

EENS 2110	Mineralogy
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<b>Mineral Chemistry</b>	

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Minerals can form by any of the following processes:

- Precipitation from a fluid like H<sub>2</sub>O or CO<sub>2</sub>. This can take place within the Earth by hydrothermal processes, diagenesis, and metamorphism, and at or near the Earth's surface as a result of evaporation, weathering, or biological activity.
- Sublimation from a vapor. This process is somewhat more rare, but can take place at a volcanic vent, or deep in space where the pressure is near vacuum.
- Crystallization from a liquid. This takes place during crystallization of molten rock (magma) either below or at the Earth's surface.
- Solid - Solid reactions. This process involves minerals reacting with other minerals in the solid state to produce one or more new minerals. Such processes take place during metamorphism and diagenesis due to changing temperature and pressure conditions.

No matter what process is involved, a particular mineral cannot form unless the chemical ingredients necessary to make the mineral are present. Thus, the most common minerals are minerals that have a chemical composition made of the common elements found in their environment. Since the environment where most observable minerals occur is the Earth's crust, we must first explore the chemical composition of the Earth's crust.

### Composition of the Crust

The Earth's crust is made up of about 95% igneous and metamorphic rocks, 4% shale, 0.75% sandstone, and 0.25% limestone. The continental crust has an average composition that approximates granodiorite (a medium to siliceous igneous rock), whereas the oceanic crust has an average composition that is basaltic (a low silica igneous rock).

Based on information compiled by Clarke and Washington in 1924, the average composition of the continental crust is as follows:

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Element	Wt%	Atomic%	Volume%
O	46.60	62.55	~94
Si	27.72	21.22	~6
Al	8.13	6.47	
Fe	5.00	1.92	
Ca	3.63	1.94	
Na	2.83	2.34	
K	2.59	1.42	
Mg	2.09	1.84	
Total	98.59	100.00	100

Note that 8 elements make up over 98% of the Earth's crust and that Oxygen is the most abundant element. This becomes even more evident if the elements are determined on an atomic basis, where we can see that about 63 out of every 100 atoms in the crust are Oxygen. On a volume basis, Oxygen makes up about 94% of the crust because Oxygen is a large anion, and the other elements occur as small cations coordinated by the Oxygen anions, as we discussed in the previous lecture.

Because of the average composition of the crust, the most common minerals found in the crust are silicates and oxides. Of the silicates, the aluminosilicates, like the feldspars and clay minerals are the most common.

Other minerals, containing the other elements in the periodic table are found in the crust. But, in order for these minerals to occur, special geologic conditions are necessary to concentrate these less abundant elements so that they occur in high enough concentrations to form a separate mineral.

Elements that occur in concentrations less than about 0.1% (usually measured in parts per million or parts per billion) are called dispersed elements or trace elements.

A complete listing of the abundances of all elements in the Earth's crust can be found in your textbook on page 92.

### **Methods of Chemical Analysis**

While the common minerals are made up mostly of the abundant elements in the Crust, and we can express the chemical composition of such minerals by a simple (and sometimes not so simple) chemical formula, all minerals exhibit some chemical variation. In fact pure minerals (those with a chemical composition exactly the same as the chemical formula) are rarely found in nature. We will discuss why this is the case later on in the lecture. For now, it is sufficient to say that if we had a technique for measuring even the smallest concentrations of elements, we would see that any given mineral probably contains every stable element in the periodic table. Of course most of these elements would occur in very low concentrations (parts per trillion or less), nevertheless they are present.

Various methods have been used to perform chemical analyses of rocks and minerals. We will discuss some of these techniques here. But, analysis of minerals is quite different from analysis of rocks. Chemical analysis of rocks involves analyzing an aggregate of minerals. So, in most

case the rock can be ground to a fine powder and subjected to one of the methods discussed here. Analysis of a mineral is more complicated because:

1. Individual minerals are much smaller than rocks and it is therefore difficult to obtain enough sample of a mineral to perform the chemical analysis.
2. In cases where a single mineral is too small to provide enough sample, several grains of the same mineral can be separated from a rock and analyzed as a single sample. But, this involves extensive work in separating the mineral from all other minerals, and still does not tell us if there is any chemical variability between individual grains. (The electron microprobe technique described below is an exception, because it allows for analysis of small areas of single grains).
3. Individual minerals may be chemically zoned. That is there may be differences in the chemical composition of the mineral from its center to its rim. Chemical analysis of single mineral grains or aggregates of mineral grains will not reveal this chemical zonation. (Again, the electron microprobe technique is an exception).

Here we discuss only the more commonly used methods of mineral analysis.

