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Genesis of Minerals

Composition of the Earth's Crust

Classifications of Minerals

Environments of Mineral Formation

Study of Minerals with Emphasis on Rock-forming Minerals

Chemical Properties of Minerals

Mineral Chemistry

Minerals can form by any of the following processes:

- Precipitation from a fluid like H_2O or CO_2. 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.

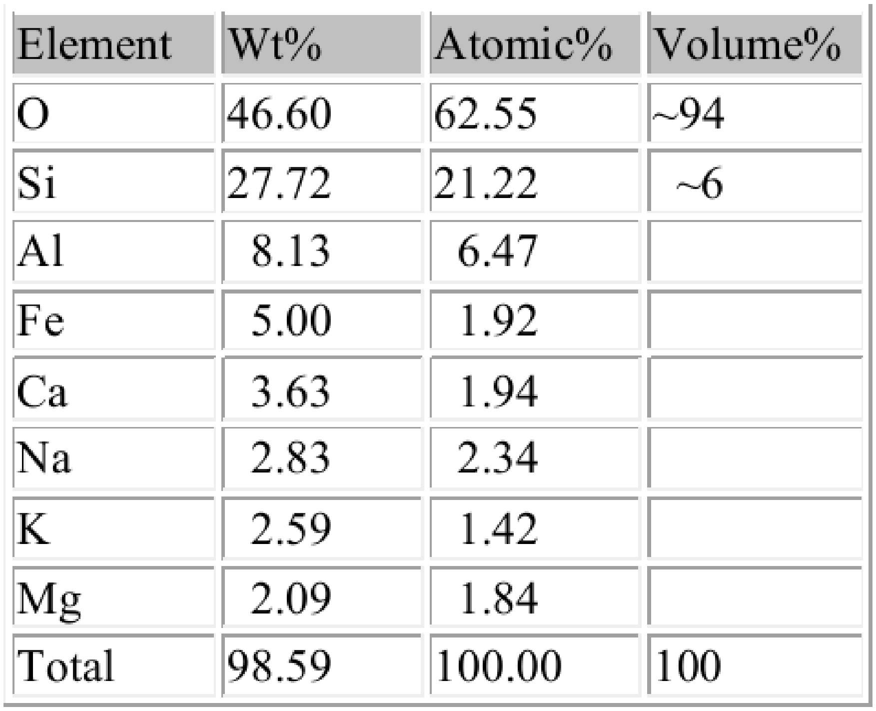
No matter what process is involved, a particular mineral cannot form unless the chemical ingredients necessary to make the mineral are present. Thus, the most common minerals are minerals that have a chemical composition made of the common elements found in their environment. Since the environment where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

(Note: **Sublimation** is the transition of a substance directly from the solid to the gas phase without passing through the intermediate liquid phase. It is an endothermic phase transition that occurs at temperatures and pressures below a substance's triple point in its phase diagram.)

Composition of the Earth’s 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:



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.

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.

