

## Ternary Phase Diagrams

### General principles:

*Construction of ternary phase diagrams:* Ternary phase diagrams are constructed by projecting the liquidus surfaces of a three dimensional diagram (a triangular prism in which T is plotted on the vertical axis against the compositions of three components on the base of the prism) onto the compositional ternary diagram (Fig. 1). On such diagrams or projections, these temperatures are shown as dashed *contours*. The intersection of two liquidus surfaces is also projected on the same compositional ternary and is known as a *boundary curve*. The areas between boundary curves where one liquid coexists with a solid are known as "*primary fields*" (Fig. 2). Because T is still a variable on these ternary projections, we can still apply the condensed phase rule to determine the variance of a system. Accordingly, any point in a primary field (at T below the liquidus for this composition) will have two degrees of freedom. Boundary curves on the other hand will be univariant (as long as the system remains isobaric, and as long as two solid phases coexist with a liquid along these curves). As will be shown later, there are several types of boundary curves, depending on the type of system.

From the above discussion, it is quite clear that ternary systems are a bit more complicated than binary ones. The primary fields on these projections have to be labelled, and the diagram has to have T contours to allow us to determine the variance of the system and to understand the sequence of equilibrium crystallization. However, many ternary diagrams do not show T contours. These can still be "read" and interpreted using several simple rules.

*Alkemade line:* An alkemade line is a straight line joining the compositions of two phases that share a boundary curve. On Fig. 3, the sides XY and XZ of the ternary diagram XYZ are alkemade lines, so are the lines Y-YZ, Z-YZ and X-YZ.

### *Rules for interpreting ternary phase diagrams:*

1- A melt of composition 30% X, 20% Y and 50% Z undergoing equilibrium crystallization will end up crystallizing 30% X, 20% Y and 50% Z!

2- A melt with a bulk composition lying in a "primary field" will first crystallize the solid phase of this primary field, and the liquid will then change its composition along a line drawn through this bulk composition and joining the composition of this solid (represented by a point on an Alkemade line if the solid phase is an intermediate compound e.g. YZ on Fig. 3, or one of the apices of the ternary diagram) and the boundary curve (Fig. 4).

3- The percentage of crystals formed at any point can be determined using the lever rule. For example, on the ternary diagram sphene - anorthite - wollastonite (Fig. 5), at a temperature represented by point "B", the % of crystals formed from a melt of composition "A" will be:

% crystals =  $100[AB/BC]$  (Fig. 5).

4- After considerable cooling, the liquid will eventually have a composition lying on a boundary curve. At this stage, the liquid will begin to crystallize another phase (so that there are two solids and a liquid in equilibrium along the curve). The percentage of crystals of each phase which have already crystallized after the liquid has reached a point on the boundary curve can again be determined by the lever rule. On Fig. 6, to determine the % of sphene which has formed by the time the liquid is at point E, we draw a line from E passing through the original bulk composition of the melt "A" to the alkemade line: sphene - wollastonite. The % of sphene that has crystallized becomes equal to the distance "wollastonite - F" divided by wollastonite - sphene" (Fig. 6). The ratio of liquid to crystals is then given by: AF : AE (Fig. 6).

5- *The tangent rule*: To determine the percentage of crystals of a particular phase which are actually crystallizing at a particular point on a boundary curve, then we have to construct a tangent from this point on the boundary curve to the corresponding alkemade line. The point of intersection of this tangent with the alkemade line can then be used to determine the percentage of the two phases as shown on Fig. 7. This is known as the tangent rule. Note that you do not need to know the original bulk composition of the melt when applying the tangent rule, since it is concerned with determining the ratios of phases actually precipitating along the boundary curve at a specific T, and which will only depend on the position of the liquid on this path (i.e. the T).

6- *The Alkemade theorem*: This theorem enables one to determine the direction of T change along a boundary curve in the absence of T contours. It states that crystallization along a boundary curve will always take place in a direction away from the alkemade line joining the two solid phases that coexist along this curve. The highest temperature on a boundary curve is that at which the boundary curve intersects its alkemade line (Fig. 8).