### **Wet Chemical Analyses**

Prior to about 1960 classical wet chemical analysis was the only means of determining the chemical composition of minerals. Such analyses were limited by the factors discussed above in terms of sampling size, although techniques were developed for analyzing very small samples. Wet chemical analyses always involves dissolving the mineral into an acidic solution. In order for the dissolution to take place completely, the mineral is usually first ground into a fine powder (to increase surface area) and the appropriate acid must be used. Wet chemical analysis can be classified into three different types:

- Gravimetric Analyses- In this case the element of interest is precipitated as a compound. The precipitate is then weighed to determine its proportion in the original sample.
- Volumetric Analyses - In this type of analysis titration is used to determine the amount of reagent that is added in order for a specific chemical reaction to occur that involves the element of interest. From the volume of reagent added, the concentration of the element can be calculated.
- Colorimetric Analyses - A reagent is added to the solution that reacts with the element of interest to produce a color change in the solution. The intensity of the color is proportional to the concentration of the element of interest, and thus when compared to standard solutions in which the concentration is known, the concentration of the element in the unknown solution can be determined.

Generally all elements cannot be determined by the same wet chemical methods and different methods are more sensitive for different elements. Thus, complete wet chemical analysis usually involves a combination of methods. Wet chemical analyses require a skilled analytical chemist, and are usually very time consuming.

### **Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)**

ICP-MS combines two instruments, an inductively coupled plasma spectrometer and a mass spectrometer to simultaneously measure most elements in the periodic table and determine concentration down to the sub part-per trillion (ppt) level. The sample of mineral or rock must

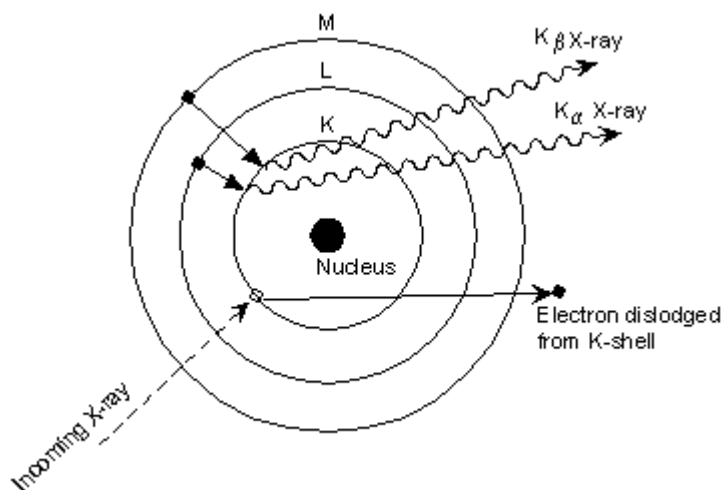
first be powdered and put into solution in acid. This solution is then injected into a plasma as an aerosol where the atoms in the sample are ionized. The plasma is produced by passing Ar gas into an energy field induced by a radiofrequency (RF) generating coil. The RF energy field causes collisions between the Ar atoms, generating a high energy plasma. The sample aerosol is instantly decomposed in the plasma (temperature of 6,000 - 10,000 K) to form analyte atoms which are simultaneously ionized. The ions produced are extracted from the plasma into a mass spectrometer which is held at high vacuum. The mass analyzer then separates the ions based on their mass/charge ratio. The mass analyzer is essentially four parallel molybdenum rods to which a combination of RF and DC voltages are applied. The combination of these voltages allows the analyzer to transmit only ions of a specific mass/charge ratio. Finally, the ions are measured using an electron multiplier, and are collected by a counter for each mass number. The mass spectrum generated is extremely simple. Each elemental isotope appears at a different mass (i.e.,  $^{27}\text{Al}$  would appear at 27 amu) with a peak intensity directly proportional to the initial concentration of that isotope. The proportionality is determined using standard solutions with known concentrations of elements.

Small parts of solid mineral samples can also be analyzed using the ICP-MS with an attached laser. The laser is focused on the part of the sample of interest and the power is increased to cause melting of that small part of the sample (this is called laser ablation). The melt is then injected into the plasma and the rest of the analysis is similar to that described above. This is a relatively new technique that is continually improving in terms of detection limit and reproducibility.

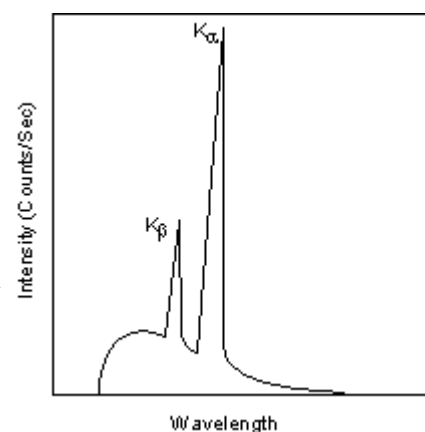
### X-ray Fluorescence (XRF) Spectrometry

XRF spectrometry uses some of the same principles we discussed in our lecture on X-ray diffraction. It is a technique now used mainly for the analysis of rocks because it requires relatively large amounts of sample (about 1 gram). It can be used to measure all of the major elements in a rock or mineral as well as a wide variety of trace elements. Sample preparation involves grinding the rock or mineral to fine powder and either pressing the powder into a pill or melting and quenching the sample to make a glass disk.

