

What is a mineral?

A mineral is a naturally occurring, homogenous solid phase, formed through inorganic processes, with a clearly described (fixed range of) chemical composition and an ordered crystal structure.

Crystal structure: The regular and repeated 3-dimensional arrangement of atoms or ions in a crystal.

Classification system based on chemical signature – 8 groups

I Elements Au, C

II Sulfides PbS, FeS₂

III (Hydr)oxides Fe₂O₃, TiO₂

IV Halides NaCl, CaF₂

V [XO₃]²⁻ e.g. Carbonates CaCO₃

VI [XO₄]²⁻ e.g. Sulfates CaSO₄

VII [XO₄]³⁻ e.g. Phosphates Ca₅(PO₄)₃(OH,F,Cl)

VIII [SiO₄]⁴⁻ e.g. Silicates (Mg,Fe)₂SiO₄

1. Silicate minerals

1.1 Introduction: After oxygen, silicon is the second most abundant element in the Earth's crust and mantle. Si-O bond is substantially stronger compared to other cations-oxygen bonds. Hence, silicate minerals make up the vast majority of crustal rocks (90.8 volume%).

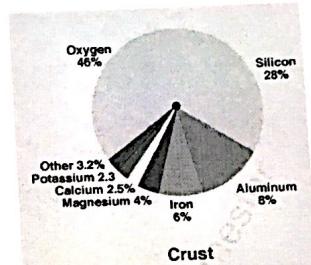


Figure 1: Major element abundances in the Earth's crust.

1.2 Si-O bond and silicate structures: Description of silicate structures is largely based on the model for the Si-O bond. In a 100% ionic bond consisting of Si⁴⁺ and O²⁻ ions, the oxygen ions would tend to be close-packed with charge balance provided by Si⁴⁺ and other cations in interstitial sites of permissible size. However, very few silicates have a density approaching that of a close-packed oxygen array. The 'cation : oxygen' radius ratios are also found to be inconsistent (not matching) with the observed coordinations. In comparison, a covalent model provides a much better match, considering the Si-O bond in terms of overlapping orbitals. In majority of silicates, Si is tetrahedrally coordinated to oxygen with the O-Si-O bond angles only slightly deviating from the ideal tetrahedral value of 109.5°, which also supports the covalent model. However, neither the 'complete covalent bond model' nor the 'complete ionic bond model', is found to provide the complete match considering all aspects and despite not being able to perfectly quantify the 'ionicity', the general consensus is that the Si-O bond has 50% ionic character and 50% covalent character. Si has valency of +4 and O has a valency of -2

Si-O bond (Figure 2): 50% Covalent bonding (electron sharing) and 50% Ionic bonding (electron exchange)

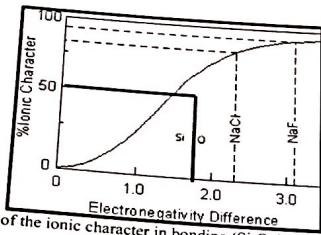


Figure 2: Comparison of the ionic character in bonding (Si-O; Na-Cl; Na-F).

Each O in the tetrahedra has a valency of -1 and individual tetrahedra can join up with other ions in lots of interesting ways. The way in which the basic unit of the "SiO₄ tetrahedra" are arranged in different silicate structures is used for classifying silicate minerals. The SiO₄ tetrahedra are either (1) present as islands i.e. isolated from each other and hence bonded to other cation polyhedral or (2) attached to other SiO₄ tetrahedra by corner-sharing. The grouping of corner-sharing SiO₄ tetrahedra is commonly considered to constitute the frame of a silicate structure, with other cations occupying appropriate interstitial positions.

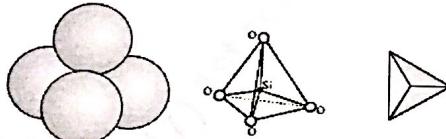


Figure 3: The [SiO₄] tetrahedron can be represented by either a packing model, a ball and stick model or a polyhedral model.

1.3 Al-Si substitution: In many silicate minerals, Al is often found to substitute for Si in the SiO₄ tetrahedron. However, considering the normal oxidation states (Si⁺⁴, Al⁺³ and O⁻²) makes it becomes essential that the Al-Si substitution should always be compensated by replacement in the cation content to maintain electrical neutrality. When Al substitutes for Si in a tetrahedron, both Al and Si play a similar structural role and the overall structural configuration remains the same. The size of the [AlO₄] tetrahedron is found to be slightly larger than that of the [SiO₄] tetrahedron since the Al-O bond (1.75 Å) is longer than the average Si-O bond (1.62 Å). In silicate structures where [AlO₄] and [SiO₄] tetrahedra are linked, the observed size difference (between [AlO₄] and [SiO₄] tetrahedra) is accommodated by a change in the T-O-T bond angle (T = tetrahedral cation). Another known effect of the Al-Si substitution is that the potential energy of the Al-O-Al bond is more than that of an Al-O-Si bond, which makes the placement of adjacent [AlO₄] tetrahedra (i.e. AlO₄ tetrahedra placed adjacent / immediately next to each other) to be energetically unfavorable. This is known as the 'aluminium avoidance principle' and plays a significant role in the ordering of Al and Si among tetrahedral sites in many aluminosilicate minerals.

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2. Subdivision of silicate minerals

This is centered on the structural signature of silicates based on polymerization of SiO₄ groups (in simple words "process of linking smaller molecules together to form larger molecules in the form of small or large chains or multi-dimensional networks"). Degree of polymerization has significant consequences for structure, chemical composition, habit (external shape), physical (cleavage) and optical properties of silicates.

Broadly there are six subgroups of silicates and these subgroups are again subdivided into groups, series, types and subspecies.

1) Isolated tetrahedra: nesosilicates / orthosilicates/ Island silicates

Ratio of Si:O = 1:4
E.g. olivine, garnet

2) Double island silicates / sorosilicates / pyrosilicates)

Ratio of Si:O = 1:3.5
E.g. Melilites, epidote, lawsonite

3) Inosilicates /chain silicates

Single chains: Ratio of Si:O = 1:3
E.g. Pyroxenes with two "bridging oxygens" per tetrahedral

Double chains: Ratio of Si:O = 2:5.5
E.g. Amphiboles with two or three bridging oxygens per tetrahedra

4) Cyclosilicates/ring silicates- usually six sided

Ratio of Si:O = 1:3
Two 'bridging oxygens' per tetrahedra
e.g. tourmaline, beryl (Be₃Al₂Si₆O₁₈)

5) Phyllosilicates / sheet silicates

Ratio of Si:O = 1:2.5
Three bridging oxygens per tetrahedra
e.g. micas, chlorite, serpentine, clay minerals

6) Tectosilicates/ framework silicates

Ratio of Si:O = 1:2
Four bridging oxygens per tetrahedra
e.g. quartz, feldspar

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2.1 Olivine

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The olivine minerals have a general formula M_2SiO_4 where M is Mg^{2+} , Fe^{2+} or Ca^{2+} . Most natural olivines have compositions in the continuous range of compositions between Mg_2SiO_4 (forsterite) and Fe_2SiO_4 (fayalite) and the formula is written as $(Mg,Fe)_2SiO_4$, indicating that Mg and Fe can substitute for each other. This type of continuous chemical mixing is called a *solid solution*. The most important factor which controls solid solution formation is the relative size of the cations.