7- *Types of boundary curves*: Boundary curves are of two types depending on (i) the nature of the ternary system considered, (ii) whether the system has compounds of intermediate composition, and (iii) whether intermediate compounds melt congruently or incongruently. The two types of boundary curves are:

(i) *subtraction curves*: boundary curves along which two phases co-precipitate. These curves are also known as "cotectic curves". Subtraction curves are designated by a single arrow pointing in the down-T direction.

(ii) *reaction curves*: boundary curves along which one solid phase dissolves in the liquid to produce another solid phase (in a fashion similar to peritectic points on binary diagrams). Reaction curves are designated by double arrows pointing in the down - T direction.

8- *Identification of the type of boundary curve*: The type of boundary curve at a certain point can be determined by constructing a tangent from that point to the corresponding alkemade line. If the tangent intersects its alkemade line, then the curve is a subtraction

curve, if it intersects the extension of its alkemade line, it becomes a reaction curve (Fig. 9). Note that a subtraction curve can turn into a reaction curve (Fig. 10).

### 1- Ternary Systems with a Ternary Eutectic The system: Fayalite - Qz - albite

This system has a ternary eutectic melting point simply because each of its binary joins (Fa - Qz, Qz - Ab, Fa - Ab) has a binary eutectic melting point.

#### **Equilibrium crystallization of composition "A"** (Fig. 11):

Liquid + Qz → Liquid + Qz + Fa → Liquid + Fa + Qz + Ab at "E" isothermally until all liquid is used up. Sum of all Qz + Fa + Ab crystallized is equal to original composition of point "A".

Note that the T range over which fayalite crystallizes with quartz is very limited (between 1200 and 1025°C). This diagram explains why Fa and Qz can coexist in some rocks, but is not a very common assemblage since it requires a rather rare bulk composition, and the period of time spent by the magma on the cotectic will be relatively short!

#### **Equilibrium melting of rock of composition "A"** (Fig. 11):

The first melt produced is of composition "E" at the eutectic melting point; system remains isothermal until all albite melts. Liquid then moves up the Fa - Qz cotectic as T rises and Fa melts, until point "B" is reached (T ~ 1125°C), at which point all Fa melts. Liquid then migrates towards point "A" along the line AB as Qz melts until the last crystal of Qz disappears.

#### **Fractional crystallization of melt "A"** (Fig. 11):

Liquid → Liquid + Qz, with Qz separating; and liquid composition changing away from the Qz apex towards cotectic. At "B", both Fa and Qz crystallize and separate out of the liquid, and the liquid changes its composition along the cotectic. At E, Fa, Qz and Ab crystallize in eutectic proportions until the last drop of liquid is used up, and the final rock composition is the eutectic composition. Note that this will be the case regardless of the starting melt composition, as long as fractional crystallization is 100% efficient.

#### **Batch melting (fractional melting) of rock of composition "A"** (Fig. 11):

Fractional melting will yield batches of composition "E", until all Ab has melted. The remaining crystals will then have the binary composition "C" (determined by drawing a line from "E" through the bulk composition "A"; Fig. 11). No melting will occur until T ~ 1190°C, when Fa + Qz will melt isothermally in binary eutectic proportions. The temperature will remain constant until all Fa is used up, leaving behind pure Qz, which will not melt except at T >> 1400°C.

**Other examples for systems with a ternary eutectic:** Di - An - Qz.

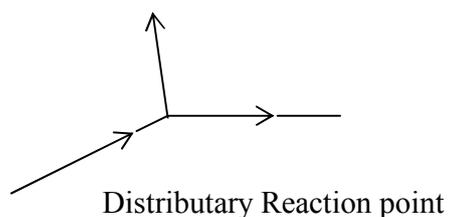
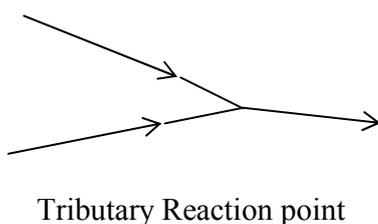
## 2- Ternary systems with congruently melting intermediate compounds The system Fa - Qz - Ne.