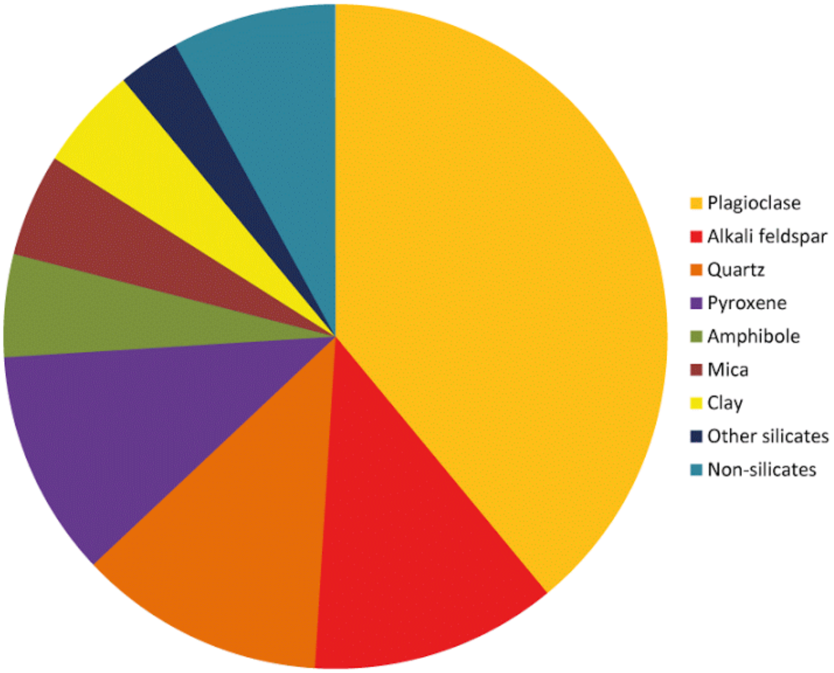
Other minerals, containing the other elements in the periodic table are found in the crust. But, in order for these minerals to occur, special geologic conditions are necessary to concentrate these less abundant elements so that they occur in high enough concentrations to form a separate mineral.

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.

The table below lists average crustal abundances of some of the important materials that are commonly sought.

Substance	Average Crustal Abundance
Al (Aluminum)	8.0%
Fe (Iron)	5.8%
Ti (Titanium)	0.86%
Cr (Chromium)	0.0096%
Zn (Zinc)	0.0082%
Cu (Copper)	0.0058%
Ag (Silver)	0.000008%
Pt (Platinum)	0.0000005%
Au (Gold)	0.0000002%
U (Uranium)	0.00016%

More than 90% on the crust is composed of silicate minerals. Most abundant silicates are feldspars (plagioclase (39%) and alkali feldspar (12%)). Other common silicate minerals are quartz (12%) pyroxenes (11%), amphiboles (5%), micas (5%), and clay minerals (5%). The rest of the silicate family comprises 3% of the crust. Only 8% of the crust is composed of non-silicates — carbonates, oxides, sulfides, etc.



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. There are technics for measuring even the smallest concentrations of elements. 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:

- Individual minerals are much smaller than rocks and it is therefore difficult to obtain enough sample of a mineral to perform the chemical analysis.
- 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 form all other minerals, and still does not tell us if there is any chemical variability between individual grains. (The electron microprobe technique is an exception, because it allows for analysis of small areas of single grains).
- 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 will only know the names of the methods which are more commonly used. Some common analytical methods are:

- Wet chemical analysis
- Inductively coupled plasma - mass spectrometry (ICP-MS)
- X-ray fluorescence (XRF) spectrometry
- Electron microprobe (EPM) analysis

Compositional Variation in Minerals

Mineral has a definite, but not necessarily fixed chemical composition. Here we explore the "not necessarily fixed" composition of minerals. 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 structures 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 sizes 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.

Solid solutions

Solid solution: A solid that has a homogeneous crystal structure in which some equivalent sites are occupied by different ions.

A **solid solution** is a solid-state solution of one or more solutes in a solvent. Such a mixture is considered a solution rather than a compound when the crystal structure of the solvent remains unchanged by addition of the solutes, and when the mixture remains in a single homogeneous phase. This often happens when the two elements (generally metals) involved are close together on the periodic table; conversely, a chemical compound generally results when two metals involved are not near each other on the periodic table.

Solid solution can also be defined as solid in which components are *compatible* and form a *unique phase*. It can be seen in Figure 1.