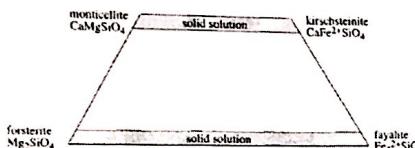


Figure 4: Compositions of natural olivines. The mineral olivine refers to the solid solution between forsterite and fayalite. Less common is monticellite, which also has solid solution due to Mg \leftrightarrow Fe substitution.

Most natural olivines have compositions in the range Mg_2SiO_4 (forsterite) to Fe_2SiO_4 (fayalite). There is virtually no solid solution between the Ca-bearing olivines and Fe,Mg olivines under normal geological conditions, as the structure cannot tolerate the strain which would be produced by random substitution of cations of such different sizes (Ca^{2+} ion is too big to substitute into sites (M2) when they are occupied by Mg^{2+} and Fe^{2+}).

Trace elements: Nickel, cobalt and zinc are also frequently present in olivines in trace amounts

2.1.1 Structure of Olivine

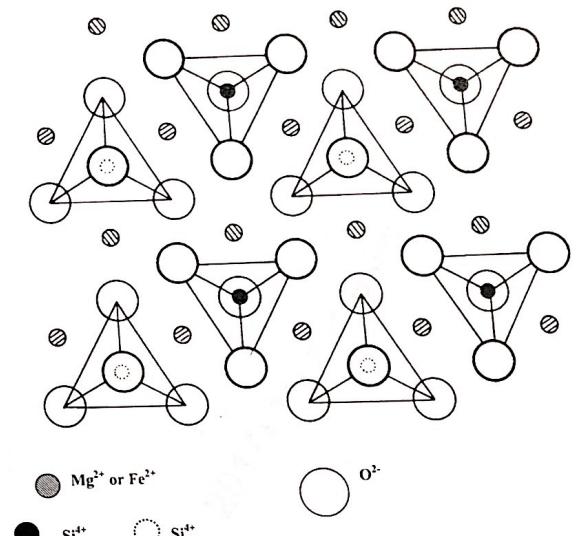


Figure 5: Structure of Olivine. Orthorhombic orthosilicates with isolated SiO_4^4 tetrahedra (pointing alternately up and down) linked by divalent Mg or Fe ions.

2.1.2 Occurrence of Olivine:

Very important rock forming mineral:

Mafic and ultramafic magmatic rocks (gabbro, basalt, peridotite), with e.g. pyroxenes and plagioclase

Dunites (almost pure olivine), Cumulate which crystallized during solidification of a

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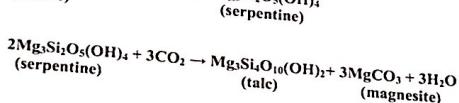
peridotitic magma

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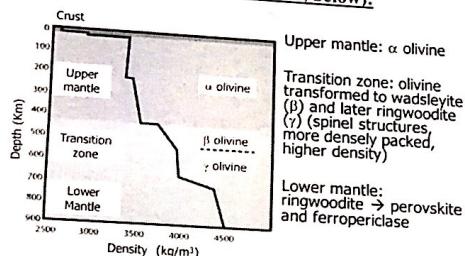
Pure forsterite: forms during metamorphism of dolomitic limestone (forsterite marble)
 $2\text{CaMg}(\text{CO}_3)_2 + 3\text{SiO}_2 \rightarrow \text{Mg}_2\text{SiO}_4 + 2\text{CaSiO}_3 + 2\text{CO}_2$

Alteration products

Olivines are highly susceptible to low grade metamorphism and weathering.
 $3\text{Mg}_2\text{SiO}_4 + 4\text{H}_2\text{O} + \text{SiO}_2 \rightarrow 2\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ (serpentine)



2.1.3 Olivine in the Earth's mantle (Figure 6, below):



2.1.4 Olivine Phase diagram

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Melting point of forsterite = 1890°C

Melting point of fayalite = 1205°C

Note that only the pure end-members of the solid solution melt at fixed temperatures. Solid solutions melt over a range of temperatures as shown in the following Composition-Temperature phase diagram.

Only pure melts (pure end members) begin to crystallise solids of the same composition as the melt. All other (intermediate) melt compositions crystallise solids more Mg rich than the melt.

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

The upper curve is the LIQUIDUS and describes the temperature range where the onset of crystallization occurs.

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

The lower curve is the SOLIDUS and describes the onset of a solid.

Between the curves both liquid and solid material exists.

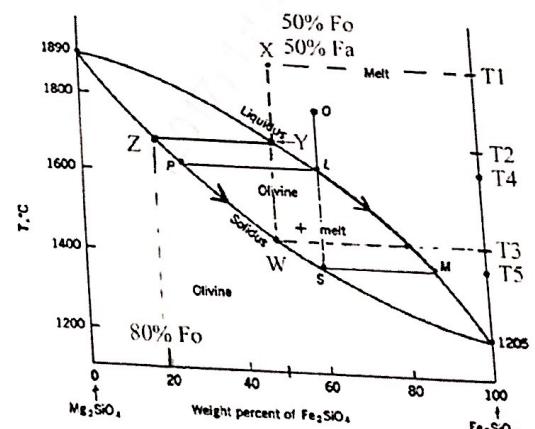


Figure 7: This (Figure 7) is an equilibrium diagram showing a plot of temperature (in °C) vs composition.

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Simple binary system (Phase diagram in Figure 7)

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Forsterite has melting point of 1890 °C

Fayalite has melting point of 1205 °C

Therefore, the first olivine crystals to form should be Mg rich Forsterite at ~1889 °C and, as a consequence, the remaining liquid would become progressively more Fe rich.

The two intercepts on the temperature axis are at 1890 ° and 1205 °C, Fo=100% and Fa=100% respectively.

Consider this example:

Equilibrium crystallization:

Consider a melt of composition **Fo50, Fa50** that exists at a temperature **T1** (X on diagram in Figure 7).

As the melt starts to cool, at temperature T2, the line for **Fo50, Fa50** hits the **liquidus** curve (point Y on diagram in Figure 7). At this point crystals of **Fo80** begin to form from the liquid. The remaining liquid becomes more Fe or Fayalite rich.

