic rocks. In hand specimen it is dark brown to black in color and shows the characteristic amphibole cleavage. In thin section, it shows high relief with a characteristic green - brown - yellow pleochroism. Optic sign and 2V angle cover a wide range and not very useful in the distinction of hornblende.

**Basaltic Hornblende (also called Oxy-hornblende)**- is a dark brown to reddish brown variety of hornblende that results from oxidation during crystallization of basalts, andesites, dacites, and rhyolites. It usually has a dark reaction rim that consists of opaque oxide, and is characteristically pleochroic in yellow to brown to reddish brown colors.

**Anthophyllite** - does not occur in igneous rocks, but is a constituent of metamorphic rocks. It is the only orthorhombic amphibole so it is easily characterized by its parallel extinction relative to the {110} cleavage.

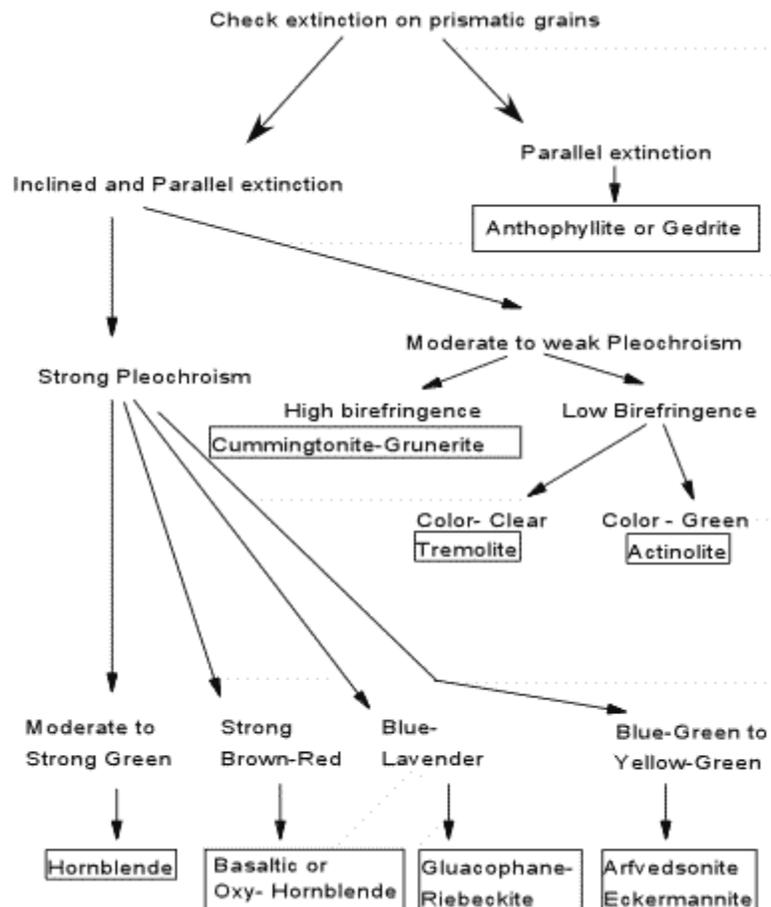
**Cummingtonite - Grunerite** - is more common in metamorphosed igneous rocks where members of the series occur with hornblende. It has been found in siliceous volcanic rocks as well. Cummingtonite is optically positive, while grunerite is optically negative.

Members of this series can be distinguished from orthorhombic Anthophyllite by the inclined extinction of the monoclinic Cummingtonite-Grunerite series, and can be distinguished from tremolite and actinolite by the higher refractive indices and higher birefringence of the Cummingtonite Grunerite series.

**Glaucophane - Riebeckite** - Glaucophane is a common mineral in blueschist facies metamorphic rocks that result from low temperature, high pressure metamorphism along ancient subduction zones. Riebeckite is found in alkali granites, syenites, and peralkaline rhyolites. Glaucophane is easily distinguished from the other amphiboles by its characteristic blue-lavender pleochroism. Glaucophane is length slow, whereas Riebeckite is length fast.

**Arfvedsonite** - occurs most commonly in peralkaline volcanic rocks and alkaline plutonic igneous rocks, where it typically occurs with the sodic pyroxene aegerine. Its blue green to yellow green pleochroism distinguish it from the other amphiboles.

The chart below, also found in your lab assignments, summarizes the properties used to distinguish the amphiboles.



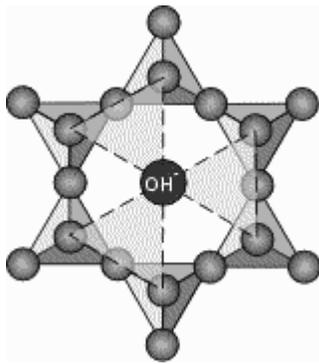
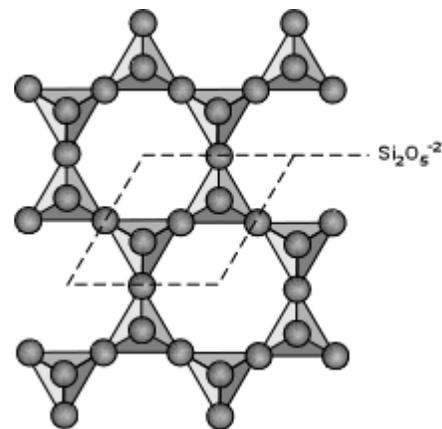
EENS 2110	Mineralogy
Tulane University	Prof. Stephen A. Nelson
<b>Phyllosilicates (Micas, Chlorite, Talc, &amp; Serpentine)</b>	

This document last updated on 18-Aug-2015

### Phyllosilicates (Sheet Silicates)

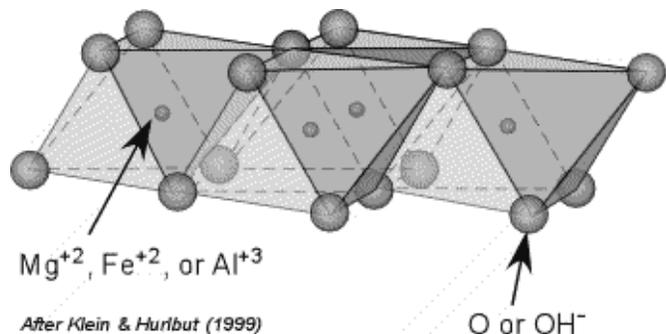
The phyllosilicates, or sheet silicates, are an important group of minerals that includes the micas, chlorite, serpentine, talc, and the clay minerals. Because of the special importance of the clay minerals as one of the primary products of chemical weathering and one of the more abundant constituents of sedimentary rocks, they will be discussed in more detail in the next lecture.

The basic structure of the phyllosilicates is based on interconnected six member rings of  $\text{SiO}_4^{-4}$  tetrahedra that extend outward in infinite sheets. Three out of the 4 oxygens from each tetrahedra are shared with other tetrahedra. This leads to a basic structural unit of  $\text{Si}_2\text{O}_5^{-2}$ .



Most phyllosilicates contain hydroxyl ion,  $\text{OH}^-$ , with the OH located at the center of the 6 membered rings, as shown here. Thus, the group becomes  $\text{Si}_2\text{O}_5(\text{OH})^{-3}$ . When other cations are bonded to the  $\text{SiO}_4$  sheets, they share the apical oxygens and the (OH) ions which bond to the other cations in octahedral coordination. This forms a layer of cations, usually  $\text{Fe}^{+2}$ ,  $\text{Mg}^{+2}$ , or  $\text{Al}^{+3}$ , that occur in octahedral coordination with the O and OH ions of the tetrahedral layer. As shown, here, the triangles become the faces of the octahedral groups that can bind to the tetrahedral layers.

The octahedral layers take on the structure of either Brucite [ $\text{Mg}(\text{OH})_3$ ], if the cations are +2 ions like  $\text{Mg}^{+2}$  or  $\text{Fe}^{+2}$ , or Gibbsite [ $\text{Al}(\text{OH})_3$ ], if the cations are +3 like  $\text{Al}^{+3}$ . In the brucite structure, all octahedral sites are occupied and all anions are  $\text{OH}^{-1}$ . In the Gibbsite structure every 3<sup>rd</sup> cation site is unoccupied and all anions are  $\text{OH}^{-1}$ .



This gives rise to 2 groups of sheet silicates:

1. The **trioctahedral** sheet silicates where each O or OH ion is surrounded by 3 divalent cations, like  $Mg^{+2}$  or  $Fe^{+2}$ .
2. The **dioctahedral** sheet silicates where each O or OH ion is surrounded by 2 trivalent cations, usually  $Al^{+3}$ .

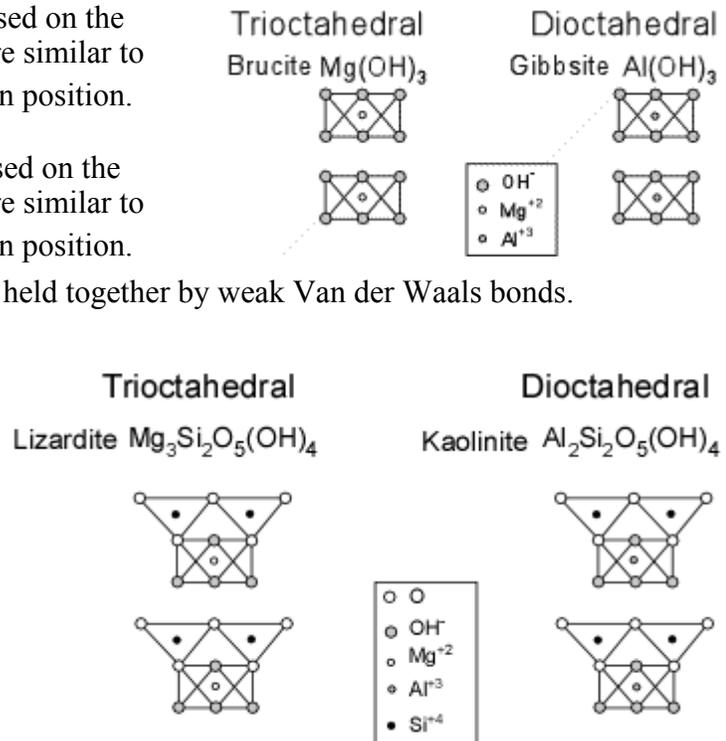
We can build the structures of the various sheet silicates by starting with the octahedral layers similar to the structures of brucite or gibbsite, as shown below.

The trioctahedral phyllosilicates are based on the structure where the octahedral layers are similar to brucite, where  $Mg^{+2}$  occupies the cation position.

The dioctahedral phyllosilicates are based on the structure where the octahedral layers are similar to gibbsite, where  $Al^{+3}$  occupies the cation position.

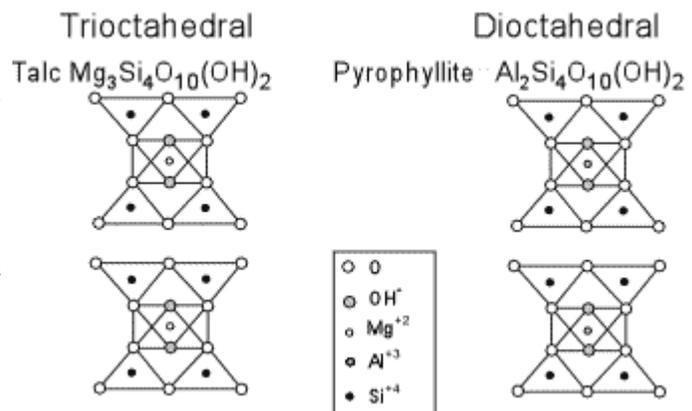
The octahedral sheets in both cases are held together by weak Van der Waals bonds.

If we start with the brucite and gibbsite structures shown above, and replace 2 of the OH ions with O, where the Oxygens are now the apical Oxygens of the tetrahedral sheets, then we get the structure of the serpentine mineral, Lizardite, if the octahedral layer is trioctahedral, containing  $Mg^{+2}$ . If the octahedral layer is dioctahedral, containing  $Al^{+3}$ , the structure of the clay mineral Kaolinite, is obtained.

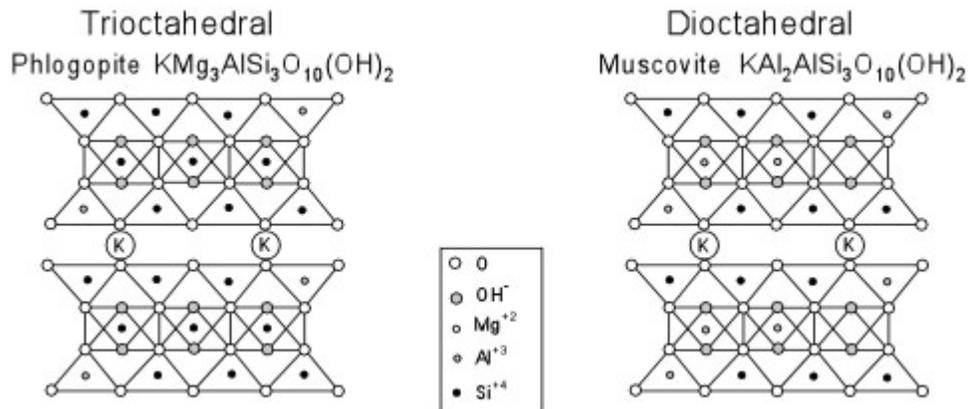


This leads to a tetrahedral - octahedral (T-O) structure, where each T-O layer is bonded to the top (or bottom) of another T-O layer by Van der Waals bonds.