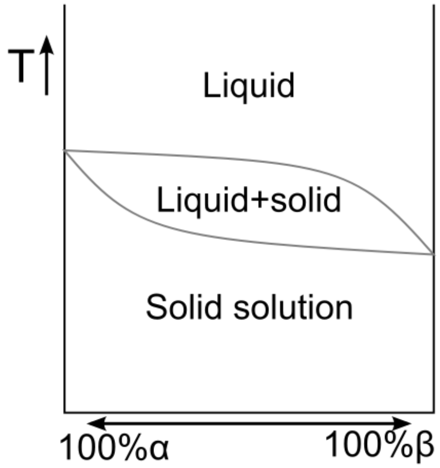


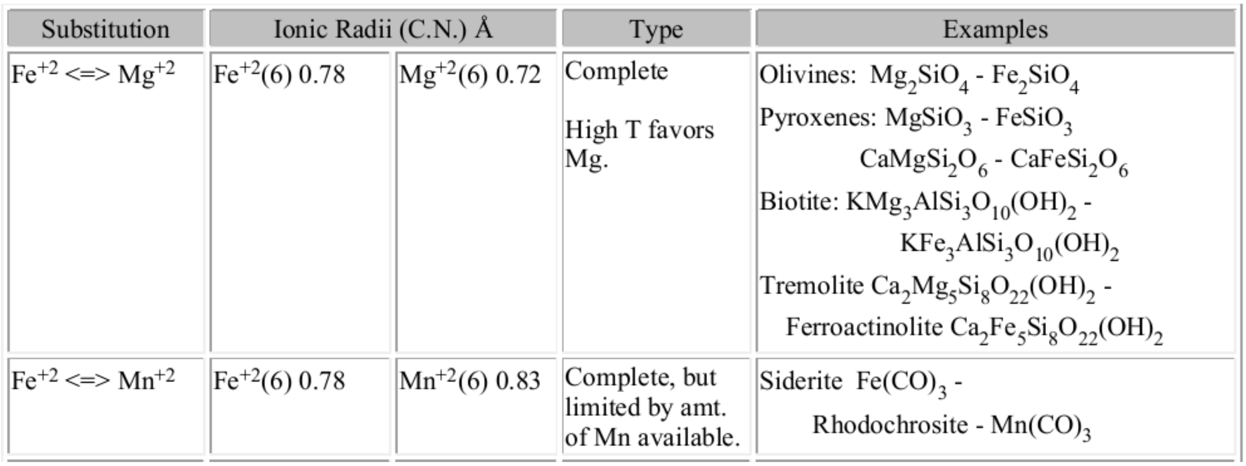
Figure 1: A binary phase diagram displaying solid solutions over the full range of relative concentrations.

Substitutional solid solutions

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.

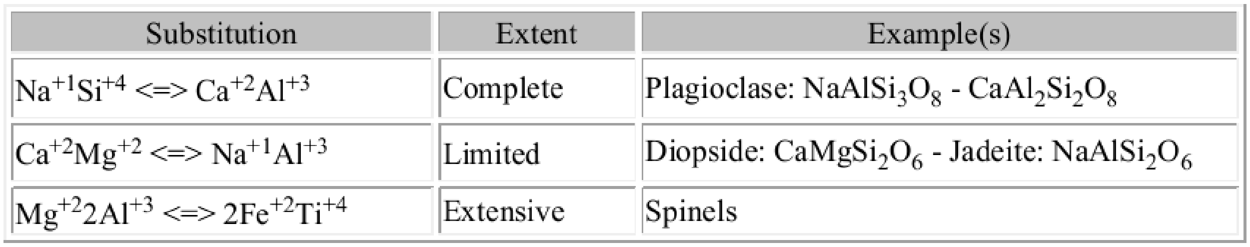
Some common examples are:



Substitution	Ionic Radii (C.N.) Å		Type	Examples
Fe^{+2} <=> Mg^{+2}	Fe^{+2}(6) 0.78	Mg^{+2}(6) 0.72	Complete High T favors Mg.	Olivines: Mg_2SiO_4 - Fe_2SiO_4 Pyroxenes: $MgSiO_3$ - $FeSiO_3$ $CaMgSi_2O_6$ - $CaFeSi_2O_6$ Biotite: $KMg_3AlSi_3O_{10}(OH)_2$ - $KFe_3AlSi_3O_{10}(OH)_2$ Tremolite $Ca_2Mg_5Si_8O_{22}(OH)_2$ - Ferroactinolite $Ca_2Fe_5Si_8O_{22}(OH)_2$
Fe^{+2} <=> Mn^{+2}	Fe^{+2}(6) 0.78	Mn^{+2}(6) 0.83	Complete, but limited by amt. of Mn available.	Siderite $Fe(CO)_3$ - Rhodochrosite - $Mn(CO)_3$