As the temperature drops further and cooling of the melt continues, the liquid becomes progressively enriched in Fe, so the crystals that are forming also become more Fe rich.

As the temperature drops down to T3, the last of the liquid is used up. A liquid of composition **Fo50, Fa50** has to completely solidify by the time the temperature drops to T3 (the **solidus**).

Under equilibrium conditions, the crystals are constantly altered and converted to a composition approaching **Fo50** (at temperature **T3**) from a **Fo80** start (at temperature **T2**). Equilibrium implies slow cooling and constant diffusion of Fe ions into the crystals.

Remember the **Lever's rule** to calculate the proportions of co-existing liquid and solid phases at any given temperature.

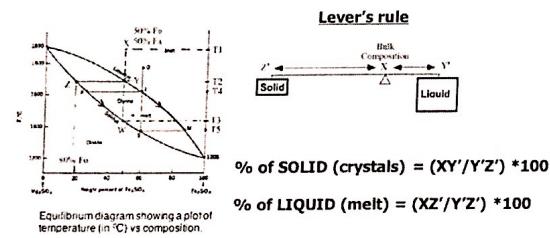


Figure 8.

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Disequilibrium processes are also quite common and can occur by:

(a) Removal of crystals: Crystals may precipitate or settle out of the melt, and sink due to higher density. As crystals are removed, the remaining liquid becomes more Fe rich e.g. $\text{Fo40} \rightarrow \text{Fo30}$. This in turn extends the range of crystallization to lower temperatures.

Result: Cumulative Rocks -many basaltic piles.

(b) Diffusion is not allowed: If crystals are layered and cooled fast enough, we get the first crystals layered off or zoned by further layers. This has the same effect as removal of crystals.



Figure 9: Zoned crystal with Mg-rich core and Fe-rich rim.

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3.1 Pyroxenes

Pyroxenes are the most important group of ferromagnesian silicates, and form an integral component of almost all igneous rocks. They constitute a major portion of mantle peridotites and are also found in many rocks formed under both regional and contact metamorphism.

Their widespread occurrence, varied chemistry, and intricate phase transition behaviour make them excellent minerals for use as geothermometers and geospeedometers (i.e. minerals which are able to record information about the thermal history and cooling rates of rocks).

Pyroxenes have a varied chemistry, which can be represented by the general structural formula $X_2YZ_4O_8$, where X and Y can be either monovalent (e.g. Na, Li), divalent (e.g. Mg, Fe²⁺, Ca), or trivalent cations (e.g. Al, Fe³⁺). Z is either Si or Al.

Common endmembers include:

- i) Enstatite $Mg_2Si_2O_6$ (or simply $MgSiO_3$)
- ii) Ferrosilite $Fe_2Si_2O_6$ (or simply $FeSiO_3$)
- iii) Diopside $CaMgSi_2O_6$
- v) Hedenbergite $CaFeSi_2O_6$
- vii) Jadeite $NaAlSi_3O_8$
- viii) Ca-Tschermak $CaAl(AlSi)O_8$

Orthorhombic pyroxenes

Enstatite—Orthofersilite $(Mg, Fe^{+2})_2Si_2O_6$

Monoclinic pyroxenes

Mostly Clinopyroxenes	Diorside—Hedenbergite	$Ca(Mg, Fe^{+2})_2Si_2O_6$
	Johannsenite	$CaMnSi_2O_6$
	Aegirine	$NaFe^{+3}Si_2O_6$
	Spodumene	$LiAlSi_2O_6$
	Jadeite	$NaAlSi_3O_8$
	Augite	$(Ca, Mg, Fe^{+2}, Al)_2(Si, Al)_2O_6$
	Pigeonite	$(Mg, Fe^{+2}, Ca)(Mg, Fe^{+2})_2Si_2O_6$
	Omphacite	$(Ca, Na)(Mg, Fe^{+2}, Fe^{+3}, Al)Si_2O_6$
	Fassaite	$Ca(Mg, Fe^{+2}, Fe^{+3}, Al)(Si, Al)_2O_6$

3.1.1 Solid solutions and the pyroxene quadrilateral

The most important natural pyroxene minerals are formed from solid solutions involving Mg, Fe²⁺, and Ca. The range of compositions can be represented by the pyroxene quadrilateral (Fig. 1). There

are three important solid solutions contained within the quadrilateral: the *orthopyroxene solid solution* (often referred to as *hypersthene*), the *pigeonite solid solution*, and the *augite solid solution*.

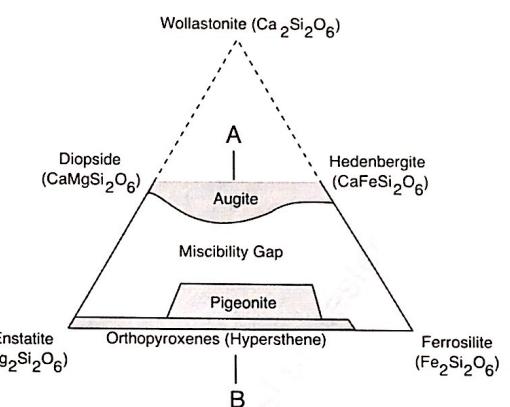
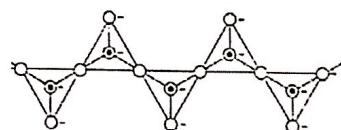


Figure 1: Pyroxene quadrilateral

3.1.1 Structure of Pyroxenes:



● Silicon

○ Oxygen

Figure 2. Single SiO_4 chains in pyroxenes with periodicity of two tetrahedra.

3.1.2 Substitution: Unlike the olivine series which was restricted to a few divalent ions, this series accepts a wide range of ions. Eg: Al, Ca, [Mn, Fe³⁺, Ti, Cr, Ni] can enter the lattice in varying amounts. The latter 5 seldom exceed 10% of the composition.

Similar to olivine, the Ni and Cr are found mainly in basic rocks or the Mg varieties. High Al Hypersthene occurs in metamorphic rocks. As well, Al³⁺ enters the structure under high pressure conditions. Therefore, the amount of Al³⁺ is roughly indicative of the pressure. Eg: you can tell if the rock is a cumulative or a very deep mantle rock, if Al³⁺ ↑ then Pressure ↑.

Ca can substitute into the lattice up to about 15% by weight. Substitution is dependent on temperature: at higher T, more Ca can enter the lattice. The lattice is usually monoclinic which is less ordered and makes Ca substitution easier.