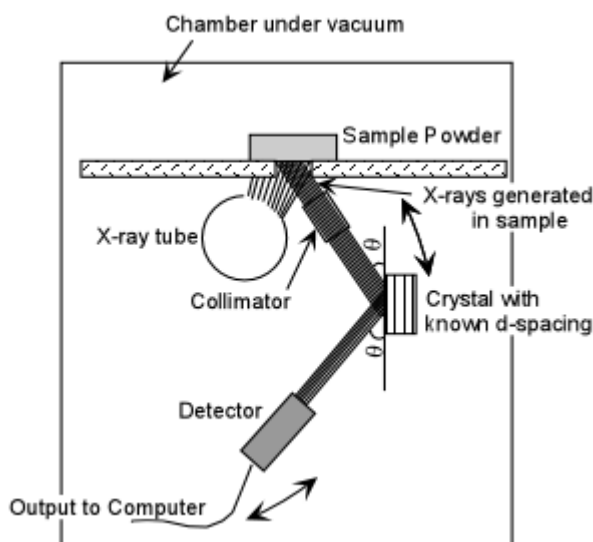
Recall from our previous discussion that when an electron is dislodged from an inner electron shell, outer shell electrons fall in to take its place resulting in the production of X-rays with a wavelength that is characteristic of the element involved. In X-ray diffraction, a beam of electrons is used to dislodge the inner shell electrons and to produce X-rays of known wavelength in the anode target of the X-ray tube. In XRF, however, we use the X-rays from the X-ray tube to dislodge the electrons in atoms of an unknown sample.



Just like in the X-ray tube, inner shell electrons that are dislodged from atoms in the unknown sample result in the production of X-rays of characteristic wavelength for each of the different atoms in the sample. For each atom in the sample, the intensity of the characteristic X-rays will be proportional to the number of atoms in the sample. Thus, if we can measure the intensity of characteristic X-rays for each element, we can compare the intensity to that of a standard with known concentration, and determine the concentration of the element in the unknown.



The instrument used for such measurements is called an X-ray Fluorescence Spectrometer. It consists of an X-ray tube to produce X-rays capable of dislodging inner shell electrons of all elements of interest in the sample. These have to be high energy X-rays, so Cr, Mo, W, and Au targets are used as the anode. The X-rays that are produced in the sample are then sent through a collimator to produce a coherent beam. These are then diffracted through a crystal of known d-spacing. Using the Bragg equation ( $n\lambda = 2d\sin\theta$ ) we can determine the  $\theta$  angle that X-rays of known wavelength will be diffracted through the crystal. Thus, the crystal and detector are set up to diffract only X-rays of the particular wavelength of interest into the detector.



Intensities of characteristic X-rays for each element of interest are determined by rotating the crystal and detector to the angle  $\theta$  required for diffraction of the characteristic X-ray wavelength. X-ray intensities are then measured for each element in the unknown and for each element in a standard that has known concentrations. The following equations are then used to determine the concentration of each element in the unknown:

$$C_i^{\text{std}} = kI_i^{\text{std}}$$

$$C_i^{\text{unk}} = kI_i^{\text{unk}}$$

where  $C_i^{\text{std}}$  = the concentration of element  $i$  in the standard,

$I_i^{\text{std}}$  = the intensity of X-rays of element  $i$  in the standard,

$C_i^{\text{unk}}$  = the concentration of element  $i$  in the unknown,

$I_i^{\text{unk}}$  = the intensity of X-rays of element  $i$  in the unknown, and

$k$  = a proportionality constant.

The proportionality constant,  $k$ , can be determined from the first equation:

$$k = C_i^{\text{std}} / I_i^{\text{std}}$$

This can then be substituted into the second equation to solve for the concentration of element  $i$  in the unknown:

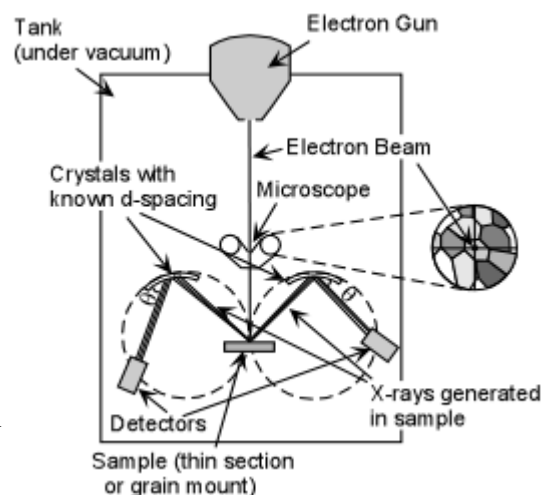
$$C_i^{\text{unk}} = (C_i^{\text{std}} / I_i^{\text{std}}) I_i^{\text{unk}}$$

In practice, this is only true if all elements in the standard and the unknown occur in about the same concentration. This is often difficult to attain, so a wide variety of standards are used to figure out all of the interfering effects and make a calibration curve which relates concentration in the unknown to a more complex equation involving the concentration and intensities in the standard.