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 Al^{+3}substitutes for Si^{+4}in tetrahedral (C.N. = 4) sites. Some examples of common coupled substitutions are given below:



Substitution	Extent	Example(s)
$Na^{+1}Si^{+4}$ <=> $Ca^{+2}Al^{+3}$	Complete	Plagioclase: $NaAlSi_3O_8$ - $CaAl_2Si_2O_8$
$Ca^{+2}Mg^{+2}$ <=> $Na^{+1}Al^{+3}$	Limited	Diopside: $CaMgSi_2O_6$ - Jadeite: $NaAlSi_2O_6$
$Mg^{+2}2Al^{+3}$ <=> $2Fe^{+2}Ti^{+4}$	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 - $Ca_2Mg_5Si_8O_{22}(OH)_2$, if Al^{+3} replaces one of the Si^{+4} ions then Na^{+1} can go into a site that is normally vacant to maintain charge balance. The resulting formula would be $NaCa_2Mg_5AlSi_7O_{22}(OH)_2$. This would be called a sodic amphibole.

Interstitial solid solution

Interstitial defects have sometimes been termed interstitial solid solution, especially those defects occurring in quantities that affect the chemical formula.

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 Pb^{+2} ion replaces 2 K^{+1} ions. One of the K sites is replaced by the 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*.

The alkali feldspars (albite - $NaAlSi_3O_8$- orthoclase - $KAlSi_3O_8$) 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.

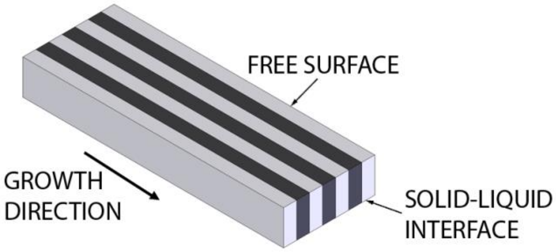


Figure 2: Typical example of lamella.

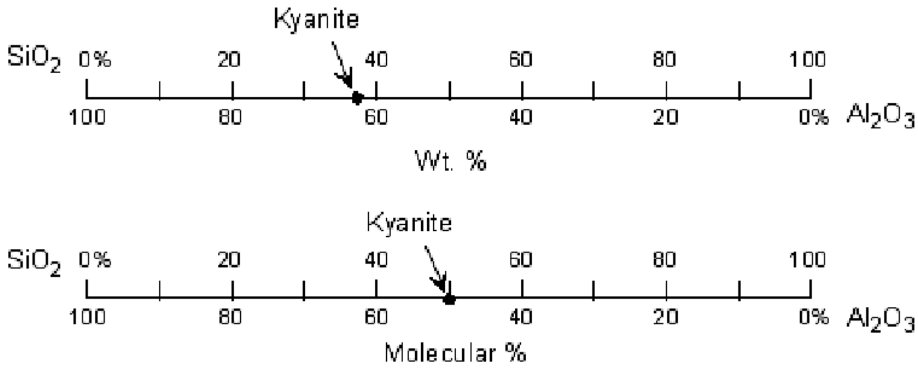
In the case of perthite, the exsolution lamellae are often large enough to see with the naked eye. In other systems, the exsolution lamellae can only be observed with the petrographic microscope.

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.