If 2 more of the OH ions in the octahedral layer are replaced by O, and these O become the apical Oxygens for another tetrahedral layer, then this builds the trioctahedral phyllosilicate talc or the dioctahedral pyrophyllite. This becomes a T-O-T layer that can bond to other T-O-T layers by weak Van der Waals bonds.

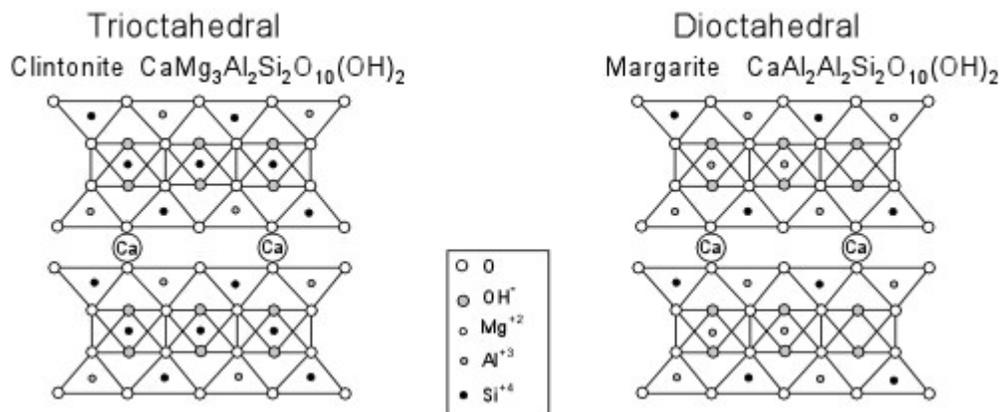


If an  $\text{Al}^{+3}$  is substituted for every 4<sup>th</sup>  $\text{Si}^{+4}$  in the tetrahedral layer, this causes an excess -1 charge in each T-O-T layer. To satisfy the charge,  $\text{K}^{+1}$  or  $\text{Na}^{+1}$  can be bonded between 2 T-O-T sheets in 12-fold coordination.



For the trioctahedral sheet silicates this becomes Phlogopite (Mg-biotite), and for the dioctahedral sheet silicates this becomes Muscovite. This makes a T-O-T - T-O-T layer that, again can bind to another T-O-T - T-O-T layer by weak Van der Waals bonds. It is along these layers of weak bonding that the prominent  $\{001\}$  cleavage in the sheet silicates occurs.

Replacing 2 more  $\text{Si}^{+4}$  ions with  $\text{Al}^{+3}$  ions in the tetrahedral layer results in an excess -2 charge on a T-O-T layer, which is satisfied by replacing the  $\text{K}^{+1}$  with  $\text{Ca}^{+2}$ .



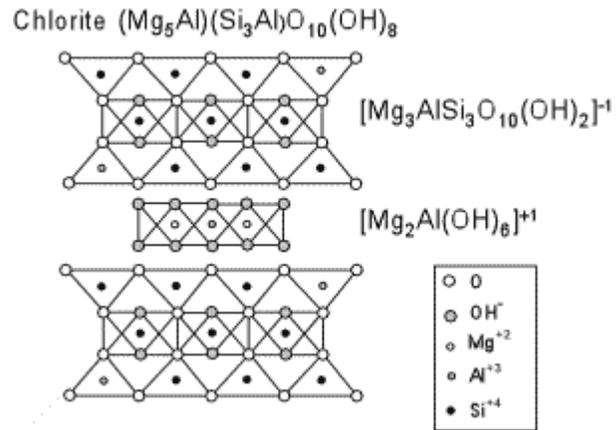
This results in the trioctahedral sheet silicate - Clintonite and the dioctahedral sheet silicate - Margarite.

Because of the differences in charge balance between the trioctahedral and dioctahedral sheet silicates, there is little solid solution between the two groups. However, within the trioctahedral sheet silicates there is complete substitution of  $\text{Fe}^{+2}$  for  $\text{Mg}^{+2}$  and limited substitution of  $\text{Mn}^{+2}$  into the octahedral sites. Within the dioctahedral sheet silicates there is limited substitution of  $\text{Fe}^{+3}$  for  $\text{Al}^{+3}$  in octahedral sites. In addition,  $\text{F}^-$  or  $\text{Cl}^-$  can substitute for  $(\text{OH})^-$  in the hydroxyl site. As previously discussed, substitution of  $\text{F}^{-1}$  stabilizes the mineral to higher pressures and temperatures.

Another group of phyllosilicates that is more of a mixture of structural types is the chlorite group. Although chlorite is complex in that the amount of Al that can substitute Mg and Si is

variable, one way of looking at the chlorite structure is shown below.

Here, the chlorite structure is depicted as consisting of a brucite-like layer (with some Al) sandwiched between tetrahedral layers that are similar to phlogopite.



Another important sheet silicate structure is that of vermiculite. This is similar to the talc structure, discussed above, with layers of water molecules occurring between each T-O-T layer.

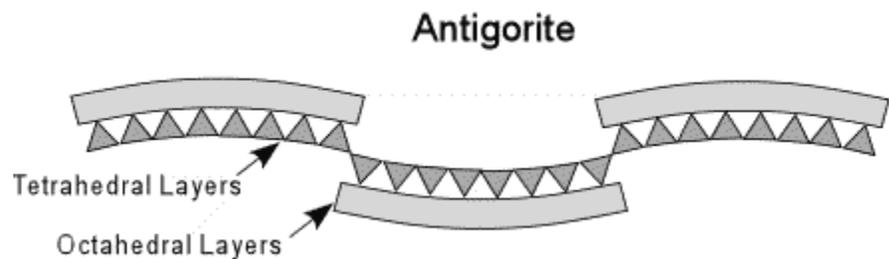
Similarly, insertion of layers of water molecules between the T-O-T sheets of pyrophyllite produces the structure of smectite clays. The vermiculite and smectite groups are therefore expanding type sheet silicates and as the water is incorporated into the structure the mineral increases its volume.

Although we have shown that the octahedral layers fit perfectly between the tetrahedral layers, this is an oversimplification. If the tetrahedral layers were stacked perfectly so that apical oxygens were to occur vertically aligned, then the structure would have hexagonal symmetry. But, because this is not the case, most of the phyllosilicates are monoclinic.

### Serpentine Group

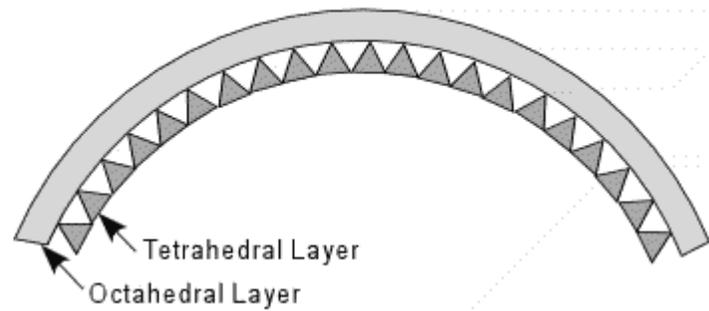
The serpentine group of minerals has the formula -  $Mg_3Si_2O_5(OH)_4$ . Three varieties of serpentine are known. Antigorite and Lizardite are usually massive and fine grained, while Chrysotile is fibrous. As discussed above, the imperfect fit of the octahedral layers and the tetrahedral layers causes the crystal structure to have to bend.

In Antigorite the bending of the sheets is not continuous, but occurs in sets, similar to corrugations, as shown here.

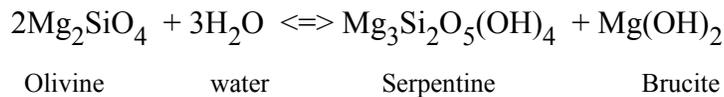


## Chrisotile

In Chrisotile, the bending of the sheets is more continuous, resulting in continuous tubes that give the mineral its fibrous habit. The Chrisotile variety is commonly referred to as asbestos.



*Occurrence* - Serpentine is found as an alteration product of Mg-rich silicates like pyroxene and olivine. It results due to hydration. For example:



Thus, serpentine is commonly found pseudomorphed after olivines and pyroxenes in altered basic and ultrabasic igneous rocks, like altered peridotites, dunites, and sometimes basalts and gabbros. It is commonly associated with minerals like magnesite ( $\text{MgCO}_3$ ), chromite, and magnetite. If the rock is made up almost entirely of serpentine, it is called a *serpentinite*.

*Properties* - Because the serpentines usually occur either as fine-grained aggregates or fibrous crystals, optical properties are difficult to determine. Most of the time, serpentine can be distinguished by its characteristic pseudomorphing of other crystals like olivines and pyroxenes. In hand specimen it generally tends to have a dark green color with a greasy luster. In thin section it is clear to pale green to pale yellow, but does not show pleochroism, shows a generally low relief compared to minerals like olivine and pyroxene with which it is associated, and show very low order interference colors due to its low birefringence.

## Talc

Talc has the chemical formula -  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ . It is probably best known for its low hardness. Although it has a micaceous structure, it is so easily deformed, that crystals are rarely seen.

*Occurrence* - Like serpentine, talc requires an environment rich in Mg. It is therefore found in low grade metamorphic rocks that originated as ultrabasic to basic igneous rocks. Rocks composed almost entirely of talc have a greasy feel and are referred to as *soapstone*.

*Properties* - Talc is most easily distinguished in hand specimen by its low hardness, greasy feel, and association with other Mg-bearing minerals. When crystals are present they show the characteristic micaceous cleavage on {001}. In thin section, talc is colorless, biaxial negative with a 2V of 0 to 30°. Like other sheet silicates, it shows the well developed {001} cleavage. Maximum interference colors, consistent with a birefringence of 0.05 is 3° yellow. Muscovite has a higher birefringence and higher 2V, properties which easily distinguish the 2 minerals.

## Mica Group

The micas can be divided into the dioctahedral micas and the trioctahedral micas, as discussed above. Muscovite, Paragonite, and Margarite are the white micas, and represent the dioctahedral group, and Biotite and Clintonite (Xanthophyllite) the black or brown mica, represents the trioctahedral group. Muscovite and Biotite are the most common micas, but the Lithium- rich, pink mica, Lepidolite,  $K(Li,Al)_2AlSi_3O_{10}(OH)_2$  is also common, being found mostly in pegmatites.

### *Muscovite*

Muscovite,  $KAl_3Si_3O_{10}(OH)_2$ , and Paragonite,  $NaAl_3Si_3O_{10}(OH)_2$ , are two potential end members of the solid solution series involving K and Na. But, there is a large miscibility gap between the two end members with Muscovite being between 65% and 100% of K-rich end member, and Paragonite showing compositions between about 80% and 100% of the Na-rich end member.

*Occurrence* - Muscovite is common constituent of Al-rich medium grade metamorphic rocks where is found in Al-rich schists and contributes to the schistose foliation found in these rocks. Muscovite is also found in siliceous, Al-rich plutonic igneous rocks (muscovite granites), but has not been found as a constituent of volcanic rocks. In these rocks it is commonly found in association with alkali feldspar, quartz, and sometimes biotite, garnet, andalusite, sillimanite, or kyanite.

*Properties* - Muscovite is easily identified in hand specimen by its white to sometimes light brownish color and its perfect {001} cleavage. In thin section, the {001} cleavage is easily seen and it's high birefringence is exhibited by the large change in relief on rotation of the stage and it's 2nd to 4th order interference colors. It is clear and shows no pleochroism (which distinguishes it from Biotite), and it is biaxial negative with a 2V between 28 and 50°. One of the most diagnostic properties of the micas, including muscovite, is the mottled or birds-eye extinction exhibited by these minerals.

### *Biotite*

Biotite is a solid solution between the end members Phlogopite  $KMg_3AlSi_3O_{10}(OH)_2$  and Annite  $KFe_3AlSi_3O_{10}(OH)_2$ , although pure Annite does not occur in nature. In addition, small amounts of Na, Rb, Cs, and Ba may substitute for K, and like in other minerals, F can substitute for OH and increase the stability of Biotite to higher temperatures and pressures.

*Occurrence* - Nearly pure phlogopite is found in hydrous ultrabasic rocks like kimberlite, and is also found in metamorphosed dolomites. Biotite, with more Fe-rich compositions is common in dacitic, rhyolitic, and trachytic volcanic rocks, granitic plutonic rocks, and a wide variety of metamorphic rocks. In metamorphic rocks, biotite usually shows a preferred orientation with its {001} forms parallel to the schistose foliation.

*Properties* - In hand specimen, Biotite is brown to black and shows the perfect {001} micaceous cleavage. In thin section, it shows the perfect cleavage and mottled extinction

typical of all micas. Its most characteristic property is its pleochroism, showing yellow to brown to green colors. Hornblende shows similar pleochroic colors, but is distinguished from biotite by the differences in cleavage of the 2 minerals. Biotite is biaxial negative with a low  $2V$  of  $0^\circ$  to  $25^\circ$ .

### **Chlorite Group**

As discussed above, the Chlorite group has a structure that consists of phlogopite T-O-T layers sandwiching brucite-like octahedral layer. There is substantial substitution of Mg for Fe, and Al can substitute for (Mg, Fe) in both the octahedral sites, as well as for Si in the tetrahedral sites. Thus, chlorite can have a rather complicated formula -  $(\text{Mg,Fe,Al})_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_6$ .

*Occurrence*- Chlorite is a common mineral in low grade metamorphic rocks, where it occurs in association with minerals like actinolite, epidote, and biotite. It also forms as an alteration product of pyroxenes, amphiboles, biotite, and garnet in igneous as well a metamorphic rocks.