In this system, the intermediate compound is albite, which melts congruently. As you may have expected, this system will show a thermal boundary similar to the one seen on binary phase diagrams. The system will also have two ternary eutectic points (Fig. 12). The composition of the final product of equilibrium or fractional crystallization will therefore be determined by the original bulk composition of the melt, i.e. whether it lies in the Fa - Qz - Ab volume of the diagram (in which case it will end up at  $E_1$ ), or in the Fa - Ne - Ab volume (ending up at  $E_2$ ; Fig. 12). Keep in mind the differences between equilibrium crystallization and fractional crystallization.

## 3- Ternary systems with an incongruently melting intermediate compound A- The system An - K-spar - Qz

As you are well aware, K-spar melts incongruently. This diagram will therefore have a primary field for leucite (Lc). The joins An - K-spar, and An - Qz are simple binary eutectics. Tangents drawn at all points for the boundary curves between An - Lc, An - Qz, and K-spar - Qz clearly intersect their respective alkemade lines (not their extensions), which makes these curves subtraction curves (represented by single arrows; Fig. 13). The boundary curve between K-spar and An is also a subtraction curve, because tangents drawn for all points on this curve will intersect the alkemade line An - K-spar (dashed line on Fig. 13), and not its extension. On the other hand, the boundary curve K-spar - Lc is a reaction curve (designated by double arrows; Fig. 13), since tangents drawn for all points on this curve intersect the alkemade line K-spar - Lc at its extension!

It is also clear from this diagram that there are two isobarically invariant points in this system (E and R). Point E is a simple ternary eutectic at which K-spar, a silica phase and anorthite coprecipitate isothermally until all liquid is used up. On the other hand, point R is a reaction point, at which Lc reacts with the liquid to give K-spar until one of these phases is used up. Depending on the bulk melt composition, it can be seen that some liquids may undergo further changes in composition beyond point R after all Lc is used up, and will migrate down the subtraction curve RE to the ternary eutectic E. This type of reaction point R (which in many ways is equivalent to the peritectic point on binary diagrams) is known as the *tributary* reaction point (because it looks like a point where two tributaries of a river meet). Keep in mind that not all reaction points are of this type; some can be "*distributary*" as shown on the sketch below.



**Sequence of equilibrium crystallization of a melt of composition "C":**

A melt of this composition lies in the compositional volume An - K-spar - Lc, and will therefore end up crystallizing these two phases in the same proportions designated by point "C".

- 1- Liquid  $\rightarrow$  An + L, liquid changes its composition away from the An apex towards the boundary curve.
- 2- At  $T = 1380^{\circ}\text{C}$ , Lc begins to crystallize along with An (so we have three phases: L + Lc + An), and the liquid changes in composition away from the An - Lc alkemade line down to point "R".
- 3- At R, liquid begins to react with Lc isothermally to form K-spar, until all liquid is used up (at  $T \sim 990^{\circ}\text{C}$ ).

**Sequence of equilibrium crystallization of a melt of composition "D":**

A melt of this composition lies in the compositional volume An - K-spar - Qz, and will therefore end up crystallizing these three phases in the same proportions designated by point "D".

- 1- Liquid  $\rightarrow$  An + L, liquid changes its composition away from the An apex towards the boundary curve.
- 2- At  $T = 1250^{\circ}\text{C}$ , Lc begins to crystallize along with An (so we have three phases: L + Lc + An), and the liquid changes composition away from the An - Lc alkemade line down to point "R".
- 3- At R, liquid begins to react with Lc isothermally to form K-spar, until all Lc is used up (at  $T \sim 990^{\circ}\text{C}$ ). The temperature is then allowed to drop, and the liquid changes its composition along curve RE, precipitating An + K-spar.
- 4- At E, a silica phase begins to crystallize together with An and K-spar in ternary eutectic proportions until all liquid is used up.

**B- The system An - Fo - Qz**

The joins An - Fo and An - Qz are both binary eutectics, whereas the join Fo - Qz is characterized by an intermediate compound (enstatite, En) which melts incongruently at low P (but congruently at higher P). A quick examination of the phase relations on this ternary (or more correctly pseudoternary because of the primary field for Spinel along the An - Fo join; Fig. 14) shows that all boundary curves are cotectics (subtraction curves), except that one between En and Fo which is a reaction curve (since it intersects the extension of the Fo - En alkemade line). There is also a field of liquid immiscibility between a  $\text{SiO}_2$  rich liquid and a more magnesian one, as well as the usual primary fields for the various silica polymorphs (cristobalite and Tridymite, herein collectively referred to as "Qz").