3.1.3 Phase relationships:

1. Enstatite – Ferrosilite phase diagram

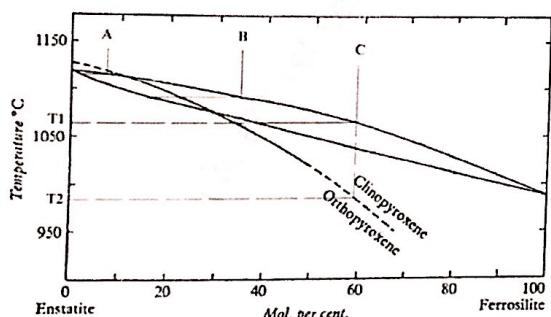


Figure 3. This is a typical Solid Solution Series, similar to olivine (Forsterite-Fayalite phase diagram), except this system has an inversion [Clinopyroxene (Monoclinic) to Orthopyroxene (orthorhombic)].

The exact position of the **inversion curve** is hard to plot. Above and to the right, any pyroxenes which crystallize are monoclinic. Below and to the left any pyroxene to crystallize are orthorhombic. Note

that in Fig 8 that the inversion curve dies out, at lower temperature you would expect conversion of monoclinic pyroxene to orthorhombic pyroxene.

A -the melt cools, hits the liquidus and crystallizes orthorhombic crystals

B -the melt cools, some crystals may be monoclinic

C -At T1 crystals are monoclinic but on further cooling to T2, they cross over the inversion curve and become orthorhombic

If you quench (rapid cooling) a monoclinic pyroxene (Pigeonite) crystal quickly, you preserve the monoclinic structure. Eg volcanic rocks at the surface such as pillow basalts.

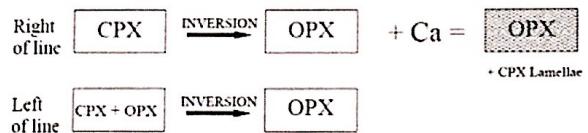
Pigeonite is monoclinic and its structure is less ordered and wider apart. This allows Ca ions into the structure more easily. The available Ca is taken up into the crystal lattice.

If a monoclinic pyroxene is allowed to cool slowly (gabbro or cumulate magma chamber) and crosses the inversion curve, the structure collapses into a more ordered, orthorhombic arrangement and the Ca ions are expelled.

This expelled Ca rich fluid can:

1) Form Ca rich Clinopyroxene under the right conditions (rapid cooling) or

2) Form Ca rich Orthopyroxene below the inversion line. In this case, exsolution lamellae will form within the monoclinic clinopyroxene. An example of this is Inverted Pigeonite where you have clinopyroxene lamellae in an orthopyroxene.



3.1.4 Orthopyroxene Paragenesis

1) Mg-rich pyroxenes are common in ultra-basic rocks. E.g.: enstatite associations Ol-Di-Augite-Spinel

2) Ultra Mafics

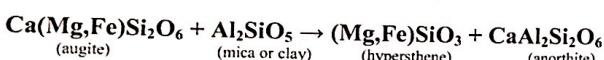
Hartzburgites (Orthopyroxenes + Olivine)
 Pyroxenites (Orthopyroxenes + Clinopyroxenes) large crystals
 Herzolites (Orthopyroxenes + Clinopyroxenes + Olivine + Plagioclase)

3) Orthopyroxenites -Gabbro (cumulates, EastBull Lake)

The Orthopyroxene crystals accumulate as layers on the bottom of the magma chamber (often interlayered with Olivine). It occurs in well-defined layers as opposed to isotropic gabbros (not well defined).

4) Volcanics. Eg andesites often contain Mg-rich phenocrysts.

5) Norites. Orthopyroxene is an essential constituent of norite (Sudbury). Some come from uncontaminated basic magmas. However, many show assimilation of Al rich sediments.



3.1.5 Alteration: It is common for Enstatite (Orthopyroxene) to be altered to Antigorite (Serpentine), often pseudomorphed.

Diopside and Jadeite (cpx) are sometimes altered to Tremolite-Actinolite (amphibole).

Augite can alter to 1) hornblende (amphibole) 2) Tremolite-Actinolite by hydrothermal alteration.

4.1 Amphiboles

Amphiboles are an important group of ferromagnesian silicates, usually found in low grade metamorphic rocks. These are normally stable up to 100 Km depth from the Earth's surface and not found beyond 200 km.

Amphiboles have a highly variable chemistry, which can be represented by the general structural formula $X_2Y_3T_2O_{22}(\text{OH})_2$, where X can be either monovalent (e.g. Na), divalent (e.g. Mg, Fe²⁺, Ca), Y (Mg, Fe³⁺, Al) and T is either Si or Al.

-Double chain silicates with (Si,Al)O₄ tetrahedra.

-Hydroxyl (OH) group is an essential part of the structure

-there are both orthorhombic and monoclinic amphiboles

-The complex structure allows a large number of different ion substitutions, therefore, you can get amphiboles occurring a very diverse number of rock types.

Chemistry

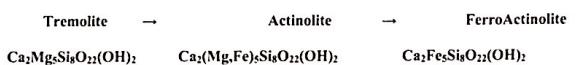
There are several amphibole groups

Anthophyllite-Cummingtonite (Ca+Na=0)

Calcium Amphiboles (Ca>Na)

Alkali Amphiboles (Na>Ca)

Within these groups there are several continuous series. A typical series is:



These are essentially metamorphic minerals and are found in all types of metamorphic regimes. They are usually found as fibrous, radiating clusters. There are many such series for the amphiboles.