*Properties* - In hand specimen, chlorite is recognized by its green color, micaceous habit and cleavage, and association with other minerals like actinolite and epidote. In thin section, Chlorite shows low relief and low birefringence, with a characteristic midnight blue to black anomalous interference color. It shows some pleochroism in the range of green to pale yellow. It is easily distinguished from biotite by its lower relief and anomalous interference color.

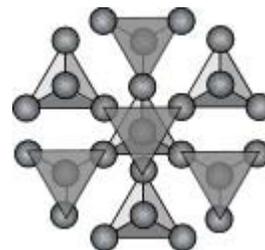
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EENS 2110	Mineralogy
Tulane University	Prof. Stephen A. Nelson
<b>Tectosilicates, Carbonates, Oxides, &amp; Accessory Minerals</b>	

This document last updated on 01-Dec-2014

### Tectosilicates (Framework Silicates)

The tectosilicates or framework silicates have a structure wherein all of the 4 oxygens of  $\text{SiO}_4^{-4}$  tetrahedra are shared with other tetrahedra. The ratios of Si to O is thus 1:2.



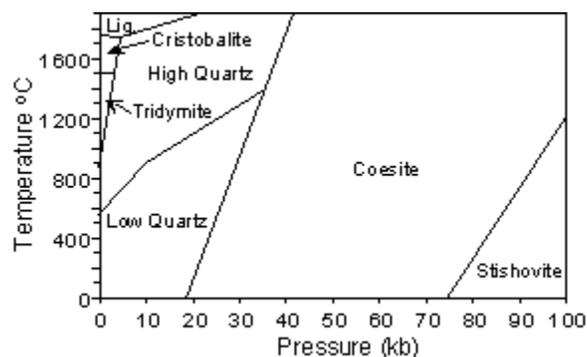
Since the Si - O bonds are strong covalent bonds and since the structure is interlocking, the tectosilicate minerals tend to have a high hardness.

### SiO<sub>2</sub> Minerals

There are nine known polymorphs of SiO<sub>2</sub>, one of which does not occur naturally. These are:

Name	Crystal System	Density (g/cm <sup>3</sup> )	Refractive Index (mean)
Stishovite	Tetragonal	4.35	1.81
Coesite	Monoclinic	3.01	1.59
Low ( $\alpha$ ) Quartz	Hexagonal	2.65	1.55
High ( $\beta$ ) Quartz	Hexagonal	2.53	1.54
Kaetite (synthetic)	Tetragonal	2.50	1.52
Low ( $\alpha$ ) Tridymite	Monoclinic or Orthorhombic	2.26	1.47
High ( $\beta$ ) Tridymite	Hexagonal	2.22	1.47
Low ( $\alpha$ ) Cristobalite	Tetragonal	2.32	1.48
High ( $\beta$ ) Cristobalite	Isometric	2.20	1.48

Stishovite and Coesite are high pressure forms of  $\text{SiO}_2$ , and thus have much higher densities and refractive indices than the other polymorphs. Stishovite is the only polymorph where the Si occurs in 6 fold (octahedral) coordination with Oxygen, and this occurs due to the high pressure under which the mineral forms. Both Stishovite and Coesite have been found associated with meteorite impact structures.



At low pressure with decreasing temperature,  $\text{SiO}_2$  polymorphs change from high Cristobalite - Low Cristobalite - High Tridymite - Low Tridymite - High Quartz - Low Quartz. The high to low transformations are all displacive transformations. Since displacive transformations require little rearrangement of the crystal structure and no change in energy, the high ( $\beta$ ) polymorphs do not exist at the surface of the earth, as they will invert to the low ( $\alpha$ ) polymorphs as temperature is lowered.

Transformations between  $\alpha$  Cristobalite,  $\alpha$  Tridymite, and  $\alpha$  Quartz, however, as well as between the high pressure polymorphs and Quartz, are reconstructive transformations. Since reconstructive transformations require significant structural rearrangement and significant changes in energy, they occur slowly, and the high temperature and high pressure polymorphs can occur as metastable minerals at the Earth's surface.

### ***Quartz***

Quartz is hexagonal and commonly occurs as crystals ranging in size from microscopic to crystals weighing several tons. Where it crystallizes unhindered by other crystals, such as in cavities in rock or in a liquid containing few other crystals, it shows well-developed hexagonal prisms and sometimes showing apparent hexagonal pyramids or dipyramid. When it crystallizes in an environment where growth is inhibited by the surroundings, it rarely shows crystal faces. It is also found as microcrystalline masses, such as in the rock chert, and as fibrous masses, such as in chalcedony.

As visible crystals, Quartz is one of the more common rock forming minerals. It occurs in siliceous igneous rocks such as volcanic rhyolite and plutonic granitic rocks. It is common in metamorphic rocks at all grades of metamorphism, and is the chief constituent of sand. Because it is highly resistant to chemical weathering, it is found in a wide variety of sedimentary rocks.

Several varieties of Quartz can be found, but these are usually only distinguishable in hand specimen.

Rock Crystal - clear Quartz in distinct crystals - usually found growing in open cavities in rock.

Amethyst - violet colored Quartz, with the color resulting from trace amounts of Fe in the crystal.

Rose Quartz - a pink colored variety, that usually does not show crystal faces, the color resulting from trace amounts of  $Ti^{+4}$ .

Smokey Quartz - a dark colored variety that may be almost black, usually forming well-formed crystals. The color appears to result from trace amounts of  $Al^{+3}$  in the structure.

Citrine - a yellow colored variety.

Milky Quartz - a white colored variety with the color being due to fluid inclusions. Milky Quartz is common in hydrothermal veins and pegmatites.

A fibrous variety of Quartz is called Chalcedony. It is usually brown to gray to translucent with a waxy luster. It is found lining or filling cavities in rock where it was apparently precipitated from an aqueous solution. When it shows bands of color, it is commonly called by the following names:

Carnelian - red colored Chalcedony

Chrysoprase - apple-green colored as a result of coloration from NiO.

Agate - alternating curving layers of Chalcedony with different colors or different porosities.

Onyx - alternating layers of Chalcedony of different colors or porosities arranged in parallel planes.

Bloodstone - green Chalcedony containing red spots of jasper (see below).

Very fine grained aggregates of cryptocrystalline quartz makes up rock like Flint and Chert. Flint occurs as nodules in limestone, whereas chert is a layered rock deposited on the ocean floor. The red variety of flint is called Jasper, where the color results from inclusions of hematite.

### *Optical Properties*

Quartz is uniaxial positive with a low relief and low birefringence, thus exhibited only 1<sup>o</sup> gray to 1<sup>o</sup> white interference colors. In thin section it is almost always colorless when viewed without the analyzer inserted. One of its most distinguishing properties in thin section is that it usually has a smooth, almost polished-like surface texture. Quartz is easily distinguished from the Feldspars by the biaxial nature of feldspars, and from Nepheline which is uniaxial

negative. Apatite, has similar birefringence to quartz, but is uniaxial negative and has a very high relief.

In Chalcedony, the fibers are usually elongated perpendicular to the c-crystallographic axis and thus are length fast. Normal quartz, when it show an elongated habit, is elongated parallel to the c axis, and is thus length slow.

### ***Tridymite***

Tridymite is the high temperature polymorph of SiO<sub>2</sub>. Thus, it is only commonly found in igneous rocks that have been cooled rapidly to surface temperatures, preventing the slow transformation to quartz, the stable form of SiO<sub>2</sub> at surface temperatures. Because of this, we only expect to find Tridymite in siliceous volcanic rocks like rhyolites, where it commonly occurs as wedge shaped crystals in cavities in the rock. In volcanic rocks, Tridymite is commonly associated with Cristobalite and Sanidine.

#### *Optical Properties*

Tridymite usually occurs as orthorhombic or monoclinic wedge shaped crystals with a positive 2V between 40 and 90°. The wedge shape of the crystals is the result of twinning on {110}, and usually as 2 to 3 twinned individuals. Although it has similar birefringence to quartz and feldspar, it has lower refractive indices, and thus shows negative relief compared to quartz and feldspars.

### ***Cristobalite***

Cristobalite is also a high temperature SiO<sub>2</sub> polymorph, and thus has a similar occurrence to Tridymite. It also occurs in thermally metamorphosed sandstones. In volcanic rocks it can occur both as a lining in open cavities, and as fine grained crystals in the groundmass of the rock.

#### *Optical Properties*

Cristobalite is tetragonal and thus uniaxial. It has a negative optic sign and shows lower relief than quartz, but has similar birefringence.

### ***Opal***

Opal is amorphous, and thus a mineraloid, with a formula - SiO<sub>2</sub>·nH<sub>2</sub>O.

### **Feldspars**

The feldspars are the most common minerals in the Earth's crust. They consist of three end-members:

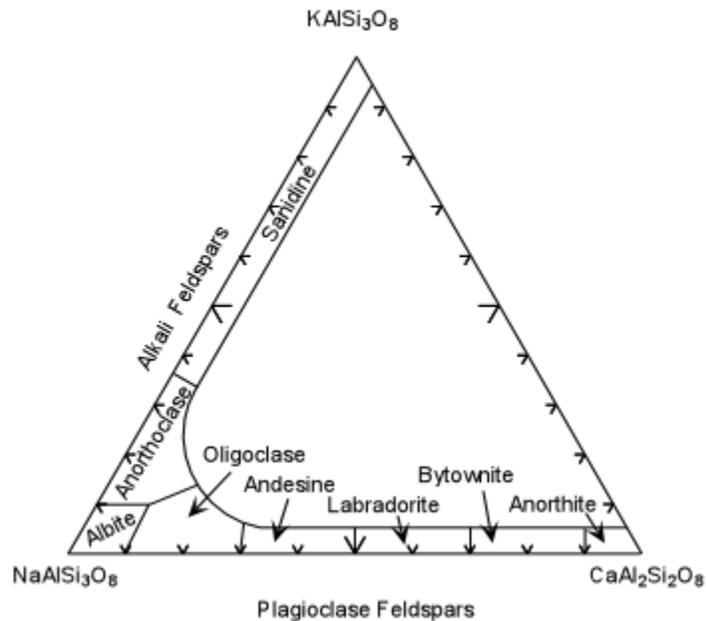
KAlSi<sub>3</sub>O<sub>8</sub> - Orthoclase (or), NaAlSi<sub>3</sub>O<sub>8</sub> - Albite (ab), and CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> -Anorthite (an)

KAlSi<sub>3</sub>O<sub>8</sub> and NaAlSi<sub>3</sub>O<sub>8</sub> form a complete solid solution series, known as the alkali feldspars

and  $\text{NaAlSi}_3\text{O}_8$  and  $\text{CaAl}_2\text{Si}_2\text{O}_8$  form a complete solid solution series known as the plagioclase feldspars.

The feldspars have a framework structure, consisting of  $\text{SiO}_4$  tetrahedra sharing all of the corner oxygens. However, in the alkali feldspars 1/4 of the  $\text{Si}^{+4}$  ions are replaced by  $\text{Al}^{+3}$  and in the plagioclase feldspars 1/4 to 1/2 of the  $\text{Si}^{+4}$  ions are replaced by  $\text{Al}^{+3}$ . This allows for the cations  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Ca}^{+2}$  to be substituted into void spaces to maintain charge balance.

Compositions of natural feldspars are shown in the diagram below based on the 3 components -  $\text{NaAlSi}_3\text{O}_8$ , - Albite (ab),  $\text{KAlSi}_3\text{O}_8$  - Orthoclase (or) and  $\text{CaAl}_2\text{Si}_2\text{O}_8$ . The Alkali Feldspars form a complete solid solution between ab and or, with up to 5% of the an component. The high temperature more K-rich variety is called Sanidine and the more Na-rich variety is called anorthoclase.

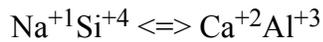


The plagioclase feldspars are a complete solid solution series between ab and an, and can contain small amounts of the or component. Names are given to the various ranges of composition, as shown here in the diagram are:

- Albite -  $\text{ab}_{90}$  to  $\text{ab}_{100}$
- Oligoclase -  $\text{ab}_{70}$  to  $\text{ab}_{90}$
- Andesine -  $\text{ab}_{50}$  to  $\text{ab}_{70}$
- Labradorite -  $\text{ab}_{30}$  to  $\text{ab}_{50}$
- Bytownite -  $\text{ab}_{10}$  -  $\text{ab}_{30}$
- Anorthite -  $\text{ab}_0$  to  $\text{an}_{10}$

### Plagioclase Feldspars

Plagioclase is the most common feldspar. It forms initially by crystallization from magma. The plagioclase solid solution series is coupled solid solution where the substitution is:

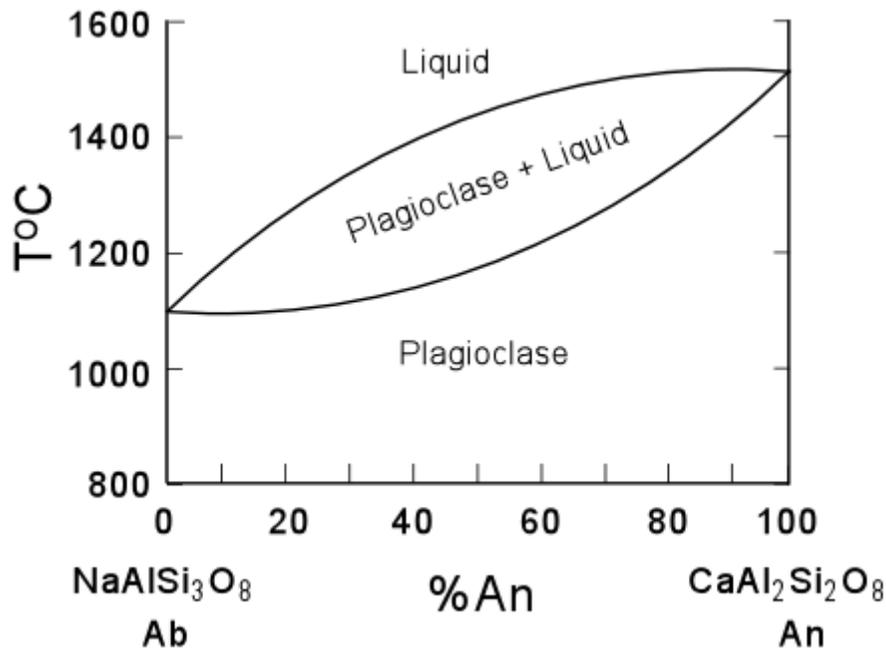


Thus, the general chemical formula for plagioclase can be written as:



where x is between 0 and 1.