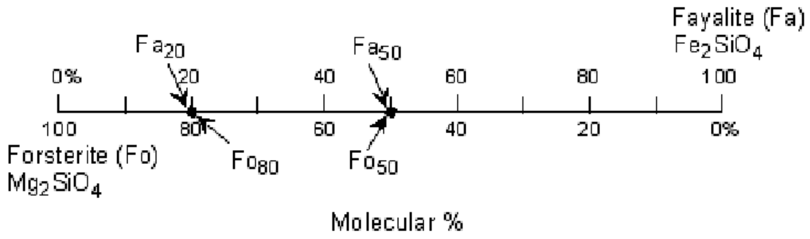
If the composition of a mineral can be expressed with *2 components*, then a linear scale can be used as a graphical representation of composition. For example, chemical analysis of the mineral kyanite shows that it is composed of about 36 weight % SiO_2 and 64 weight % Al_2O_3.

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



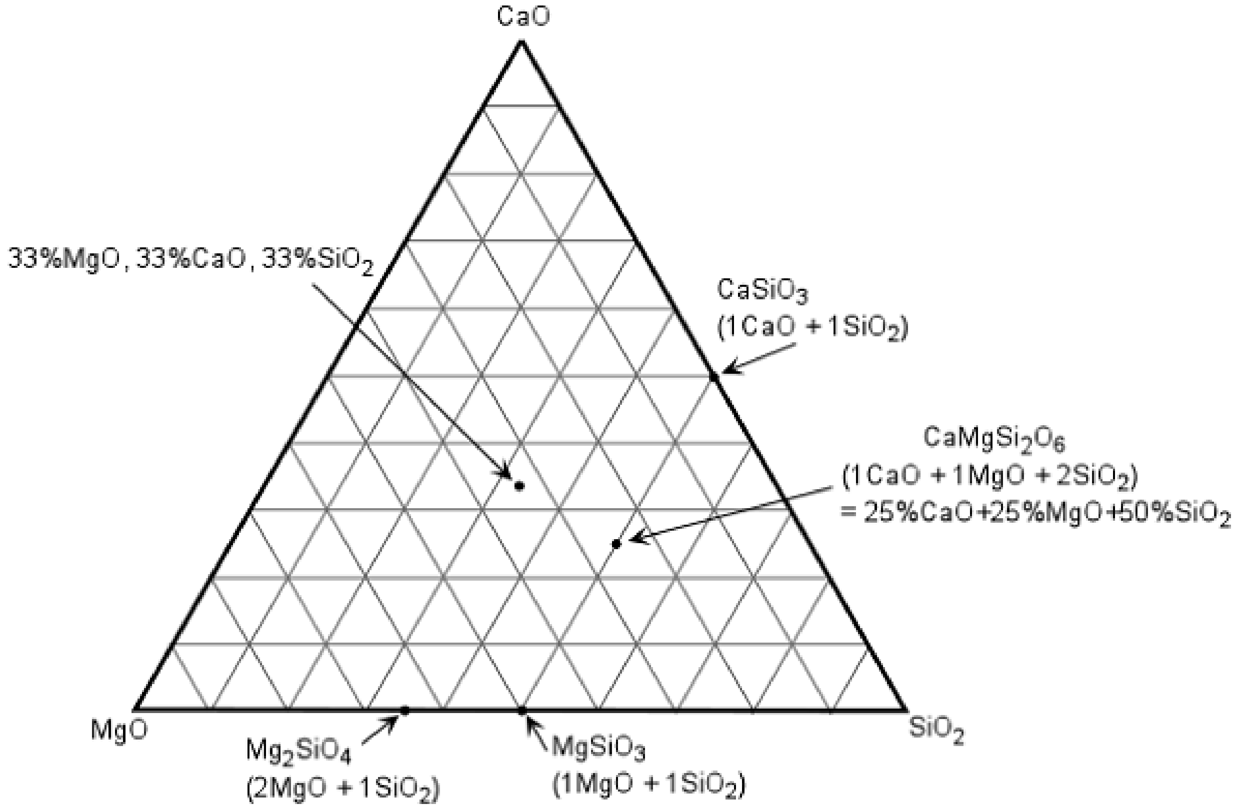
We could divide each of these weight percentages by the molecular weight of each of the oxides and recalculate in the analysis in terms of molecular %. But the chemical formula of Kyanite - Al_2SiO_5 - tells us that kyaniteis made up of $1Al_2O_3$+$1SiO_2$. So in molecular percent 50% of kyanite is Al_2O_3 and 50% is SiO_2, as shown in the lower diagram above.