4.1.1 Common endmembers and series:

- | | |
|---|--|
| 1. Anthophyllite-Cummingtonite sub-group. | |
| $\text{Ca} + \text{Na} = 0$ | $(\text{Mg}, \text{Fe}^{+2}, \text{Fe}^{+3}, \text{Li})_{5-7}\text{Al}_{2-0}[\text{Si}_{6-8}\text{Al}_{2-0}\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Orthorhombic. | |
| Anthophyllite | $(\text{Mg}, \text{Fe}^{+2})_7[\text{Si}_8\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Gedrite | $(\text{Mg}, \text{Fe}^{+2})_{6-5}\text{Al}_{1-2}[\text{Si}_6(\text{Si}, \text{Al})_2\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Ferrogedrite | $(\text{Fe}^{+2}, \text{Mg})_5\text{Al}_2[\text{Si}_6\text{Al}_2\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Holmquistite | $\text{Li}_2(\text{Mg}, \text{Fe}^{+2})_3(\text{Al}, \text{Fe}^{+3})_2[\text{Si}_5\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Monoclinic. | |
| Cummingtonite | $(\text{Mg}, \text{Fe}^{+2})_3[\text{Si}_8\text{O}_{22}] (\text{OH})_2$ |
| Grunerite | $(\text{Fe}^{+2})_4(\text{Fe}^{+2}, \text{Mg})_3[\text{Si}_8\text{O}_{22}] (\text{OH})_2$ |
| 2. Calcium amphiboles. | |
| $\text{Ca} > \text{Na}$ | $\text{Ca}_2\text{Na}_{0-1}(\text{Mg}, \text{Fe}^{+2})_{3-5}(\text{Al}, \text{Fe}^{+3})_{2-0}[\text{Si}_{6-8}\text{Al}_{2-0}\text{O}_{22}] (\text{O}, \text{OH}, \text{F})_2$ |
| Monoclinic. | |
| Tremolite | $\text{Ca}_2\text{Mg}_5[\text{Si}_8\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Ferroactinolite | $\text{Ca}_2\text{Fe}_5^{+2}[\text{Si}_8\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Hornblendite | $(\text{Na}, \text{K})_{0-1}\text{Ca}_{1-5-2-0}(\text{Mg}, \text{Fe}^{+2})_{3-5}(\text{Al}, \text{Fe}^{+3})_{2-0} [\text{Si}_6-7\text{Al}_{2-1}\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Common hornblendite | |
| Edenite | $(\text{Ca}, \text{Na}, \text{K})_{2-3}(\text{Mg}, \text{Fe}^{+2}, \text{Fe}^{+3}, \text{Al})_5 [\text{Si}_6(\text{Si}, \text{Al})_2\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Ferroedenite | $\text{NaCa}_2\text{Mg}_3[\text{Si}_7\text{Al}_2\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Tschermakite | $\text{NaCa}_2\text{Fe}_5^{+2}[\text{Si}_7\text{Al}_2\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Ferrotschermakite | $\text{Ca}_2\text{Mg}_5(\text{Al}, \text{Fe}^{+3})_2[\text{Si}_6\text{Al}_2\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Pargasite | $\text{Ca}_2\text{Fe}_3^{+2}(\text{Al}, \text{Fe}^{+3})_3[\text{Si}_6(\text{Si}, \text{Al})_2\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Ferrohastingsite | $\text{NaCa}_2\text{Mg}_4(\text{Al}, \text{Fe}^{+3})_3[\text{Si}_6\text{Al}_2\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Basaltic hornblende | $\text{Na}_2(\text{Na}, \text{K})_{0-5-1-0}(\text{Mg}, \text{Fe}^{+2})_{3-4}(\text{Fe}^{+3}, \text{Al})_{2-1} [\text{Si}_6\text{Al}_2\text{O}_{22}] (\text{O}, \text{OH}, \text{F})_2$ |
| Kaersutite | $\text{Ca}_2(\text{Na}, \text{K})(\text{Mg}, \text{Fe}^{+2}, \text{Fe}^{+3})_4\text{Ti}[\text{Si}_6\text{Al}_2\text{O}_{22}] (\text{O}, \text{OH}, \text{F})_2$ |
| Barkvikite | $\text{Ca}_2(\text{Na}, \text{K})(\text{Fe}^{+2}, \text{Mg}, \text{Fe}^{+3}, \text{Mn})_5[\text{Si}_{6-8}\text{Al}_{1-5}\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| 3. Alkali-amphiboles. | |
| $\text{Na} > \text{Ca}$ | $\text{Na}_2-3\text{Ca}_{1-0}(\text{Mg}, \text{Fe}^{+2})_{3-3}(\text{Al}, \text{Fe}^{+3})_{0-2}[\text{Si}_7-8\text{Al}_{1-0}\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Monoclinic. | |
| Glaucophane | $\text{Na}_2\text{Mg}_3\text{Al}_2[\text{Si}_8\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Magnesiolebeckite | $\text{Na}_2\text{Mg}_3\text{Fe}^{+2}[\text{Si}_8\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Riebeckite | $\text{Na}_2\text{Fe}_5^{+2}\text{Fe}^{+3}[\text{Si}_8\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Richterite | $\text{Na}_2\text{Ca}(\text{Mg}, \text{Fe}^{+2}, \text{Mn}, \text{Fe}^{+3}, \text{Al})_3[\text{Si}_8\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Katophorite | $\text{Na}_2\text{Ca}\text{Fe}^{+2}(\text{Fe}^{+3}, \text{Al})_3[\text{Si}_8\text{Al}_2\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Magnesiokatophorite | $\text{Na}_2\text{CaMg}_4(\text{Fe}^{+2}, \text{Al})_3[\text{Si}_7\text{Al}_2\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Eckermannite | $\text{Na}_2\text{s}_2\text{Ca}_{0.5}(\text{Mg}, \text{Fe}^{+2}, \text{Fe}^{+3}, \text{Al}, \text{Li})_5[\text{Si}_{7.5}\text{Al}_{0.5}\text{O}_{22}] (\text{OH}, \text{F})_2$ |
| Arfvedsonite | $\text{Na}_2\text{Ca}_2\text{Ca}_2(\text{Fe}^{+2}, \text{Mg}, \text{Fe}^{+3}, \text{Al})_3[\text{Si}_{7.5}\text{Al}_{0.5}\text{O}_{22}] (\text{OH}, \text{F})_2$ |

4.1.2 Structure of Amphiboles:

The structure and the behaviour of amphiboles are similar in many ways to the pyroxenes but more complex. The essential feature of the amphibole minerals is the double chain of $[\text{SiO}_4]$ tetrahedra, which can be thought of as two single chains joined by corner sharing, with a mirror plane along the join. The mirror plane is preserved in all amphiboles, even when the chains are not straight. Half of the tetrahedra have two bridging and two nonbridging oxygens, the other half have three bridging oxygens and one non-bridging.

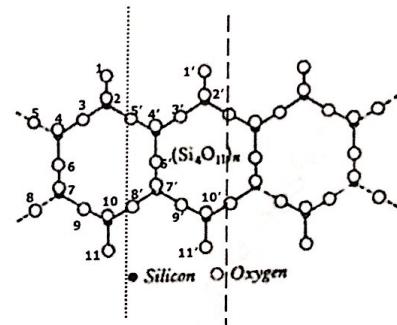


Figure 1. Si:O ratio = 4:11

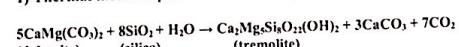
4.1.3 Alteration:

Anthophyllite (orthorhombic), Tremolite/Actinolite, and Nephrite alter to Talc.

Riebeckite alters to an iron-stained fibrous quartz known as "tigers-eye".

4.1.4 Amphibole Paragenesis

1) Thermal metamorphism of sediments (common reaction)



If you increase the grade of metamorphism, tremolite breaks down to diopside and at very high pressure, forsterite can form. All such reactions liberate CO_2 and H_2O and are therefore pressure

dependent.

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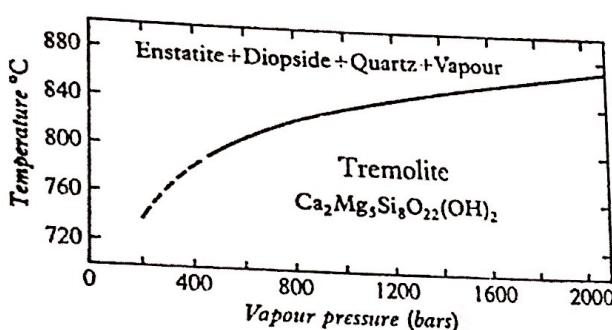


Figure 2: Tremolite = Enstatite + Diopside + Quartz + Vapour

2) Regional Metamorphism

-tremolite occurs where calcareous sediments dominate.