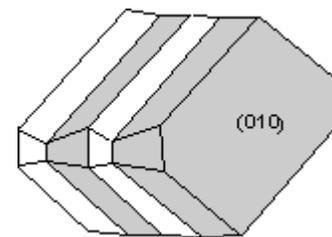
The phase diagram for the plagioclase series is shown here, and shows that the Anorthite component has a higher melting temperature than the Albite component. Thus, on crystallization, higher temperatures will favor more An-rich plagioclase which will react with the liquid to produce more Ab-rich plagioclase on cooling.



Plagioclase occurs in basalts, andesites, dacites, rhyolites, gabbros, diorites, granodiorites, and granites. In most of these igneous rocks, it always shows the characteristic albite twinning. Plagioclase also occurs in a wide variety of metamorphic rocks, where it is usually not twinned. In such rocks where the plagioclase is not twinned, it is difficult to distinguish from the alkali feldspars. Plagioclase can be a component of clastic sedimentary rocks, although it is less stable near the Earth's surface than alkali feldspar and quartz, and usually breaks down to clay minerals during weathering.

### *Properties*

In hand specimen, plagioclase is most commonly white colored and shows perfect {100} and good {010} cleavage. It is most easily identified and distinguished from quartz, sanidine, orthoclase, and microcline, by its common polysynthetic twinning on {010}. If this twinning is not present, plagioclase can still be distinguished from quartz by its cleavage, but cannot easily be distinguished from the alkali feldspars. If both plagioclase and alkali feldspar occur in the same rock, the two can usually be distinguished by differences in color or differences in the extent of weathering.



In thin section, plagioclase commonly shows the characteristic albite polysynthetic twinning. This twinning is the most characteristic identifying feature of plagioclase, and makes its identification easy when present. Although some cross-hatched twinning may also occur in plagioclase, it is always very simple with only one or two cross twins per grain. Thus, be careful not to identify plagioclase as microcline. The cross-hatched twinning in microcline is always much more complex.



Plagioclase often shows zoning. This is exhibited by the extinction position changing from the rim to the core of the crystal. Remember that zoning is caused by incomplete reaction of crystals with liquid during cooling of a solid solution. Often the zoning is very complex, and is sometimes oscillatory. Normal zoning would show Ca - rich cores and Na - rich rims, but reverse zoning is possible under certain conditions.

In metamorphic rocks plagioclase may not show twinning making it difficult to distinguish from orthoclase. The two can be distinguished by staining the thin section with stains that make the K-feldspars one color and the more Ca-rich feldspars another color. In this class, we will not have time to look at these staining techniques. You should, however, be aware, that such staining techniques exist, so that if you need them in the future, you can use them.

The optical properties of the plagioclase series vary widely as a function of composition of the plagioclase. In general, all plagioclases show low order interference colors, and thus, low birefringence. Optic sign and 2V vary widely, and are thus, not very distinguishing features of plagioclase. Although, as you have seen in lab, it is possible to estimate the composition of plagioclase from a combination of extinction angle and twinning.

### **Alkali Feldspars (K,Na)AlSi<sub>3</sub>O<sub>8</sub>**

As an alkali feldspar cools from high temperature to lower temperature, the crystal structure changes from that of sanidine, which is monoclinic, through orthoclase, also monoclinic, but with a different crystal structure than sanidine, to microcline, which is triclinic. These transformations are order-disorder transformations, and thus require large amounts of time. Furthermore, if the feldspar is allowed to cool very slowly, then exsolution will occur, and the solid solution will separate into a Na-rich phase and a K-rich phase. Thus, one expects to find sanidine in rocks that were cooled very rapidly from high temperature, i.e. volcanic rocks. Orthoclase and microcline will be found in plutonic igneous rocks (cooled slowly at depth in the earth) and in metamorphic rocks. In addition, in the plutonic rock types if the cooling takes place slowly enough, then perthitic exsolution lamellae may also form.

All of the alkali feldspars have low relief and low birefringence. Thus the interference colors may range up to 1<sup>o</sup> white. Since this is the same interference color we expect for quartz, care must be taken to avoid confusing feldspars and quartz.

### ***Sanidine***

Sanidine generally occurs with an equant habit (almost square) and shows perfect {001} and {010} cleavages, which readily distinguish it from quartz. Rarely does sanidine show twinning, but when it does, it is usually simple twinning. Optic axis figures will only be found on sections showing both cleavages. Sanidine is optically negative with a 2V of 20 - 50°. This distinguishes it from quartz, which is uniaxial positive, and from the other alkali feldspars which show larger values of 2V.

### ***Orthoclase***

Orthoclase is a common alkali feldspar in granitic rocks and K - Al rich metamorphic rocks. It often shows perfect {001} and {010} cleavages which will distinguish it from quartz. Also, quartz usually shows a smooth surface texture, while orthoclase appears much rougher. Orthoclase is also biaxial, which further distinguishes it from quartz. The 2V of orthoclase varies from 60 to 105°, and thus it may be either positive or negative. The 2V angle distinguishes orthoclase from sanidine, but is otherwise not very useful because of its wide range.

### ***Microcline***

Microcline is the lowest temperature form of alkali feldspar. Upon cooling, orthoclase must rearrange its structure from monoclinic to triclinic. When this happens, twinning usually results. The twinning characteristic of microcline is a combination of albite twinning and pericline twinning. This results in a cross-hatched pattern (often called tartan twinning) that is the most distinguishing characteristic of microcline.

### ***Anorthoclase***

Anorthoclase is a Na - rich feldspar with approximately equal amounts of the Anorthite (Ca) and orthoclase (K) components. Generally anorthoclase occurs in Na - rich volcanic rocks. Like the other alkali feldspars, it has perfect {001} and {010} cleavages. Sections showing both of the cleavages are best for determining the optic sign and 2V. Anorthoclase sometimes shows twinning, but generally not the multiple twinning seen in the plagioclase feldspars, but a cross-hatched twinning similar to that seen in microcline, but on a very fine scale. Anorthoclase, like sanidine shows a low 2V of 5 to 20°, and is optically negative. Anorthoclase can sometimes be distinguished from sanidine by the fact that anorthoclase usually forms crystals with a tabular, elongated habit, while sanidine forms crystals with a more equant habit.

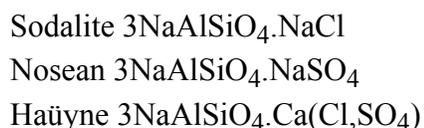
### **Feldspathoids**

The feldspathoid group of minerals are SiO<sub>2</sub> poor, alkali rich minerals that occur in low SiO<sub>2</sub>, high Na<sub>2</sub>O - K<sub>2</sub>O igneous rocks. In general, these minerals are not compatible with quartz, and therefore, are rarely, if ever, seen in rocks that contain quartz. They do, however, often occur with feldspars. Because of the alkalic nature of the rocks that contain feldspathoids, associated pyroxenes and amphiboles are of the sodic variety, i.e. aegerine or riebeckite.

The main feldspathoids are Nepheline (Na,K)AlSi<sub>3</sub>O<sub>8</sub>, Kalsilite KAlSi<sub>2</sub>O<sub>6</sub>, and Leucite KAlSi<sub>2</sub>O<sub>6</sub>. At high temperature there is complete solid solution between Nepheline and

Kalsilite, but at low temperature Nepheline can contain only about 12 wt%  $K_2O$ .

Other similar members of the feldspathoid group are:



### ***Nepheline***

Nepheline occurs in both volcanic and plutonic alkaline igneous rocks. In hand specimen, Nepheline is difficult to distinguish from the feldspars, and thus must usually be identified by its association with other alkalic minerals. Nepheline has a yellowish colored alteration product, called cancrinite. Nepheline is hexagonal, and thus uniaxial, making it easy to distinguish from the feldspars. Furthermore, it is optically negative, making it distinguishable from quartz. It usually shows no cleavage, has low birefringence, and low relief (refractive indices are smaller than the feldspars). The only other common mineral with which nepheline could be confused is apatite, which is also uniaxial negative. Apatite, however, shows much higher relief than does nepheline.

### ***Sodalite***

Sodalite occurs predominantly in alkali-rich plutonic igneous rocks, like syenites, but can also be found in volcanic rocks. It is essentially 3 nepheline molecules with an added NaCl molecule. It is a clear colored isometric mineral with low relief. Thus, the only thing sodalite might be confused with is a hole in the thin section. The blue color of sodalite in hand specimen and its association with other alkali-rich minerals is usually necessary to detect its presence in a rock.

### ***Leucite***

Leucite is found in alkalic volcanic rocks, and is rarely found in plutonic rocks. It is a tetragonal mineral, however, its refractive indices  $e$  and  $w$  are so close together that it almost always appears isometric. It usually occurs as small, slightly rounded, low relief grains that go extinct upon insertion of the analyzer. Commonly, leucite contains tiny inclusions within the mineral, and sometimes shows a slight twinning, barely visible with the analyzer inserted.

## **Oxides**

The oxide minerals are very common and usually occur as accessory minerals in all kinds of rocks. The most common oxide minerals are the following:

### **Corundum - $Al_2O_3$**

Corundum is hexagonal and optically negative. It occurs in Al-rich igneous and metamorphic rocks. If transparent blue, it is the gemstone sapphire, if transparent red, it is the gemstone ruby. When it occurs as an accessory mineral it usually shows its hexagon shaped outline when looking down the  $c$ -axis. It has high refractive indices, thus shows very high relief in thin section. But it has low birefringence and commonly shows lamellar twinning.

**Spinel** -  $\text{MgAl}_2\text{O}_4$ 

Spinel is an isometric mineral that occurs ultrabasic rocks like peridotite, and in many low silica igneous rocks like basalts, where it contains high concentrations of Cr. It is also found in Al-rich contact metamorphic rocks. It shows a wide variety of colors depending on trace amounts of other ions substituting for both Mg and Al. Because of the isometric nature, Spinel is difficult to distinguish from garnet, although spinel tends to occur as much smaller crystals.

**Chromite** -  $\text{Fe}^{+2}\text{Cr}_2\text{O}_4$ 

Chromite is a major ore of Cr. It is found in in low silica, Mg-rich igneous rocks, usually associated with Olivine. Often it is seen as small inclusions in Olivine, indicating that it is an early crystallizing phase in basaltic and gabbroic magmas. Chromite is isometric, and usually opaque in thin section. Electron Microprobe analysis is usually necessary to distinguish it from other opaque oxide minerals.

**Magnetite** -  $\text{Fe}_3\text{O}_4$ 

Magnetite is one of the most common oxide minerals. It is a major ore of Fe, and is found as an accessory mineral in all rock types. It is isometric and commonly crystallizes with an octahedral habit. In hand specimen it is most easily identified by its strongly magnetic nature, black color, and hardness of 6. In thin section it is opaque and thus difficult to distinguish from the other opaque oxide minerals. As discussed below, it forms a solid solution with Ulvospinel -  $\text{Fe}_2\text{TiO}_4$ .

**Ilmenite** -  $\text{FeTiO}_3$ 

Ilmenite is a major ore of Ti. It is found as a common accessory mineral in a wide range of igneous volcanic and plutonic rocks, as well as metamorphic and clastic sedimentary rocks. It forms a solid solution series with Hematite, as will be discussed below, and commonly occurs along with Magnetite. Ilmenite is hexagonal, but is usually opaque which makes its distinction from other oxide minerals difficult. Ilmenite, however, often shows an elongated or acicular habit, whereas Magnetite usually crystallizes as more equant crystals with an octahedral habit.

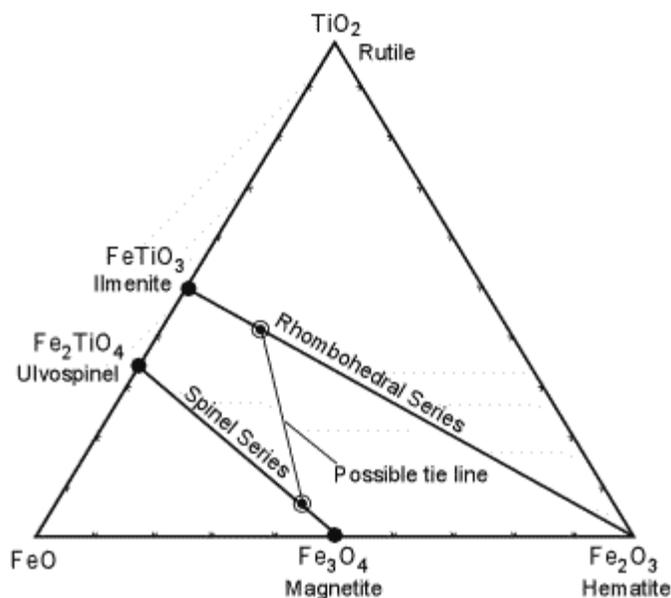
**Hematite** -  $\text{Fe}_2\text{O}_3$ 

Hematite is one of the most important ores of Fe. It is more oxidized than Magnetite, and thus forms as an alteration product of magnetite as well as other Fe bearing minerals. In most unaltered igneous rocks, hematite occurs as a component of Ilmenite in solid solution. Hematite is hexagonal, but rarely occurs in crystals where its symmetry can be determined. It is found in a variety of forms, ranging from oolitic spherules, to massive fine grained aggregates, to botryoidal masses. It is most easily distinguished by its black to dark red color and reddish brown streak. In thin section it is not easily distinguished from other opaque oxide minerals.