### Electron Microprobe (EMP) Analysis

The electron microprobe is an instrument that uses principles similar to XRF. The main difference is that instead of using X-rays to dislodge inner shell electrons of elements in the unknown, an electron beam is used. The electron beam can be focused down to a spot size of about  $1\ \mu\text{m}$  ( $1\ \mu\text{m} = 10^{-6}\text{m}$ ), and thus the X-rays in the sample will only be generated within a very small volume of the sample. Thus, one can measure the concentrations in small parts of single mineral grains, and chemical zoning patterns or changes in the concentration of elements through an individual grain can be determined. The sample can either be a highly polished thin section of a rock or mineral or can be grain mounts wherein individual grains are mounted in epoxy and polished to a smooth surface.

The instrument consists of a large tank that is evacuated to produce a vacuum. At the top is an electron gun that has a filament, similar to that in an X-ray tube, that generates electrons. The electron beam is accelerated down to a sample stage that is moveable. The electron beam is focused to a diameter of about  $1\ \mu\text{m}$  by a series of magnets along its path. Most electron microprobes have at least 3 X-ray spectrometers inside, so that more than one element can be measured at once. A microscope with binocular viewfinders allows the user to focus the electron beam anywhere on the sample, as shown in the inset. This can be accomplished by moving the sample stage.



Electrons striking the small area of the sample produce X-rays with wavelengths characteristic of the elements in the sample. The spectrometers consist of curved crystals of known  $d$ -spacing. These crystals diffract X-rays of each element into the detectors at the diffraction angle  $\theta$ . Several elements can be measured at once, then the spectrometers are set to new angles to measure the X-ray intensities of several more elements.

Just like in XRF analyses, standards have to be measured to determine the proportionality constants or calibration curves, and equations similar to those used in the XRF method are used

to determine element concentrations in the unknowns.

Electron microprobe analysis is useful for determining the major element concentration in small parts of minerals. But, it is much less sensitive than the XRF in terms of trace element concentrations.

### Compositional Variation in Minerals

In our definition of a mineral we said that a mineral has a definite, but not necessarily fixed chemical composition. Here we explore the "not necessarily fixed" portion of the definition. Chemical compositional variation in minerals is referred to ***solid solution***. Although most of us think of solutions as a liquid containing dissolved ions, solids can form solutions as well, in which case we think of one solid as being dissolved in another solid.

Solid solution occurs as the result of ions substituting for one another in a crystal structure. The factors that control the amount of solid solution that can take place in any given crystal structure are:

1. The size of the ions and the size of the crystallographic sites into which they substitute. Generally ions of about the same size can substitute for one another, although the size of the crystallographic site can also play a role if one of the ions is of nearly the same size, but is too large to fit into the site.
2. The charges on the ions that are substituting for one another. If the charges are the same, then the crystal structure can remain electrically neutral. If the charges are not the same then other substitutions must take place to maintain charge balance.
3. The temperature and pressure at which the substitution takes place. In general there is a greater amount of substitution that takes place at higher temperature. This is because the atoms vibrate at a higher rate and the size of crystallographic sites are larger. Pressure can also have an effect because it can change the size of both the crystallographic sites and the ions, thus resulting in different substitutions than might take place at lower pressure.

Three different types of solid solution are recognized - substitutional, interstitial, and omission.

### Substitutional Solid Solution

- Simple substitution

When ions of equal charge and nearly equal size substitute for one another, the solid solution is said to be simple. Generally if the sizes of the ions are nearly the same, the solid solution can occur over the complete range of possible compositions and the solid solution series is said to be ***complete***. If the sizes are similar, but still very different the substitution may only occur over a limited range of compositions and the solid solution series is said to be ***partial*** or ***limited***. Partial or limited solid solution can also occur because the substituting ion does not occur in high enough concentrations in the

environment in which the mineral is formed.

Some common examples are:

Substitution	Ionic Radii (C.N.) Å		Type	Examples
$\text{Fe}^{+2} \rightleftharpoons \text{Mg}^{+2}$	$\text{Fe}^{+2}(6) 0.78$	$\text{Mg}^{+2}(6) 0.72$	Complete High T favors Mg.	Olivines: $\text{Mg}_2\text{SiO}_4$ - $\text{Fe}_2\text{SiO}_4$ Pyroxenes: $\text{MgSiO}_3$ - $\text{FeSiO}_3$ $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFeSi}_2\text{O}_6$ Biotite: $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ - $\text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ Tremolite $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ - Ferroactinolite $\text{Ca}_2\text{Fe}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
$\text{Fe}^{+2} \rightleftharpoons \text{Mn}^{+2}$	$\text{Fe}^{+2}(6) 0.78$	$\text{Mn}^{+2}(6) 0.83$	Complete, but limited by amt. of Mn available.	Siderite $\text{Fe}(\text{CO})_3$ - Rhodochrosite - $\text{Mn}(\text{CO})_3$
$\text{Mg}^{+2} \rightleftharpoons \text{Mn}^{+2}$	$\text{Mg}^{+2}(6) 0.72$	$\text{Mn}^{+2}(6) 0.83$	Partial	
$\text{Na}^{+1} \rightleftharpoons \text{K}^{+1}$	$\text{Na}^{+1} (8) 1.18$	$\text{K}^{+1}(8) 1.51$	Complete at high T Partial at low T	Alkali Feldspars: $\text{NaAlSi}_3\text{O}_8$ - $\text{KAlSi}_3\text{O}_8$
$\text{Fe}^{+3} \rightleftharpoons \text{Al}^{+3}$	$\text{Fe}^{+3} (6) 0.65$	$\text{Al}^{+3} (6) 0.54$	Limited	Alkali Feldspar
$\text{Br}^{-1} \rightleftharpoons \text{Cl}^{-1}$	$\text{Br}^{-1}(6) 1.96$	$\text{Cl}^{-1}(6) 1.81$	Complete	KCl - KBr
$(\text{OH})^{-1} \rightleftharpoons \text{F}^{-1}$	$(\text{OH})^{-1} (4) 1.38$	$\text{F}^{-1}(4) 1.31$	Complete	Biotite: $\text{K}(\text{Mg,Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH,F})_2$

- Coupled Substitution

Coupled substitution occurs if an ion of different charge is substituted. This results in having to make another substitution in order to maintain charge balance. Such coupled substitution is common in the silicate minerals where  $\text{Al}^{+3}$  substitutes for  $\text{Si}^{+4}$  in tetrahedral (C.N. = 4) sites. Some examples of common coupled substitutions are given below:

Substitution	Extent	Example(s)
$\text{Na}^{+1}\text{Si}^{+4} \rightleftharpoons \text{Ca}^{+2}\text{Al}^{+3}$	Complete	Plagioclase: $\text{NaAlSi}_3\text{O}_8$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$
$\text{Ca}^{+2}\text{Mg}^{+2} \rightleftharpoons \text{Na}^{+1}\text{Al}^{+3}$	Limited	Diopside: $\text{CaMgSi}_2\text{O}_6$ - Jadeite: $\text{NaAlSi}_2\text{O}_6$
$\text{Mg}^{+2}2\text{Al}^{+3} \rightleftharpoons 2\text{Fe}^{+2}\text{Ti}^{+4}$	Extensive	Spinels

Another type of coupled solid solution involves filling a site that is normally vacant in order to achieve charge balance. For example, in the amphibole mineral tremolite -  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ , if  $\text{Al}^{+3}$  replaces one of the  $\text{Si}^{+4}$  ions then  $\text{Na}^{+1}$  can go into a site that is normally vacant to maintain charge balance. The resulting formula would be  $\text{NaCa}_2\text{Mg}_5\text{AlSi}_7\text{O}_{22}(\text{OH})_2$ . This would be called a sodic amphibole.



## Interstitial Solid Solution

In some crystal structures there are sites that are not normally occupied by ions. These are considered voids. However, when an ion does occupy one of these voids it is called interstitial solid solution.

## Omission Solid Solution

Omission solid solution occurs when an ion of higher charge substitutes for an ion of lower charge. In order to maintain charge balance, two of the lower charged ions will be replaced, but the higher charged ion will occupy only one site, thus the other site will become vacant, or omitted.

An example of this type of solid solution is found in the blue variety of microcline, in which a  $\text{Pb}^{+2}$  ion replaces 2  $\text{K}^{+1}$  ions. One of the K sites is replaced by the  $\text{Pb}^{+2}$  and the other site is left vacant.

## Exsolution

As mentioned above, the extent of solid solution is sometimes dependent on temperature and pressure since the sizes of ions and the sizes of the crystallographic sites can change with temperature and pressure. Thus, some minerals show complete solid solution under one set of temperature/pressure conditions, and only limited solid solution under different temperature/pressure conditions. When the conditions change to those where limited solid solution is favored, the mineral exsolves or unmixes. But, because the process is taking place in the solid state, exsolution or unmixing cannot easily form two separate phases, because the ions must diffuse through the solid. In fact, what happens is that two separate phases form in discrete domains within a single mineral grain. These domains are crystallographically oriented, so they appear as lamellae or lines across the mineral grain.