3) Regional metamorphism of Ultrabasic rocks

-both tremolite and actinolite (common) + talc, carbonates and chlorite.

Other Amphiboles:

4) Hornblende - occurs in a wide variety of T-P conditions in both igneous and metamorphic rocks. - stable in most siliceous rocks and very common in intermediate plutonic rocks.

Gabbros	Mg rich (Mg:Fe = 3:1)
Syenites and granites	Fe rich (Mg:Fe=5:95)
Diorites	(Mg:Fe = 1:15)

5) Basaltic Hornblende - only in igneous rocks - occur as phenocrysts in andesites

6) Kaersutite (Ti bearing amphibole) - occur as large phenocrysts (glomophyritic) in alkalic volcanic rocks such as trachyte

7) Alkali Amphiboles - Ca (Na, K)

Glauconite - occur under high pressure, low temperature conditions such as subduction zones (also large amounts of Na from seawater). Eg: Glauconite schists.

Riebeckite - occurs in alkali igneous rocks (plutonic) such as quartz syenites, granites, trachyte and

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rhyolite.

Amphibole P-T stability diagrams:

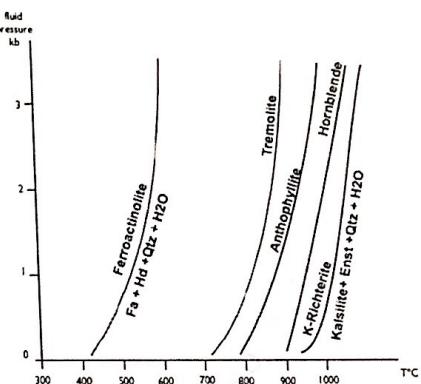
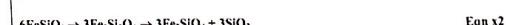
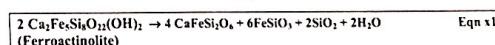


Figure 3: Amphibole P-T stability diagram: Univariant equilibrium curves for the reactions (Gupta and Venkatesh, 1993)

Some amphibole breakdown reactions:



Combining eqns x1 and x2, we obtain the breakdown reaction for Ferroactinolite:
 $2 \text{Ca}_2\text{Fe}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 \rightarrow 4 \text{CaFeSi}_3\text{O}_8 + 3\text{Fe}_2\text{SiO}_4 + 5\text{SiO}_2 + 2\text{H}_2\text{O}$
(Ferroactinolite)

*Fe (Iron) reduces the stability of amphiboles.

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5.1 Micas:

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Micas are the most important minerals within the sheet silicates. The atomic structures consist of sheets (layers) of $(\text{Si}, \text{Al})\text{O}_4$ tetrahedra with alkalis and other cations in between. In this subclass, chains of tetrahedra are linked by shared oxygens to other chains in a two dimensional plane that produces a sheet-like structure. The silicon to oxygen ratio is generally 1:2.5 (or 2:5) because only one oxygen is exclusively bonded to the silicon and the other three are half shared (1.5) to other siliconos. The typical crystal habit of this subclass is therefore flat, platy, book-like and displays good basal cleavage. Typically, the sheets are then connected to each other by layers of cations. These cation layers are weakly bonded and often have water molecules and other neutral atoms or molecules trapped between the sheets. Bonding within a sheet is much stronger compared to bonding between sheets.

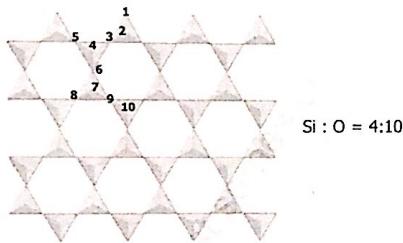


Figure 1a: Mica structure. Chains of tetrahedra are linked by shared oxygens to other chains in a two-dimensional plane that produces a sheet-like structure.

The typical crystal habit of mica is flat, platy, book-like and displays good basal cleavage. Typically, the sheets are then connected to each other by layers of cations. These cation layers are weakly bonded and often have water molecules and other neutral atoms or molecules trapped between the sheets. Bonding within a sheet is much stronger compared to bonding between sheets.

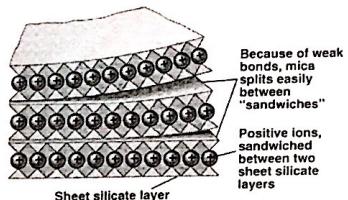


Figure 1b: Weak bonding between sheets

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5.1.1 General formulas for micas is: $\text{K}(\text{Al, Mg, Fe})_{2-3} (\text{AlSi}_3\text{O}_{10})(\text{OH})_2$

Most mica compositions can be described in terms of three end members:

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

Annite: $\text{KFe}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$

Phlogopite: $\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$

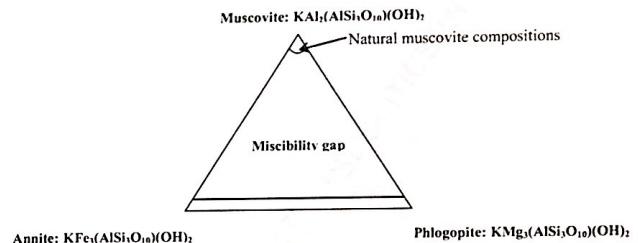


Figure 2: Ternary diagram showing the principal mica end members: muscovite, phlogopite and annite.

The two most important micas are Muscovite and Biotite.

Muscovite is common constituent of Al-rich medium grade metamorphic rocks. It 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.

Lepidolite is a lithium rich mica similar to muscovite. It occurs as a large euhedral mineral in pegmatites and is often associated with the lithium aluminium pyroxene spodumene.

Biotite is a solid solution between the end members Phlogopite $\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ and Annite $\text{KFe}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$, 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

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substitute for OH and increase the stability of Biotite to higher temperatures and pressures. Nearly pure phlogopite is found in hydrous ultrabasic rocks like kimberlite, and is also found in nearly 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. Compositions between muscovite and biotite do not exist due to large miscibility gap.