**Iron-Titanium Oxide Geothermometer**

Under magmatic conditions, Ilmenite and Hematite form a complete solid solution series, often called the rhombohedral series since both minerals crystallize in the hexagonal system. Similarly Magnetite and Ulvospinel form a complete solid solution series, called the spinel series.

The possible ranges of solid solution are shown in the diagram to the right. Coexisting compositions (as illustrated by the tie line) depend on temperature and the fugacity (similar to partial pressure) of Oxygen. If magma is rapidly cooled so as to preserve the compositions of the high temperature solid solutions, it is possible to calculate the temperature and fugacity of Oxygen that were present just before eruption of the magma. Minerals that allow for determination of the temperature of formation of minerals are referred to as a geothermometer. The example illustrated here is an important one, called the Iron-Titanium Oxide Geothermometer.



## Carbonates

The carbonates are an important group of minerals near the Earth's surface. Carbonate minerals make up the bulk of limestones and dolostones. Are found as cementing agents in clastic sedimentary rocks, and make up the shells of many organisms. The carbonates are based on the  $\text{CO}_3^{2-}$  structural unit, which has carbon surrounded by 3 oxygens in triangular coordination. Thus each Oxygen has a residual charge of  $-2/3$ . In the carbonate structure, no two triangles share the corner oxygens and the C-O bonds are highly covalent.

There are three structural types of carbonates:

Calcite Group	Aragonite Group	Dolomite Group
Calcite $\text{CaCO}_3$	Aragonite $\text{CaCO}_3$	Dolomite $\text{CaMg}(\text{CO}_3)_2$
Magnesite $\text{MgCO}_3$	Witherite $\text{BaCO}_3$	Ankerite $\text{CaFe}(\text{CO}_3)_2$
Siderite $\text{FeCO}_3$	Strontianite $\text{SrCO}_3$	
Rhodochrosite $\text{MnCO}_3$	Cerussite $\text{PbCO}_3$	
Smithsonite $\text{ZnCO}_3$		

In addition, there are the hydroxyl Cu carbonates - Malachite,  $\text{Cu}_2\text{CO}_3(\text{OH})_2$  and Azurite  $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ .

### The Calcite Group

The calcite group minerals are all hexagonal. They have Ca, Mg, Fe, Mn, or Zn divalent cations in 6-fold coordination with the  $\text{CO}_3^{2-}$  groups, in a structure that is similar to that of NaCl. All members of this group show rhombohedral cleavage  $\{01\bar{1}2\}$ , thus breaking into rhomb-shaped cleavage blocks.

**Calcite**  $\text{CaCO}_3$ - The most common carbonate mineral is calcite. It is the principal constituent of limestone and its metamorphic equivalent - marble. Deposits of fine grained calcite in powder form are referred to as chalk. It forms the cementing agent in many sandstones, and is one of the more common minerals precipitated by living organisms to form their skeletal structures.

Calcite is also precipitated from groundwater where it forms veins, or in open cavities like caves and caverns can form the cave decorations - like stalactites and stalagmites, and encrustations. It is also precipitated from hot springs where it is called travertine.

Calcite does occur in rare igneous rocks called carbonatites. These form from carbonate magmas. Calcite is also precipitated from hydrothermal fluids to form veins associated with sulfide bearing ores.

### *Properties*

In hand specimen, calcite is distinguished by its rhombohedral cleavage, its hardness of 3, and by its effervescence in dilute HCl. It can range in color from white, to slightly pink, to clear, but dark colored crystals can also occur. In thin section it is most readily distinguished by its high birefringence, showing high order white interference colors, by its rhombohedral cleavage and its uniaxial negative character. Because of its high birefringence, it shows a large change in relief on rotation of the stage. Furthermore, its  $\epsilon$  refractive index direction (low RI direction) when parallel to the polarizer shows a negative relief when compared to the mounting medium of the thin section. Calcite can be distinguished from Aragonite by the lack of rhombohedral cleavage and biaxial nature of Aragonite.

### **Magnesite** $\text{MgCO}_3$

Magnesite is a common alteration product of Mg-rich minerals on altered igneous and metamorphic rocks. Like calcite, it shows perfect rhombohedral cleavage, but unlike calcite, it does not readily effervesce in dilute HCl. It does, however, effervesce in hot HCl. These properties and its association with Mg-rich minerals and rocks make it distinguishable from Calcite.

### **Siderite** $\text{FeCO}_3$

Siderite forms complete solid solution series with Magnesite, although the environment in which the two minerals occur usually determines that either Mg-rich Magnesite or Fe-rich Siderite will form, and one rarely sees intermediate end members. In hand specimen, siderite is usually brown colored and effervesces only in hot HCl. In thin section it resembles Calcite, but has a much higher  $\epsilon$  refractive index than Calcite and is commonly pale yellow to yellow brown in color without the analyzer inserted.

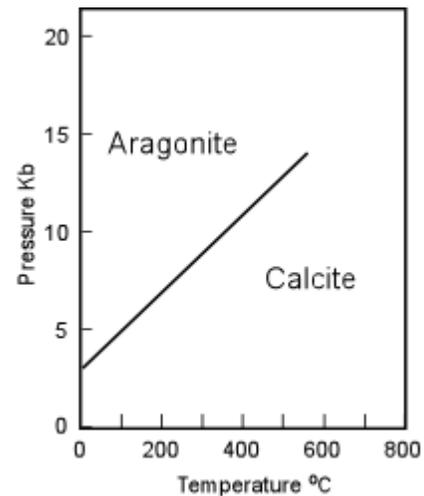
### **Rhodochrosite** $\text{MnCO}_3$

Rhodochrosite is the Mn bearing carbonate, and is thus found only in environments where there is an abundance of Manganese. It is relatively rare and occurs as hydrothermal veins and as an alteration product of Mn rich deposits. In hand specimen it shows a distinctive pink color along with the rhombohedral cleavage common to the Calcite group minerals. Hot HCl is required to make the mineral effervesce.

## **The Aragonite Group**

The Aragonite group of minerals are all orthorhombic, and can thus be distinguished from minerals of the calcite group by their lack of rhombohedral cleavage. Aragonite ( $\text{CaCO}_3$ ) is the most common mineral in this group.

Aragonite is the higher pressure form of  $\text{CaCO}_3$  but, nevertheless occurs and forms at surface temperatures and pressures. When found in metamorphic rocks it is a good indicator of the low temperature, high pressure conditions of metamorphism, and is thus commonly found in Blueschist Facies metamorphic rocks along with Glaucophane. Water containing high concentrations of Ca and carbonate can precipitate Aragonite. Warm water favors Aragonite, while cold water favors calcite, thus Aragonite is commonly found as a deposit of hot springs. Aragonite can also form by biological precipitation, and the pearly shells of many organisms are composed of Aragonite. Fine needle-like crystals of Aragonite are produced by carbonate secreting algae.



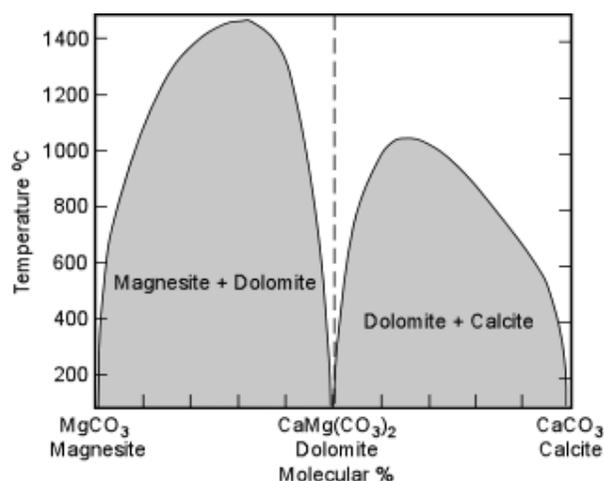
### Properties

In hand specimen, Aragonite, like calcite effervesces in cold HCl. But, unlike Calcite, Aragonite does not show a rhombohedral cleavage. Instead it has single good  $\{010\}$  cleavage. It is usually transparent to white in color and forms in long bladed crystals. Twinning is common on  $\{110\}$ , and this can produce both cyclical twins, which, when present, make it look pseudo-hexagonal, and single twins. In thin section Aragonite is distinguished by its high birefringence, showing high order white interference colors, its biaxial character with a  $2V$  of about  $18^\circ$ , and extinction parallel to the  $\{010\}$  cleavage.

### The Dolomite Group

Dolomite -  $\text{CaMg}(\text{CO}_3)_2$  and Ankerite -  $\text{CaFe}(\text{CO}_3)_2$  form a complete solid solution series, although because Mg-rich environments are much more common than Fe-rich environments, Mg-rich dolomites are much more common than Ankerites. Ankerite is common mineral in Pre-Cambrian iron formations. Dolomite is a common constituent of older limestones, probably the result of secondary replacement of original calcite. It is also found as dolomitic marbles, and in hydrothermal veins.

Dolomite is a unique chemical composition, as can be seen in the Magnesite - Calcite phase diagram shown here. Two solvi exist at low temperatures. Thus, any high Mg-calcite - dolomite solid solutions that might exist at high temperatures would form nearly pure calcite and pure dolomite at surface temperatures, and similarly, any Magnesite - Dolomite solid solutions that might exist at high temperatures would form nearly pure Magnesite and pure Dolomite at low temperatures. Thus, Magnesite and Dolomite commonly occur together, as do Calcite and Dolomite.

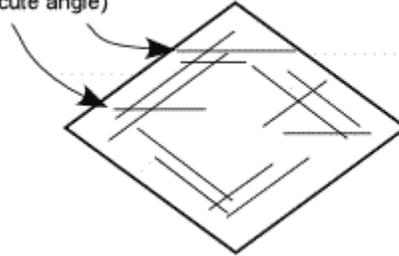


*Properties* Dolomite, and therefore rocks containing large amounts of dolomite, like dolostones, is easily distinguished by the fact that dolomite only fizzes in cold dilute HCl if broken down to a fine powder. Also, dolostones tend to weather to a brownish color rock, whereas limestones tend to weather to a white or gray colored rock. The brown color of dolostones is due to the fact that Fe occurs in small amounts replacing some of the Mg in dolomite.

In thin section it is more difficult to distinguish from calcite, unless it is twinned. In order to facilitate its identification in thin section, the sections are often stained with alizarin red S. This turns calcite pink, but leaves the dolomite unstained.

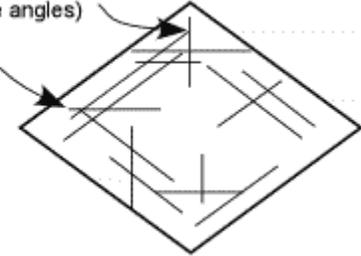
If calcite and dolomite are twinned, they are easily distinguishable from one another. Calcite shows twin lamellae that are parallel to the rhombohedral cleavage traces and parallel to the long direction of the cleavage rhombs.

Twin planes parallel to the long dimension of the rhomb (bisect the acute angle)



**Calcite**

Twin planes parallel both the long and short dimension of the rhomb (bisect both the acute and obtuse angles)



**Dolomite**

Thus, the lamellae bisect the acute angle between the cleavages. Dolomite also has twins parallel to the cleavage faces and parallel to the long direction of the rhombs, but also has twin lamellae that are parallel to the short dimension of the rhomb. Thus, dolomite would also show twin lamellae that would bisect the obtuse angle between the cleavage traces.

### **Apatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F})$**

Apatite is another very common and almost ubiquitous (always present) accessory mineral in igneous rocks and many metamorphic rocks. If the rock contains any phosphorous it is usually found in apatite. Apatite is hexagonal, hence uniaxial with a negative optic sign. Its refractive indices  $\omega = 1.624$  to  $1.666$  and  $\epsilon = 1.629$  to  $1.667$  are higher than both quartz and nepheline, giving apatite a higher relief than these minerals. Its birefringence, expressed as  $1^\circ$  gray interference colors is similar to that of quartz and nepheline. Quartz, however, is optically positive. Nepheline, while optically negative, shows much lower relief than does apatite. The crystal form of apatite is usually distinctive. If cut parallel to  $\{0001\}$ , it usually has a hexagonal outline. If cut parallel to the C axis, it appears as doubly terminated prisms.

## Phase Diagrams

A phase diagram is a graphical representation of chemical equilibrium. Since chemical equilibrium is dependent on the composition of the system, the pressure, and the temperature, a phase diagram should be able to tell us what phases are in equilibrium for any composition at any temperature and pressure of the system. First, a few terms will be defined.

### Definitions

**System** - A system is that part of the universe which is under consideration. Thus, it may or may not have fixed boundaries, depending on the system. For example, if we are experimenting with a beaker containing salt and water, and all we are interested in is the salt and water contained in that beaker, then our system consists only of salt and water contained in the beaker.

If the system cannot exchange mass or energy with its surroundings, then it is termed an **isolated system**. (Our salt and water system, if we put a lid on it to prevent evaporation, and enclosed it in a perfect thermal insulator to prevent it from heating or cooling, would be an isolated system.)