Although we will explore this further in our discussion of phase diagrams, an example is given here. The alkali feldspars (albite -  $\text{NaAlSi}_3\text{O}_8$  - orthoclase -  $\text{KAlSi}_3\text{O}_8$ ) form a complete solid solution at high temperature. At lower temperature the solid solution becomes progressively more limited, and as a result lamellae of albite-rich feldspar begin to grow in the orthoclase-rich alkali feldspar. This produces a texture called *perthite*, where the lighter colored albite-rich feldspar is seen to occur as irregular lines or streaks (the lamellae) within the pink orthoclase-rich feldspar.

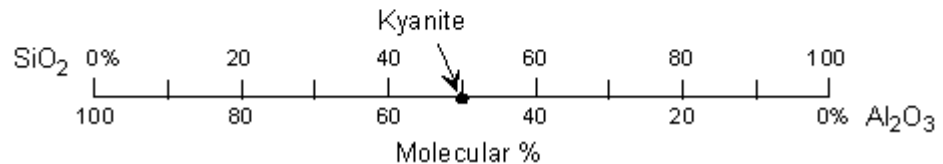
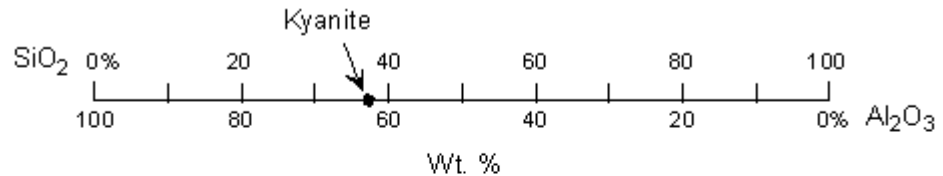
In the case of perthite, the exsolution lamellae are often large enough to see with the naked eye. In other systems, the exsolution lamellae can only be observed with the petrographic microscope. Photographic examples of exsolution lamellae can be seen in your textbook on pages 279-280 and 540 (fig. 19.77).

## Graphical Representation of Mineral Composition

For simple compositional variation it is often convenient to visualize the compositions in some kind of graphical form. Most chemical analyses of oxide and silicate minerals are reported in weight % oxide components. In weight percent because the classical technique of chemical analyses was once gravimetric, and in oxide components because it is difficult to obtain concentrations of Oxygen, so in oxides and silicates it is assumed that there is enough Oxygen to balance the cationic charges.

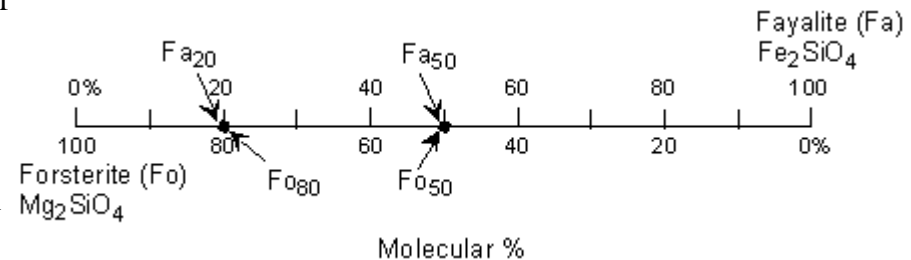
If the composition of a mineral can be expressed with 2 components, then a linear scale can be used as a graphical representation of composition. For example, chemical analysis of the mineral kyanite shows that it is composed of about 36 weight %  $\text{SiO}_2$  and 64 weight %  $\text{Al}_2\text{O}_3$ .

We can plot this on a linear scale as shown here in the upper diagram. Note that in this two component compositional diagram 0% plots at the same point as 100%.