5.1.2 Mica P-T stability

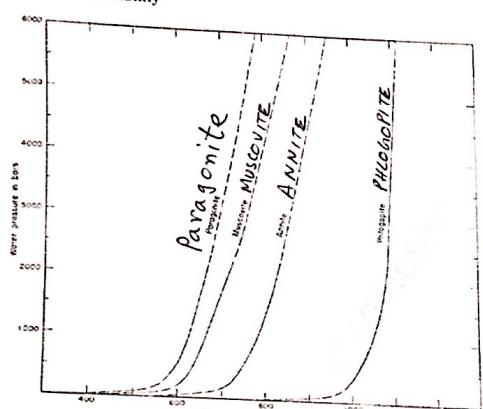
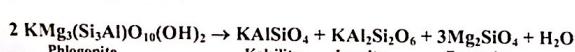
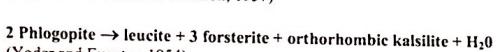
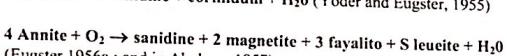


Figure 4: Mica P-T stability. Univariant equilibrium curves for the reactions:



These curves represent the upper stability limit of the pure micas indicated. The dashed portions of the curves are obtained by calculation. A pressure of 5000 bars obtains at a depth of approximately 20 km (= 12.4 miles).

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6.1 Feldspars

These aluminosilicate framework minerals are the most abundant minerals in the Earth's crust. Feldspars found in igneous, metamorphic and many sedimentary rocks make up about 65% by volume. Mineralogically they are also the most interesting and challenging from the point of view of the response of the structure to temperature, pressure and composition changes.

6.1.1 Structure

Feldspars are framework silicates where each silica tetrahedra share all corners with its four neighbouring tetrahedra. A portion of the tetrahedra contain Al^{+3} instead of Si^{+4} . The charge is balanced by incorporating Na^+ , Ca^{+2} or K^+ .

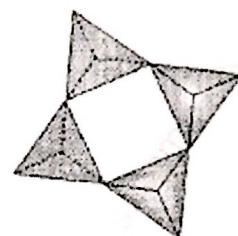


Figure 1: The basic building unit of the feldspar structure is the four-membered ring of tetrahedra with a pair of tetrahedral pointing up and a pair pointing down.

6.1.2 Chemistry

The feldspar group approximates a ternary system consisting of three components: Albite, Anorthite and Orthoclase. There are continuous and limited solid solution between the three. Plagioclase -solid solution (continuous) between Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and Albite ($\text{NaAlSi}_3\text{O}_8$). Alkali feldspars -solid solution between Albite and Orthoclase (KAISi_3O_8) is limited (dependent on temperature).

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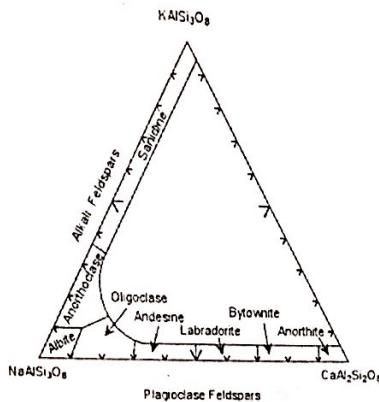


Figure 2: Feldspar ternary

Plagioclase Feldspar Solid Solution Series: There is a complete solid solution between Albite and Anorthite. Intermediate phases are Oligoclase, Andesine, Labradorite and Bytownite.

6.1.3 Varieties of Feldspar

The general formula for the feldspars is $X\text{Al}(\text{Al},\text{Si})\text{Si}_2\text{O}_8$.

where X is potassium, sodium, calcium, or barium. The Al occupies some of the tetrahedra. All the X ions are big, much larger than iron or magnesium, which are too small to occupy the voids in the structure fully. The radii of the principal feldspar cations in Angstrom units are: K 1.6; Ba 1.5; Na 1.4 and Ca 1.25. Also, Ba and Ca are divalent, but Na and K have a valence of +1.

The factors that influence feldspar structure are:

- Ionic radius
- Charge balance
- Ordering of aluminum-silicon tetrahedra, and also ordering of the large X ions.

The ordering of Al and Si tetrahedra depend on temperature and the number of Al necessary to maintain charge balance. If there are both +1 and +2 X ions, the +2 ions will tend to avoid areas of high Si (+4) concentration.

From the above we can expect K, Ba and Na to be most compatible based on ionic radius, and the K-Na and Ba-Ca pairs to be compatible based on charge. We might expect the most compatibility between K and Na and the least between K and Ca. Since Na is in the middle of the ionic radius between K and Na and the least between K and Ca. Since Na is in the middle of the ionic radius between K and Na and the least between K and Ca.

From actual spectrum we might expect it to be compatible with all the other ions. It turns out, from actual mineralogy, that ionic radius is most important and charge balance and ordering are secondary.

The barium feldspars are quite minor and consist of *celsian* ($\text{BaAl}_2\text{Si}_2\text{O}_8$) and *hyalophane* ($((\text{K},\text{Na},\text{Ba})(\text{Al},\text{Si}),\text{O}_8)$, a general solid solution of potassium, sodium and barium feldspar.

The potassium feldspars (KAlSi_3O_8) differ in the ordering of Al-Si tetrahedra. At high temperatures the tetrahedra are randomly mixed (although Al-O-Al links never occur) and the lattices are therefore of high symmetry. They have long range order even if on a local scale the lattice is disordered.

Sanidine is the highest temperature variety and is completely disordered, *orthoclase* forms below about 800°C and is partially ordered, and *microcline* forms below about 600°C and is highly ordered. The complete ordering of Al in microcline breaks down the mirror plane symmetry and microcline becomes triclinic. The a-b and b-c angles of the unit cell depart from 90 degrees by a fraction of a degree (that's what *micro-cline* means - small angle).

Potassium feldspar (KAlSi_3O_8) and the sodium feldspar *albite* ($\text{NaAlSi}_3\text{O}_8$) are completely compatible at high temperatures. Sanidine can contain up to 60% Na, a mixture of K and Na feldspar that is 60-90% Na is termed *anorthoclase*. However, at low temperatures the difference in ionic radius starts to have a strong effect and the feldspar separates into discrete streaks and patches of K and Na feldspar. This process is called *exsolution* and is analogous to cream separating from milk. If the dominant feldspar is K-feldspar the resulting mixture is termed *perthite*, and if it is albite the mixture is termed *antiperthite*.

Despite the difference in charge, Na^{+1} and Ca^{+2} are not that different in ionic radius, and there is a complete solid solution series, the *plagioclase* series, between *albite* ($\text{NaAlSi}_3\text{O}_8$) and *anorthite* ($\text{CaAl}_2\text{Si}_2\text{O}_8$). The different members of the series are arbitrarily divided at 10, 30, 50, 70 and 90 per cent anorthite. The different members are:

Albite
0-10% anorthite. Found only in very sodic rocks, hence usually metamorphic or formed in marine conditions as a sedimentary cement, or by ion exchange with more calcic plagioclase.

Oligoclase
10-30% anorthite. The dominant plagioclase in granitic rocks

Andesine
30-50% anorthite. Found in intermediate igneous rocks

Labradorite
50-70% anorthite. The dominant plagioclase in gabbro and basalt. Also, despite their name, most anorthosites are made up of labradorite.