If the system can exchange energy, but not mass with its surroundings, we call it a **closed system**. (Our beaker, still sealed, but without the thermal insulator is a closed system).

If the system can exchange both mass and energy with its surroundings, we call it an open system. (Our beaker - salt - water system open to the air and not insulated is thus an open system).

**Phase** - A phase is a physically separable part of the system with distinct physical and

chemical properties. A system must consist of one or more phases. For example, in our salt-water system, if all of the salt is dissolved in the water, consists of only one phase (a sodium chloride - water solution). If we have too much salt, so that it cannot all dissolve in the water, we have 2 phases, the sodium chloride - water solution and the salt crystals. If we heat our system under sealed conditions, we might have 3 phases, a gas phase consisting mostly of water vapor, the salt crystals, and the sodium chloride - water solution.

In a magma a few kilometers deep in the earth we might expect one or more phases. For example if it is very hot so that no crystals are present, and there is no free vapor phase, the magma consists of one phase, the liquid. At lower temperature it might contain a vapor phase, a liquid phase, and one or more solid phases. For example, if it contains crystals of plagioclase and olivine, these two minerals would be considered as two separate solid phases because olivine is physically and chemically distinct from plagioclase.

**Component** - Each phase in the system may be considered to be composed of one or more components. The number of components in the system must be the minimum required to define all of the phases. For example, in our system salt and water, we might have the components Na, Cl, H, and O (four components), NaCl, H, and O (three components), NaCl and HO (two components), or NaCl-H<sub>2</sub>O (one component). However, the possible phases in the system can only consist of crystals of halite (NaCl), H<sub>2</sub>O either liquid or vapor, and NaCl-H<sub>2</sub>O solution. Thus only two components (NaCl and H<sub>2</sub>O) are required to define the system, because the third phase (NaCl - H<sub>2</sub>O solution) can be obtained by mixing the other two components.

## The Phase Rule

The phase rule is an expression of the number of variables and equations that can be used to describe a system in equilibrium. In simple terms, the number of variables are the number of chemical components in the system plus the extensive variables, temperature and pressure. The number of phases present will depend on the variance or degrees of freedom of the system. The general form of the phase rule is stated as follows:

$$F = C + 2 - P$$

where F is the number of degrees of freedom or variance of the system.

C is the number of components, as defined above, in the system.

P is the number of phases in equilibrium,

and the 2 comes from the two extensive variables, Pressure and Temperature.

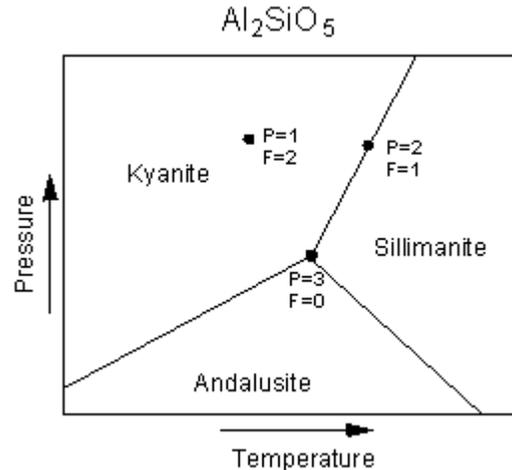
To see how the phase rule works, let's start with a simple one component system - the system Al<sub>2</sub>SiO<sub>5</sub>, shown in the Pressure, Temperature phase diagram below.

First look at the point in the field of kyanite stability. Since kyanite is the only phase present,  $P=1$ .  $F$  is 2 at this point, because one could change both temperature and pressure by small amounts without affecting the number of phases present. We say that this area of kyanite stability on the phase diagram is a divariant field (variance,  $F=2$ ).

Next look at the point on the phase boundary between kyanite and sillimanite. For any point on such a boundary the number of phases,  $P$ , will be 2. Using the phase rule we find that  $F=1$ , or there is one degree of freedom. This means there is only one independent variable.

If we change pressure, temperature must also change in order to keep both phases stable. The phase assemblage is said to be univariant in this case, and the phase boundaries are univariant lines (or curves in the more general case).

Finally, we look at the point where all three univariant lines intersect. At this point, 3 phases, kyanite, andalusite, and sillimanite all coexist at equilibrium. Note that this is the only point where all three phases can coexist. For this case,  $P=3$ , and  $F$ , from the phase rule, is 0. There are no degrees of freedom, meaning that any change in pressure or temperature will result in a change in the number of phases. The three phase assemblage in a one component system is said to be invariant.



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EENS 2110	Mineralogy
Tulane University	Prof. Stephen A. Nelson
<b>TWO COMPONENT (BINARY) PHASE DIAGRAMS</b>	

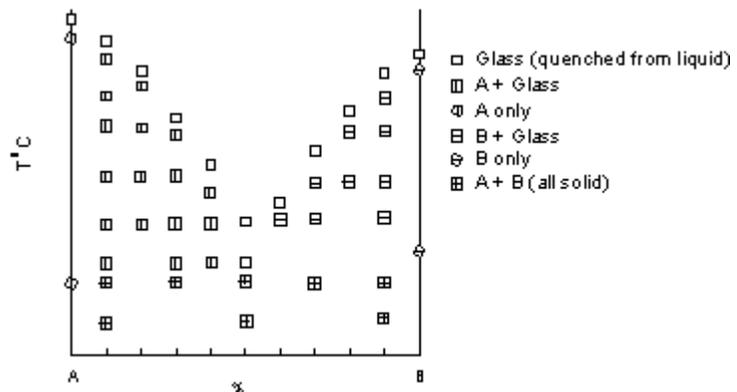
This document last updated on 07-Feb-2011

### Experimental Determination of 2-Component Phase Diagrams

As an example, we're going to look at how one might go about determining the stability of a mixture of 2 mineral phases, A and B. To perform these experiments we start with pure minerals A and B and then make mixtures in varying proportions. Each one of these mixtures, plus the pure A and pure B represent different compositions. In this case, we are only going to look at how the stability varies as with temperature and composition, holding Pressure constant at 1 atmosphere.

This type of experiment can be done in a furnace with controlled temperature. Pressure does not have to be controlled because the phase relations will be determined at atmospheric pressure. The various compositions are placed in a capsule that will not react with any of the phases produced. Usually this would be Platinum. Each mixture is then placed in the furnace, the temperature is raised to some point and held at that temperature long enough for equilibrium between all of the phases to occur. The capsules are then quickly removed from the furnace and quenched rapidly. The rapid decrease in temperature that occurs during quenching helps to assure that no further reactions take place and the phase assemblage that was present at the higher temperature is preserved at room temperature. During quenching, any liquid that may have been present at high temperature is found to be glass.

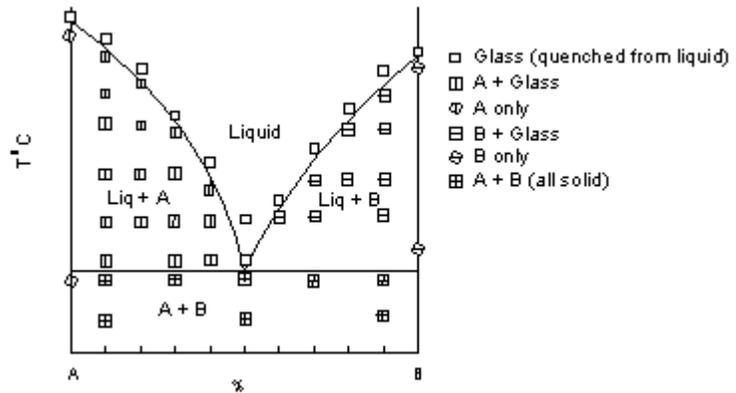
After quenching, each capsule is opened and the phases present are determined using a microscope. In the example shown, we use different symbols to represent the mineral phase assemblages present for each composition run. In this set of experiments 6 different assemblages are found, and are plotted on a diagram with Temperature of the experiment plotted on the vertical axis, and composition in terms of %A or %B plotted on the horizontal axis.



Note that pure A plots at 100% A which corresponds to 0% B, and pure B plots at 100%B, which corresponds to 0% A.

Note also that no experiments were run at temperatures higher than those where the first complete liquid appeared for each composition.

Once the points are plotted, we can then draw best-fit curves or lines between the data points to determine the Temperature - Composition stability fields for the various phase assemblages. These curves/lines are shown here, and the stability fields for each phase assemblage are labeled. the resulting phase diagram is called a binary eutectic diagram. Not all binary melting diagrams look like this, but this is the simplest and the type that we will discuss first.



## TWO COMPONENT EUTECTIC SYSTEMS

Figure 1 shows the simplest of two component phase diagrams. The components are A and B, and the possible phases are pure crystals of A, pure crystals of B, and liquid with compositions ranging between pure A and pure B. Compositions are plotted across the bottom of the diagram. Note that composition can be expressed as either a percentage of A or a percentage of B, since the total percentage must add up to 100. (Compositions might also be expressed as mole fraction of A or B, in which case the total must add up to 1). Temperature or pressure is plotted on the vertical axis. For the case shown, we consider pressure to be constant, and therefore have plotted temperature on the vertical axis.

The curves separating the fields of A + Liquid from Liquid and B + Liquid from Liquid are termed *liquidus curves*. The horizontal line separating the fields of A + Liquid and B + Liquid from A + B all solid, is termed the *solidus*. The point, E, where the liquidus curves and solidus intersect, is termed the *eutectic point*. At the eutectic point in this two component system, all three phases, that is Liquid, crystals of A and crystals of B, all exist in equilibrium. Note that the eutectic is the only point on the diagram where this is true.

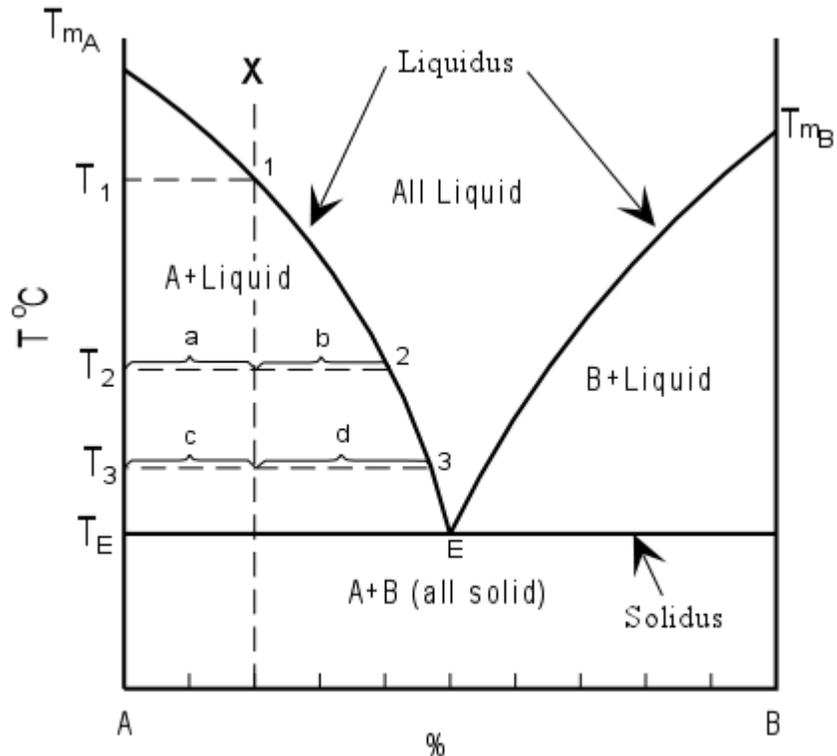


Figure 1

Since we looking at a system at constant pressure, the phase rule in this case is  $F = C + 1 - P$ . The eutectic point is therefore an invariant point. If we change the composition of the liquid or the temperature, the number of phases will be reduced to 2.

If the system contains only pure A, then the system is a one component system and phase A melts at only one temperature, the melting temperature of pure A,  $T_{mA}$ . If the system contains only pure B, then it is a one component system and B melts only at the melting temperature of pure B,  $T_{mB}$ .

For all compositions between pure A and pure B, the melting temperature is drastically reduced, and melting begins at the eutectic temperature  $T_E$ . Note that for all compositions between A and B the melting also occurs over a range of temperatures between the solidus and the liquidus. This is true for all compositions except one, that of the eutectic. The eutectic composition melts at only one temperature,  $T_E$ .

We will now consider the crystallization of a liquid with composition X in Figure 1. First, however, we must state the following rule, which must always be obeyed:

**Rule 1 - *In equilibrium crystallization or melting in a closed system, the final composition of the system will be identical to the initial composition of the system.***

Therefore, according to rule 1, composition X, which is made up of a mixture of 80% A and 20% B, will have, as its final crystalline product a mixture of 80% crystals of A and 20% crystals of B.

Composition X will be all liquid above the temperature  $T_1$ , because it will lie in the field of all Liquid. If the temperature is lowered to  $T_1$ , at  $T_1$  crystals of A begin to form.

Further lowering of the temperature causes more crystals of A to form. As a result, the liquid composition must become more enriched in B as more crystals of A form out of the liquid. Thus, with lowering of temperature, the liquid composition will change from point 1 to point 2 to point 3 to point E as the temperature is lowered from  $T_1$  to  $T_2$  to  $T_3$  to  $T_E$  respectively. At all temperatures between  $T_1$  and  $T_E$ , two phases will be present in the system; liquid and crystals of A. At the eutectic temperature,  $T_E$ , crystals of B will begin to form, and three phases will coexist; crystals of A, crystals of B, and liquid. The temperature must remain at  $T_E$  until one of the phases disappears. Thus when the liquid crystallizes completely, only pure solid A and pure solid B will remain and mixture of these two solid phases will be in the proportions of the original mixture, that is 80% A and 20% B.