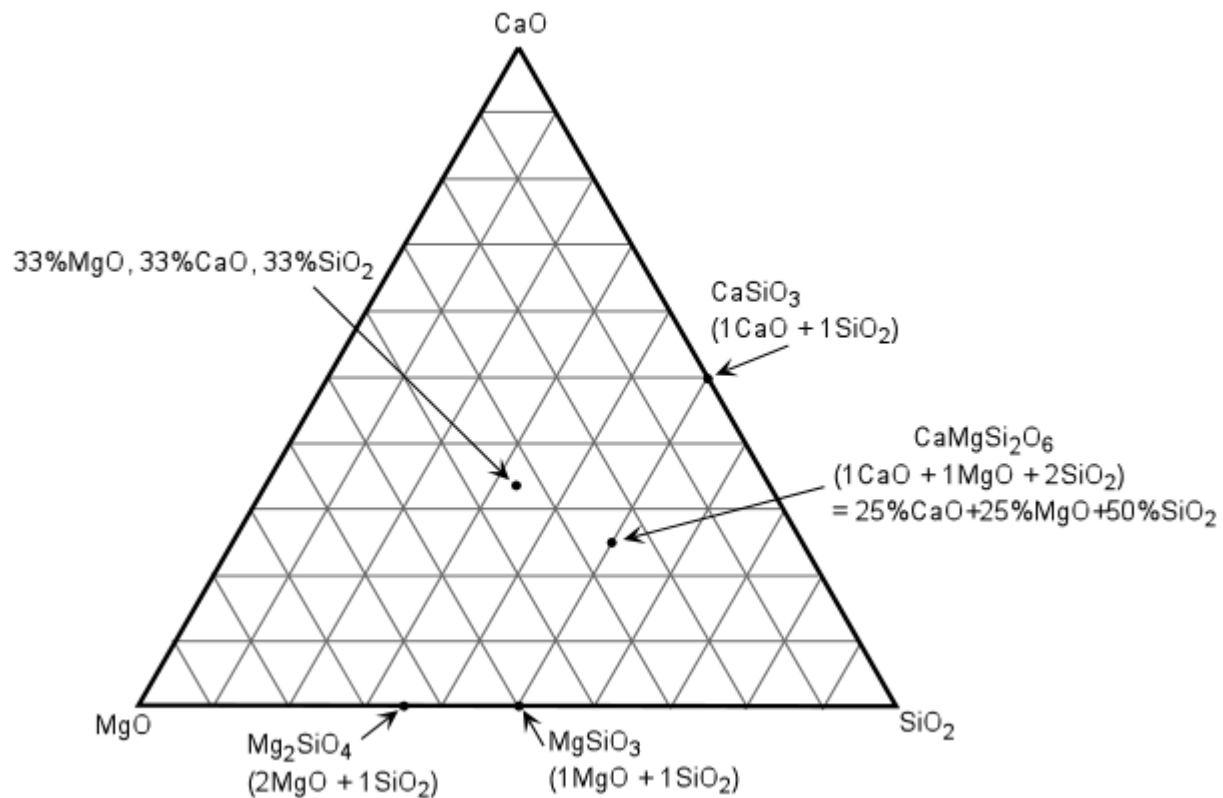
We could divide each of these weight percentages by the molecular weight of each of the oxides and recalculate in the analysis in terms of molecular %. But the chemical formula of Kyanite -  $\text{Al}_2\text{SiO}_5$  - tells us that kyanite is made up of  $1\text{Al}_2\text{O}_3 + 1\text{SiO}_2$ . So in molecular percent 50% of kyanite is  $\text{Al}_2\text{O}_3$  and 50% is  $\text{SiO}_2$ , as shown in the lower diagram above.

Similarly, olivine can be thought of as a mixture of forsterite, Fo ( $\text{Mg}_2\text{SiO}_4$ ) and fayalite, Fa ( $\text{Fe}_2\text{SiO}_4$ ). If these are the only two components involved, then note again that 100% Fo corresponds to 0% Fa, and vice versa.



An olivine solid solution that has 50% of the  $\text{Mg}^{+2}$  ions replaced by  $\text{Fe}^{+2}$  ions would be said to have a composition  $\text{Fo}_{50}$  or  $\text{Fa}_{50}$ . Note that it could be expressed either way, because both ways indicate the same composition. The chemical formula for such a composition would be written as  $\text{MgFeSiO}_4$ . Similarly, for an olivine composition where 20% of the  $\text{Fe}^{+2}$  ions are replaced by  $\text{Mg}^{+2}$  ions, the composition could be expressed as  $\text{Fa}_{20}$  or  $\text{Fo}_{80}$ .

If there are three components that need to be plotted, a triangular graph can be used. Such a graph for the three components  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SiO}_2$  is shown below.



Each of the corners of the triangular graph represent 100% of the component plotted at that corner, and 0% of the other two components. Lines parallel to the sides of the triangle in this case are marked off in 10% increments, so that the horizontal lines represent the % of CaO starting from 0% at the bottom to 100% at the CaO corner. Lines parallel to the SiO<sub>2</sub> - CaO side of the triangle represent the %MgO starting from 0% at the SiO<sub>2</sub> - CaO join to 100% MgO at the MgO corner. Lines parallel to the MgO - CaO side of the diagram represent the % SiO<sub>2</sub>.

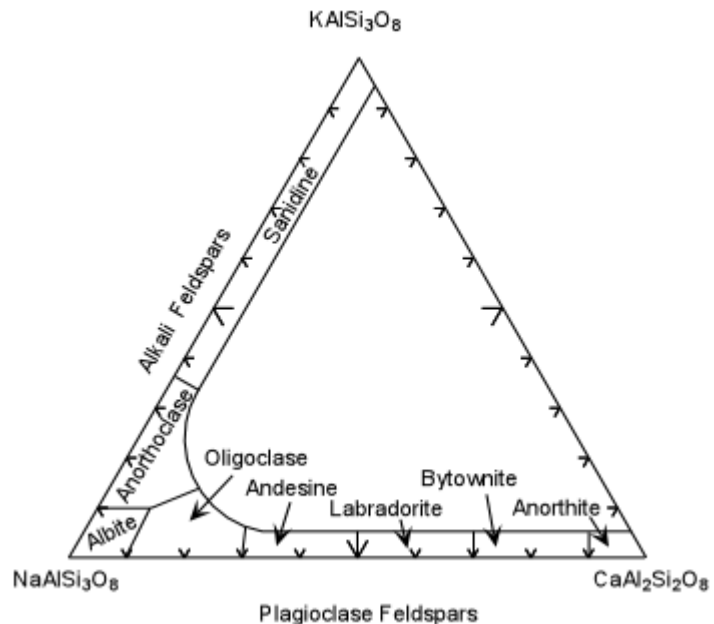
Note that the composition 33%MgO, 33%CaO, 33%SiO<sub>2</sub> plots at the exact center of the triangle.