Bytownite
70-90% anorthite. The rarest. Requires both a lot of calcium and also significant sodium. Most igneous settings have too much sodium, most calc-silicate metamorphic settings have too little sodium.

Anorthite
90-100% anorthite. Generally a metamorphic mineral in calc-silicate rocks.
The plagioclases are triclinic and their a-b and b-c angles are a bit more oblique than microcline. Hence the name: *plagi-*, oblique and *cline*, break.
Since Na and Ca differ in valence, Al has to substitute for Si to compensate. The Al-Si orderings of albite and anorthite are different, and at low temperatures, plagioclases in the middle of the

composition range also exsolve, but on a submicroscopic scale. These submicroscopic textures are probably responsible for the iridescence of some plagioclases.

Plagioclase

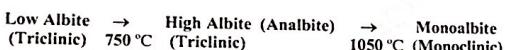
In the plagioclase series, there is usually high and low temperature structural states. At high temperatures the structure remains the same over the complete solid solution. E.g. anorthite has the same structure as high albite. This would be the case for rapidly quenched volcanic rocks. At lower temperatures the series is often not continuous but contains structural divisions (due to position of Al in the crystal structure):

Eg: An0-3, Ab97-100 low albite

An3-22, Ab78-97 Peristerites

An22-73, Ab27-78 Intermediate Structure

An73-100 Ab0-27 Anorthite Structure



The structure stays same but unit cell volume is different between Low Albite and High Albite.

Peristerites: sub-microscopic intergrowth of Na rich and Ca rich phases with alternate low albite structure and intermediate structure. Optically peristerites produce a "schiller" (iridescent) effect on cleavage surfaces.

6.1.4 Plagioclase phase diagram:

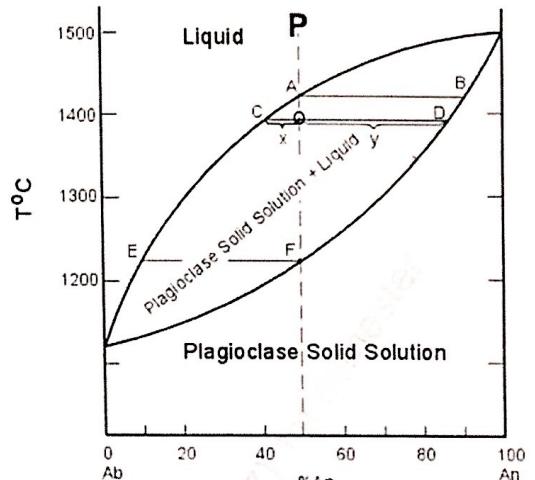


Figure 3: Phase diagram for the plagioclase system

A complete solid solution is displayed in the plagioclase feldspars. The solid solution exists between the end members albite ($\text{NaAlSi}_3\text{O}_8$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$).

For maintaining charge balance Na^{+1} cannot simply be substituted for Ca^{2+} . This solid solution is called a coupled solid solution, and $\text{Na}^{+1}\text{Si}^{4+}$ is substituted for $\text{Ca}^{2+}\text{Al}^{3+}$ in the plagioclase structure to produce intermediate compositions of plagioclase.

Since 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.

Temperature-composition phase diagram for plagioclase:

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). (Remember the definition of the 'liquidus' and 'solidus' curves from the olivine lecture). At temperatures above the liquidus curve only liquid (melt) exists, below the solidus curve only solid exists (crystals of

plagioclase solid solution). At temperatures between the solidus and liquidus crystals of plagioclase solid solution coexist in equilibrium with liquid (melt).

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Pure albite melts (or crystallizes) at 1118°C.

Pure anorthite melts (or crystallizes) at 1500°C.

Albite (Ab); Anorthite (An)

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.

From the temperature-composition phase diagram (Figure 3): if a melt of composition Ab50An50 is cooled it will begin to crystallize at 1410°C and will be completely crystalline at 1220°C.

In order to understand this, we can trace the crystallization history of composition P, which is Ab50An50.

Composition P is completely molten (liquid) above the liquidus (above 1410°C). As the temperature cools down and we touch the liquidus at point A, this 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°C. 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 P will have the composition Ab10An90. It is important to 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 further 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 melt (liquid) will change along the liquidus, thus also becoming more enriched in the Ab component. At a temperature of 1395°C 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°C, 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 Ab50An50.

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 (rich in Na/Sodium), 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 (Remember the lever's rule from the olivine lecture). As an example, we will determine the proportions of liquid and solid in the system at a temperature

of 1395°C. At this point, we measure the distances oC, oD, and CD. The percentages of liquid and solid are then given as follows:

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

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

For the above discussion, it was assumed that equilibrium is maintained throughout the course of crystallization. This means that with falling temperature and continuing crystallization, the earlier-formed, more calcic (Ca/Calcium rich) 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.

Here are three contrasting scenarios:

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.

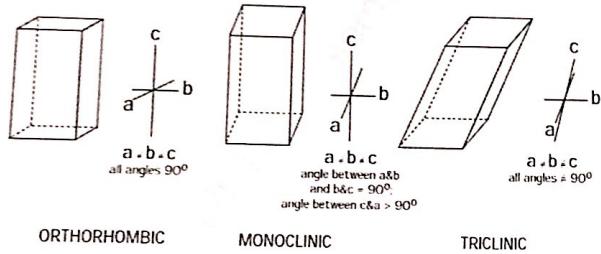
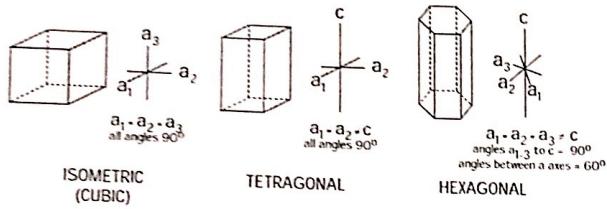
2) **Continuous removal of crystals from the melt**, by sinking or some natural filtering process. Reaction of crystals with the melt is prevented, and the composition of the liquid will continue to change along the liquidus curve toward the sodic feldspar component. The only limit to this change of 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 zones contain differing compositions: 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 P.

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Crystal system basics:



Find three examples for each crystal class mentioned above.

Solid solution in minerals

Solid solution: exhibiting variable composition represented by the substitution of one chemical species for another due to **continuous chemical mixing** (*in the mineralogical context*)

Basic rules of solid solution:

Ionic charge: the ions substituting each other should not exceed a charge difference of ± 1

Ionic radius: the ions substituting each other should not have a radius difference of more than 15%.

Consideration of temperature and pressure: influencing substitution



Recommended reading:

- **Rutley's Elements of Mineralogy**
- **Mineralogy; Dexter Perkins (2014)**
- **Minerals; Wenk & Bulakh (2004)**