The crystallization history of composition X can be written in abbreviated form as follows:

$T > T_1$  -- all liquid

$T_1 - T_E$  -- liquid + A

at  $T_E$  -- liquid + A + B

$T < T_E$  -- A + B all solid

If we were to stop the crystallization process at any point during crystallization and observe how much of each phase is present we can use the following example to determine what we would see.

For example, at a temperature  $T_2$  the amount of crystals of A and liquid (the only two phases present at this temperature) could be determined by measuring the distances a and b on figure 1. The percentages would then be given by the lever rule:

$$\% \text{ crystals of A} = b/(a + b) \times 100$$

$$\% \text{ liquid} = a/(a + b) \times 100$$

Note that since the amount of crystals must increase with falling temperature the proportional distance between the vertical line which marks the initial composition and the liquidus increases as temperature falls. Thus the distance used to calculate the amount of solid is always measured toward the liquid side of the initial composition.

At the temperature  $T_3$ , note that more crystals must have formed since the proportional distance  $d/(c+d)$  is greater than the proportional distance  $b/(a+b)$ . Thus at  $T_3$  the lever rule gives:

$$\% \text{ crystals of A} = d/(d + c) \times 100$$

$$\% \text{ liquid} = c/(c + d) \times 100$$

At  $T_3$ , note that the composition of the liquid is given at point 3, i.e. 53% A, the composition of the solid is pure A, and the composition of the system is still 80% A and 20% B. Make sure you understand the difference between composition of the phases and the amount or percentages of the phases.

The melting process is exactly the reverse of the crystallization process. That is if we started with composition X at some temperature below  $T_E$  the first liquid would form at  $T_E$ . The temperature would remain constant at  $T_E$  until all of the crystals of B were melted. The liquid composition would then change along the liquidus curve from E to point 1 as temperature increased until the temperature  $T_1$  was reached. Above  $T_1$  the system would contain only liquid with a composition of 80% A and 20% B. The melting process in abbreviated form is listed below:

$T < T_E$  -- all solid A + B

at  $T_E$  -- Liquid + A + B

$T_E - T_1$  -- Liquid + A

$T > T_1$  -- all Liquid

## INCONGRUENT MELTING

Definition of terms:

**Liquidus** - The line separating the field of all liquid from that of liquid plus crystals.

**Solidus** - The line separating the field of all solid from that of liquid plus crystals.

**Eutectic point** - the point on a phase diagram where the maximum number of allowable phases are in equilibrium. When this point is reached, the temperature must remain constant until one of the phases disappears. A eutectic is an invariant point.

**Peritectic point** - The point on a phase diagram where a reaction takes place between a previously precipitated phase and the liquid to produce a new solid phase. When this point is reached, the temperature must remain constant until the reaction has run to completion. A peritectic is also an invariant point.

**Intermediate compound** - A phase that has a composition intermediate between two other phases.

**Congruent melting** - melting wherein a phase melts to a liquid with the same composition as the solid.

**Incongruent melting** - melting wherein a phase melts to a liquid with a composition different from the solid and produces a solid of different composition to the original solid.

For the case of incongruent melting, we will use the system forsterite ( $\text{Mg}_2\text{SiO}_4$ ) - silica ( $\text{SiO}_2$ ), which has an intermediate compound, enstatite ( $\text{MgSiO}_3$ ).

This system is a prime example of the phenomena of incongruent melting in rocks, and therefore gives insights into many aspects of mineral formation.

A simplified version of the system forsterite - silica with its intermediate compound enstatite is shown in Figure 2. The crystallization histories for compositions X, Y, and Z will be documented in the following discussion. Each of these compositions behaves in a slightly different manner

### Crystallization of Composition X

Composition X is a mixture of 13 wt. %  $\text{SiO}_2$  and 87 wt. %

$\text{Mg}_2\text{SiO}_4$ . Because this composition falls between the compositions of pure forsterite and pure enstatite, it must end its crystallization history containing only crystals of forsterite and enstatite. i.e. no quartz will occur in the final crystalline mixture.

If a mixture such as composition X is taken to a temperature above its liquidus (i.e. above  $1800^\circ\text{C}$  in Figure 2) it will be in an all liquid state. We now trace the cooling history of composition X.

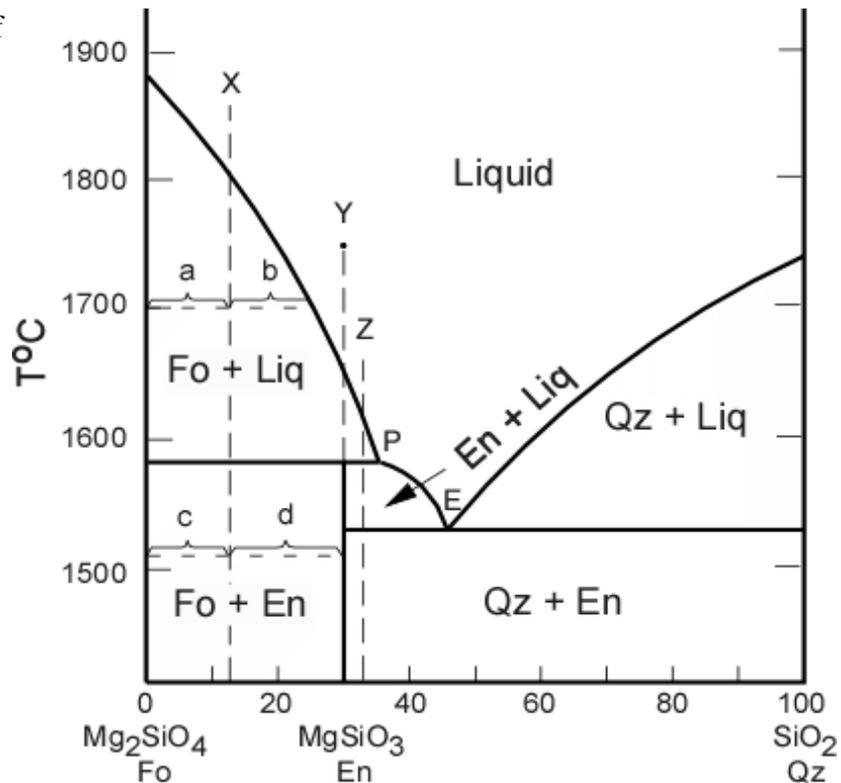
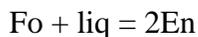


Figure 2

As a liquid of composition X is cooled, nothing will happen until the temperature is equal to the liquidus temperature at  $1800^\circ$ . At this point crystals of forsterite (Fo) begin to precipitate out of the liquid. As the temperature is further lowered, the composition of the liquid will change along the liquidus toward the peritectic (P), and the crystals forming from the liquid will always be pure Fo until P is reached.

At the temperature of the peritectic, about  $1580^\circ$ , note that three phases must be in equilibrium, Fo, liquid, and enstatite (En). At this point some of the crystals of Fo react with the liquid to produce crystals of En. The reaction that takes place can be written as follows:



(Where  $\text{SiO}_2$  in the reaction refers to the component of  $\text{SiO}_2$  in liquid with composition P).

After all of the liquid is consumed by this reaction, only crystals of Fo and En will remain. The proportions of Fo and En in the final crystalline product can be found by applying the lever rule.

$$\% \text{Fo crystals} = [d/(c + d)] \times 100$$

$$\% \text{En crystals} = [c/(c + d)] \times 100$$

At any intermediate stage in the process, such as at 1700° the proportion of all phases present (Fo and liquid in this case) can similarly be found by applying the lever rule.

at 1700°C

$$\% \text{Fo crystals} = [b/(a + b)] \times 100$$

$$\% \text{liquid} = [a/(a + b)] \times 100$$

Note that melting of composition X is exactly the reverse of crystallization. Mixture X will begin to melt at the peritectic temperature. At this point En will melt to crystals of Fo plus liquid (incongruent melting). As soon as all of the En crystals have been consumed by this reaction, the temperature can be increased until it reaches 1800° at which point all of the Fo crystals will have been consumed and the only phase left will be liquid with a composition of the starting material.

### **Crystallization of Composition Y**

Composition Y is equivalent to pure En. Thus only En may appear in the final crystalline product if perfect equilibrium is maintained.

If composition Y is cooled from an all liquid state it first begins to crystallize at about 1650°.

At 1650° crystals of Fo will begin to precipitate from the liquid. This will continue with further cooling until the temperature of the peritectic is reached. In this interval, the composition of the liquid must become more enriched in SiO<sub>2</sub> and will thus change along the liquidus until it has the composition of the peritectic, P. At the peritectic temperature (1580°) all of the remaining liquid will react with all of the previously precipitated Fo to produce crystals of En. The temperature will remain constant until this reaction has gone to completion, after which the only phase present will be pure En.

Thus, it can be seen that enstatite melts incongruently. If pure enstatite is heated to a temperature of 1580° it melts to Fo plus liquid.

### **Crystallization of Composition Z**

Since composition Z lies between En and SiO<sub>2</sub>, it must end up with crystals of En and Qz (Quartz). If such a composition were cooled from some high temperature where it is in the all liquid state, it would remain all liquid until it reached the liquidus temperature at about 1600°. At this temperature crystals of Fo would begin to precipitate and the composition of the liquid would begin to change along the liquidus toward the peritectic, P. At P, all of the Fo previously precipitated would react with the liquid to produce crystals of En. After this reaction has run to completion, and all of the previously precipitated Fo is consumed, there would still remain some liquid. With decreasing temperature, more crystals of En would form, and the liquid composition would change along the liquidus toward the eutectic, E. At E crystals of Qz would begin to form, the temperature would remain constant until all of the liquid was used up, leaving crystals of Qz and En as the final solid. Note that because composition Z lies very close to the composition of pure En, the final crystalline product would consist mostly of En with a very small amount of Qz.

For all compositions between P and 100% SiO<sub>2</sub> the system would behave in an identical fashion to the simple Eutectic system discussed previously.

### **Fractional Crystallization in the System**

Up to this point we have always been discussing the case of equilibrium crystallization. That is all solids remain in contact with the liquid until any reaction that takes place has run to completion. As is often the case in natural systems crystals can somehow become separated from the system so that they will not react at reaction points such as P. This is the case of fractional crystallization. Under fractional crystallization conditions the cooling and crystallization histories will be drastically different. In particular, the rule that the final composition must equal the initial composition will not be followed.

As an example of this phenomena we will examine the fractional crystallization of composition X. Furthermore, we will look at the case of perfect fractional crystallization. During perfect fractional crystallization of composition X all of the Fo that is precipitated will be somehow removed from the system. (In nature this can occur by crystals sinking to the bottom of the liquid due to the fact that crystals generally tend to be more dense than liquids.) Note that if only some of the crystals are removed from the liquid we will have a case intermediate between perfect fractional crystallization and equilibrium crystallization.

Cooling a liquid of composition X to the liquidus at 1800° will cause Fo to precipitate as before. With further cooling the liquid composition will change along the liquidus and more Fo will be precipitated. In this case, however, all of the Fo will be removed from the system as it crystallizes. Since the Fo is no longer present, the composition of the system will have the composition of the liquid (the Fo removed can no longer contribute to the composition of the system). Therefore, when the temperature reaches the peritectic temperature, 1580°, there will be no Fo available to react with the liquid, and the liquid (and system) will have a composition, P. Thus the liquid will now precipitate crystals of En and continue cooling to the eutectic, E, where crystals of Qz will form. The final crystalline product will consist of Qz and En.

Compare this case with the previously discussed case of equilibrium crystallization of composition X. Note that under equilibrium conditions the final crystalline product of composition X contained crystals of Fo and En, while in the fractional crystallization case the final product contains En and Qz. Thus fractional crystallization has allowed an originally Fo rich composition to produce an SiO<sub>2</sub> rich liquid and Qz appears in the final crystalline product.

If you go back and look at simple eutectic systems, or look at fractional crystallization of composition Z in the more complex system, you should be able to see that fractional crystallization will have no effect on the phases produced in the final crystalline product, but will only change the proportions of the phases produced. Fractional crystallization is only effective in producing a different final phase assemblage if there is a reaction relationship of one of the phases to the liquid.

## **SOLID SOLUTION SYSTEMS**

In the systems we've discussed so far, all of the mineral or solid phases have been pure phases, that is they have one and only one possible composition. This is not usually the case in nature, since substitution of one element for another often occurs due to the fact that some elements behave in a chemically similar fashion to other elements. When such substitutions occur, the phase can have a range of possible compositions, depending on the amount of substitution that

takes place. Such solids that can have various amounts of elemental substitution are called solid solutions. A good example of a solid solution mineral is the mineral olivine. The general chemical formula for olivine is  $(\text{Mg,Fe})_2\text{SiO}_4$ . Since  $\text{Mg}^{+2}$  and  $\text{Fe}^{+2}$  are about the same size and have the same charge, they may substitute for one another in the crystal structure of olivine. Thus olivine may have a composition anywhere between the pure Mg end member, forsterite ( $\text{Mg}_2\text{SiO}_4$ ), and the pure Fe end member, fayalite ( $\text{Fe}_2\text{SiO}_4$ ). When all compositions between two end members are possible, the solid solution is said to be a complete solid solution.

Another good example of a complete solid solution is displayed in the plagioclase feldspars. In this case the solid solution is between the end members albite ( $\text{NaAlSi}_3\text{O}_8$ ) and anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ). In order to maintain charge balance we cannot simply substitute  $\text{Na}^+$  for  $\text{Ca}^{+2}$ , so this solid solution is what is called a coupled solid solution. In this case  $\text{Na}^+\text{Si}^{+4}$  is substituted for  $\text{Ca}^{+2}\text{Al}^{+3}$  in the plagioclase structure to produce intermediate compositions of plagioclase.