Similarly, olivine can be thought of as a mixture offorsterite, Fo (Mg_2SiO_4) and fayalite, Fa (Fe_2SiO_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 Mg^{+2}ions replaced by Fe^{+2}ions would be said to have a composition Fo_{50} or 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 $MgFeSiO_4$. Similarly, for an olivine composition where 20% of the Fe^{+2} ions are replaced by Mg^{+2} ions, the composition could be expressed as Fa_{20}or 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 MgO, CaO, 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 horizontals lines represent th*e % of CaO starting from 0% at the bottom to 100%* at the CaO corner. Lines parallel to the SiO_2 - CaO side of the triangle represent the % MgO starting from 0% at the SiO_2 - CaO join to 100% MgO at the MgO corner. Lines parallel to the MgO - CaO side of the diagram represent the % SiO_2.

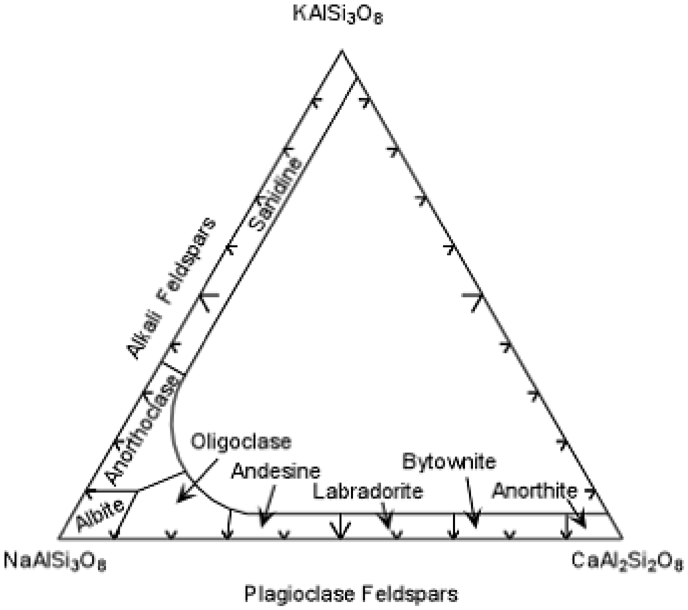
Note that the composition 33%MgO, 33%CaO, 33%SiO2plots at the exact center of the triangle.

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,

- $CaSiO_3$ (wollastonite) which can alsobe written as 1CaO + $1SiO_2$, plots 50% of the way between CaO and SiO_2.
- $MgSiO_3$ (enstatite) can also bewritten as 1MgO + $1SiO_2$, and plots 50% of the way between MgO and SiO_2.
- $CaMgSi_2O_6$ (diopside) can also be written as 1CaO + 1MgO +$2SiO_2$. There are a total of 4 molecules, with 1/4 as CaO, 1/4 as MgO, and 2/4 as SiO_2. So diopside plots at 25% CaO, 25%MgO, and 50% SiO_2.

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) - $NaAlSi_3O_8$, Orthoclase (Or) - $KALSi_3O_8$, and Anorthite (An) - $CaAl_2Si_2O_8$. 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) -$MgSiO_3$, Wollastonite (Wo) - $CaSiO_3$, Ferrosilite (Fs) - $FeSiO_3$. Wo does not have a pyroxene structure. Complete solid solution exists between Diopside, Di, (CaMgSi2O6) and Hedenbergite, Hd, (CaFeSi2O6). 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 thathas slightly more of the Wo component than the orthopyroxenes.