Minerals that only contain 2 of the three components plot along the sides of the triangle, with the scale being similar to the 2-component graphs discussed above. So, for example if we are using molecular percentages,

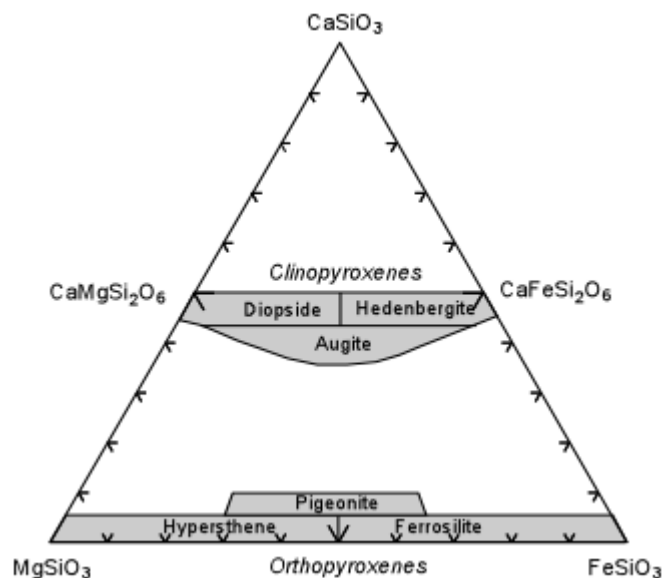
- CaSiO<sub>3</sub> (wollastonite) which can also be written as 1CaO + 1SiO<sub>2</sub>, plots 50% of the way between CaO and SiO<sub>2</sub>.
- MgSiO<sub>3</sub> (enstatite) can also be written as 1MgO + 1SiO<sub>2</sub>, and plots 50% of the way between MgO and SiO<sub>2</sub>.
- CaMgSi<sub>2</sub>O<sub>6</sub> (diopside) can also be written as 1CaO + 1MgO + 2SiO<sub>2</sub>. There are a total of 4 molecules, with 1/4 as CaO, 1/4 as MgO, and 2/4 as SiO<sub>2</sub>. So diopside plots at 25% CaO, 25%MgO, and 50%SiO<sub>2</sub>.

Triangular diagrams are often used to show the compositional ranges in minerals. We here look at 2 examples.

The feldspars can be looked at in terms of the three components Albite (Ab) -  $\text{NaAlSi}_3\text{O}_8$ , Orthoclase (Or) -  $\text{KAlSi}_3\text{O}_8$ , and Anorthite (An) -  $\text{CaAl}_2\text{Si}_2\text{O}_8$ . At high temperature, complete solid solution exists between Ab and Or, to form the alkali feldspar solid solution series. But, as shown in the diagram, the alkali feldspar solid solutions can contain up to 5% of the An component. Similarly a complete solid solution series exists between Ab and An, to form the plagioclase solid solution series. Plagioclase can contain up to about 5% of the Or component.



Another example is shown by the pyroxene minerals. These plot in the three component system Enstatite (En) -  $\text{MgSiO}_3$ , Wollastonite (Wo) -  $\text{CaSiO}_3$ , Ferrosilite (Fs) -  $\text{FeSiO}_3$ . Wo does not have a pyroxene structure. Complete solid solution exists between Diopside, Di, ( $\text{CaMgSi}_2\text{O}_6$ ) and Hedenbergite, Hd, ( $\text{CaFeSi}_2\text{O}_6$ ). These pyroxenes are monoclinic and are thus called the clinopyroxenes. Augite is also a clinopyroxene, but note that it is depleted in the Wo component relative to the Di - Hd series. En - Fs also forms a complete solid solution series. These minerals are orthorhombic, so the series is often referred to the orthopyroxenes.. Pigeonite is a monoclinic pyroxene that has slightly more of the Wo component than the orthopyroxenes.



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

1. By what processes can minerals form in nature?
2. What are the three most abundant elements in the earth's crust?
3. What factors make it difficult to determine the chemical composition of minerals?

4. What is the best method for determining the chemical variability in a small mineral grain?
5. What is a solid solution? Give examples of at least three minerals that show solid solution, giving the end-members for each?
6. Why is solid solution by ionic substitution so common in nature?
7. What is exsolution? Give at least one example of a mineral that commonly shows exsolution.

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