Because the elements that substitute are not exactly the same size (they are similar in size) the amount of substitution is dependent on temperature and pressure and the solid solutions behave in a somewhat orderly fashion as illustrated below.

Since plagioclase is one of the most common minerals in the earth's crust, we will discuss the phase diagram for the plagioclase system. The phase relations in the plagioclase system are shown in Figure 3 at constant pressure equal to that of the atmosphere (atmospheric pressure is 1 bar). In Figure 3 the upper curve is called the liquidus and the lower curve is called the solidus. At temperatures above the liquidus everything is liquid, below the solidus everything is solid (crystals of plagioclase solid solution). At temperatures between the solidus and liquidus crystals of plagioclase solid solution coexist in equilibrium with liquid.

Pure albite melts (or crystallizes) at  $1118^\circ\text{C}$ , and pure anorthite melts (or crystallizes) at  $1500^\circ\text{C}$ . Note that any composition of plagioclase between the two end members melts or crystallizes over a range of temperatures unlike the pure end members which have only one melting point. Thus we can read from the diagram that a solid solution containing 50% albite and 50% anorthite ( $\text{Ab}_{50}\text{An}_{50}$ ) begins to melt at  $1220^\circ$ , point F, and the melting is complete at  $1410^\circ$ , point A. Inversely, if a melt of composition  $\text{Ab}_{50}\text{An}_{50}$  is cooled it will begin to crystallize at  $1410^\circ$  and will be completely crystalline at  $1220^\circ$ .

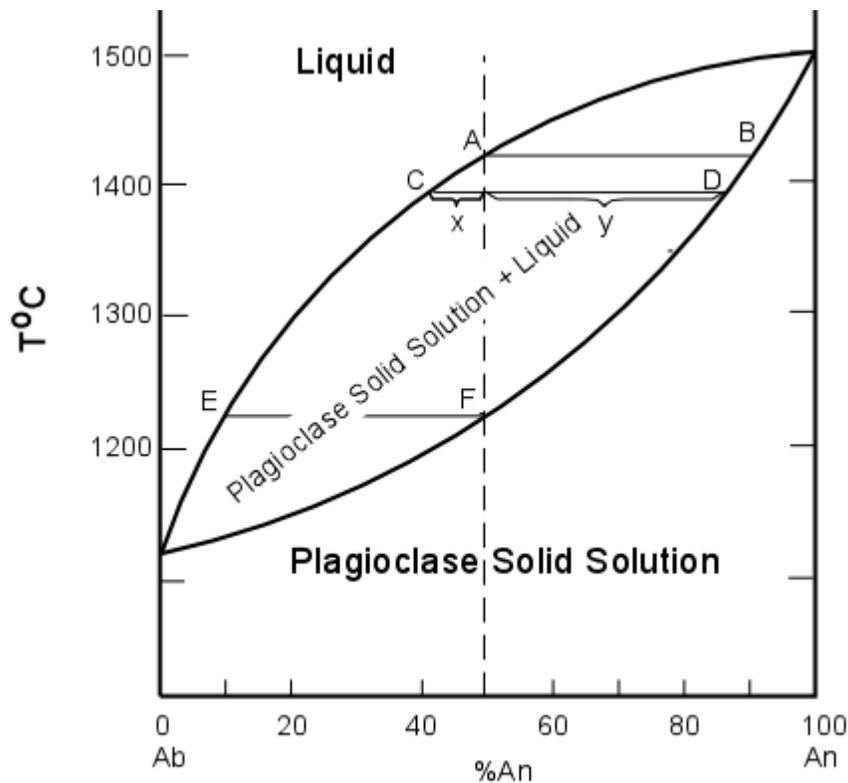


Figure 3

We will now trace the crystallization history of composition X, which is  $Ab_{50}An_{50}$ .

Composition X is completely liquid above the liquidus (above  $1410^{\circ}$ ). Cooling to the liquidus at point A results in the crystallization of a small amount of plagioclase solid solution. The composition of this plagioclase can be found by drawing an isotherm (line of constant temperature, a horizontal line in this diagram) through the temperature  $1410^{\circ}$ . Where this isotherm intersects the solidus (at point B), the composition of the solid can be found by drawing a vertical line to the base of the diagram. Thus it is seen that the first crystals precipitated from composition X will have the composition  $Ab_{10}An_{90}$ . Note that in this diagram crystals that are in equilibrium with liquid will always be enriched in anorthite component relative to the liquid. As crystallization continues with lowering of temperature the composition of the plagioclase will change along the solidus, continually reacting with the liquid to produce crystals more enriched in the Ab component. Meanwhile, the composition of the liquid will change along the liquidus, thus also becoming more enriched in the Ab component. At a temperature of  $1395^{\circ}$  the liquid composition will be at point C, while the solid composition will be at point D. Crystallization proceeds until a temperature of about  $1220^{\circ}$ , at which point the last remaining liquid will have a composition at E, and the solid will have a composition equal to the original starting composition at point F.

At this point all of the liquid will be consumed and the final crystalline product will have the composition  $Ab_{50}An_{50}$ .

During crystallization the proportion of the solid continually increases while that of the liquid continually decreases. Thus as the composition of the liquid becomes more sodic, approaching E, its volume steadily decreases. Thus it can be seen that the amount of liquid in equilibrium with the solid of composition F will be extremely small.

If at any point during the crystallization we wish to determine the amount of solid and liquid, we can apply the lever rule. As an example, we will determine the proportions of liquid and solid in the system at a temperature of 1395°. At this point, we measure the distances oC, oD, and CD. The percentages of liquid and solid are then given as follows:

$$\% \text{ solid (with composition D)} = [x/(x + y)] \times 100$$

$$\% \text{ liquid (with composition C)} = [y/(x + y)] \times 100$$

The foregoing discussion assumes that equilibrium is maintained throughout the course of crystallization. This means that with falling temperature and continuing crystallization, the earlier-formed, more calcic crystals must react continuously with the liquid to produce homogeneous crystals that will become continuously more enriched in the sodic component. If this equilibrium cannot be maintained, then fractional crystallization will take place.

We will distinguish between three contrasting conditions.

1. In equilibrium crystallization, the crystals remain suspended in the melt, and cooling and crystallization are slow enough to allow continuous, complete reaction between crystals and melt. The early formed crystals will, on cooling, react with the melt continuously and thereby gradually change their composition along the solidus from B to F, while simultaneously the liquid changes from A to E. In such circumstances the crystals will not change composition beyond F, and the end product is a homogeneous mixed crystal (solid solution) having the same composition as the initial melt.
2. Assume that the crystals are continuously removed from the melt, by sinking or some natural filtering process. Reaction of crystals with the melt is prevented, and the composition of the liquid will continue to change along the liquidus curve toward the sodic feldspar component. The only limit to this change of composition of the liquid is the composition of the pure Na feldspar, but the relative amount of very sodic liquid would be very small. As the liquid phase changed composition with continuing removal of crystals, the successively formed crystals would become continuously more sodic; the final product would be pure albite, but it would constitute a very small proportion of the initial amount.
3. If the crystals remain suspended in the liquid, but relatively rapid crystallization does not allow complete reaction between crystals and liquid, the effect will be somewhat different. In effect, failure to react completely partially removes the already formed crystals from the system. The melt becomes increasingly more sodic, and earlier formed more calcic crystals serve as nuclei on which increasingly more sodic feldspar crystallizes. The resulting crystal contain zones of differing composition; the inner zones being more calcic, and the outer zones more sodic. The bulk (average) composition of the zoned crystal is that of the initial system, but the range of composition between the inner and outer zones might theoretically be as large as from B to pure Ab in the example shown for composition X.

### **EXSOLUTION**

Many minerals that show complete solid solution at higher temperatures do not show such solid solution at lower temperatures. When this is the case, the phenomenon of exsolution occurs. Since solid solutions are really one mineral phase dissolved in another mineral phase to form a

single mineral phase, exsolution implies that one or the other of the mineral phases in the solution must "exsolve" or come out of solution with the other mineral phase.

Figure 4 illustrates a phase diagram (much simplified) of the alkali feldspar system which exhibits such exsolution behavior at low temperatures. At high temperatures the diagram shows that albite (Ab) or  $\text{NaAlSi}_3\text{O}_8$  and orthoclase (Or) or  $\text{KAlSi}_3\text{O}_8$  form a complete solid solution series. This solid solution series is different from the plagioclase solid solution series only in that it has a minimum composition in the middle rather than at the composition of one of the pure end members. At temperatures just below the solidus, alkali feldspar solid solutions are stable. At lower temperatures, along the curve labeled "solvus" the solid solution is no longer stable.

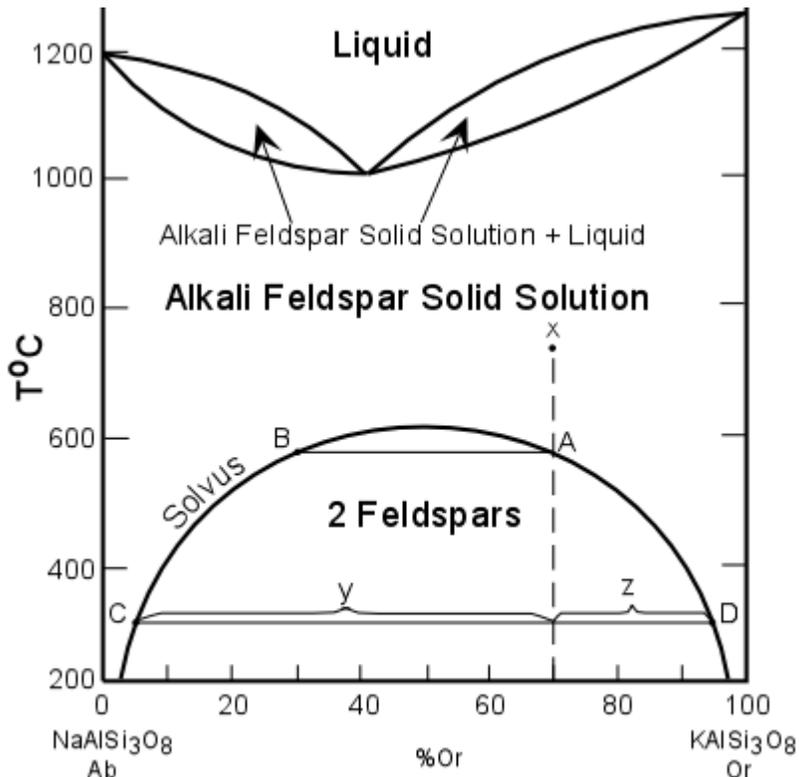


Figure 4

In this case the exsolution phenomena occurs below the solidus and so is a "sub-solidus" reaction. In order to see what happens during exsolution we will examine what happens to a composition labeled X in Figure 4. We will start at a temperature of  $750^\circ$  in the region where alkali feldspar solid solutions are stable. At  $750^\circ$  the composition of the alkali feldspar solid solution is 70% orthoclase and 30% albite ( $\text{Or}_{70}\text{Ab}_{30}$ ).

This solid solution remains stable with lowering of temperature until the temperature of the solvus is obtained at point A (a temperature of about  $590^\circ$ ). At this temperature the solid solution is no longer stable and begins to exsolve. The composition of coexisting exsolved phases can be found by drawing an isotherm until it intersects the solvus. Such an isotherm at  $590^\circ$  shows that at this temperature a solid solution having the composition of point B ( $\text{Or}_{32}\text{Ab}_{68}$ ) coexists with an alkali feldspar solid solution with the composition of point A ( $\text{Or}_{70}\text{Ab}_{30}$ ). With further lowering of temperature further exsolution occurs. At a temperature of  $300^\circ$  our original composition X has exsolved into two alkali feldspar solid solutions, one with the composition of point C and one with a composition of point D. To find the relative proportions or percentages of each of the solid solutions, the lever rule can once again be applied. For example at  $300^\circ$  for composition X the percentage of the albite-rich solid solution is  $[z/(z+y)] \times 100$ , while that of the orthoclase-rich solid solution is  $[y/(z+y)] \times 100$ . With further lowering of temperature all of the albite and orthoclase in the two solid solutions could exsolve completely to produce a pure albite phase and a pure orthoclase phase. Such complete exsolution does occur in nature, but only if the temperature is lowered very slowly. Complete

exsolution is only common in metamorphic rocks. More often, especially in granitic rocks, the two exsolved phases do not separate as individual crystals, but occur as intergrown crystals with exsolution lamellae of one crystal occurring within the other crystal. In the alkali feldspars containing such exsolution lamellae the result is to produce a texture called perthitic or perthite. Perthite on a microscopic scale is illustrated on page 540, figure 19.77 of your mineralogy text (Klein and Dutrow).

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### **Examples of Questions on this material that could be asked on an exam**

1. First note that phase diagrams similar to any of the above could be presented on an exam and you could be asked to (a) trace the crystallization history of any specified composition, (b) determine the temperatures of first melting of any specified composition, (c) determine the composition of all all phases present in any specified composition at a specified temperature and pressure, and (c) determine the proportions of all phases present in a specified composition at a specified temperature.
  2. Define the following: (a) liquidus, (b) solidus, (c) solvus, (d) fractional crystallization (e) solid solution, (f) incongruently melting compound.
  3. Draw examples of phase diagrams that show the following - be sure to label everything.
    - a. a phase diagram that has an intermediate compound that melts incongruently.
    - b. a phase diagram that shows complete solid solution between two endmembers.
    - c. a phase diagram that shows complete solidi solution at high temperature and exsolution at low temperature.
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