**Sequence of equilibrium crystallization of melt of composition "A" (Fig. 14):**

This melt lies in the compositional volume Fo - En - An, and will therefore crystallize these three phases in the proportions given by "A" if allowed to crystallize under equilibrium conditions.

- 1-  $L \rightarrow L + Fo$  after hitting the liquidus surface, L changes its composition with continued cooling and precipitation of Fo away from the Fo apex until it reaches point C on the boundary curve between Fo and En.
- 2- At point C, Fo reacts with L to precipitate En along the isobarically univariant reaction curve. L changes its composition with continued cooling along this curve until point B is reached.
- 3- At point B (a tributary reaction point), An begins to precipitate isothermally while L + Fo react to form more En until the last drop of liquid is used up. The T is then allowed to drop as all three phases cool below 1260°C.

**Sequence of Equilibrium crystallization of melt of composition "D" (Fig. 14):**

This melt lies in the alkemade triangle An - En - "Qz", and will therefore crystallize these three phases in the proportions given by "D" if allowed to crystallize under equilibrium conditions.

- 1-  $L \rightarrow L + Fo$  after hitting the liquidus surface, L changes its composition with continued cooling and precipitation of Fo away from the Fo apex until it reaches point F on the boundary curve.
- 2- At point F, Fo reacts with L to precipitate En along the isobarically univariant reaction curve. L changes its composition with continued cooling along this curve until point I is reached.
- 3- At point I, all Fo will have reacted with L and formed En. This can be represented by drawing a line from I through the bulk composition "D" and extending it to the alkemade line Fo - En: the intersection is exactly at the location of En! Because all Fo has been used up, the system is no longer univariant, and the liquid must leave the reaction curve (away from the En "apex") as it cools and continues to precipitate En **directly** from the liquid. This process continues until the liquid reaches point "J" on the cotectic An - En.
- 4- At "J", An begins to precipitate directly from the melt together with En, the system cools and L changes its composition along the curve An - En until "E" is reached.
- 5- At the ternary eutectic "E", tridymite begins to crystallize along with An and En isothermally until all liquid is used up. The T then drops below 1222°C as all three phases cool.

**Applications:**

This system is useful for understanding the crystallization of basaltic magmas, and can explain many textures and reactions observed in basalts and some layered tholeiitic intrusions. Examples include:

- 1- Ol phenocrysts in Ol-tholeiites commonly show Opx reaction rims (known as Bowen - Anderson rinds). The rock may also contain euhedral phenocrysts of Opx and (rarely) matrix Opx. This can be explained by "near equilibrium" crystallization (incomplete fractional crystallization) of a melt with composition similar to "D" (Fig. 14), where the Opx rims on Ol form as a result of cooling along the reaction curve (e.g. between F and I). When all the Ol crystals are "used up" (in real life, they were not fully reacted, but were completely mantled by Opx thus preventing further reaction with the liquid), euhedral Opx (phenocrysts?) can crystallize directly from the melt. The matrix may then

consist of Opx and Plag (in our example representing crystallization along the cotectic between J and E; Fig. 14).

2- Corona textures in many gabbros where Ol crystals are rimmed by Opx (and subsequently Cpx). This can be explained by incomplete fractional crystallization of a melt of composition similar to D (Fig. 14).

3- The occurrence of layers of Qz-gabbros (or Qz-gabbro-norites) with granophyric textures within layered intrusions of an Ol-tholeiitic magma can also be explained by this diagram. Fractionation of Ol from the tholeiitic magma (to form early cumulates) will push the melt composition across the plane of SiO<sub>2</sub> oversaturation, and this liquid will end up crystallizing Plag + Opx + Qz at the ternary eutectic.

4- In a layered complex, the layers dunite, bronzitite, norite and granophyre closely represent the compositional evolution of a tholeiitic melt undergoing fractional crystallization. (Can you work this out from Fig. 14?).

5- The diagram can be used to explain why scientists believe that norite does not form from a noritic magma, but by fractional crystallization of a tholeiitic melt. This is simply because the first melt to form by partial melting in this system will always be "granitic" (rather than noritic) in composition (i.e. a liquid which is fairly rich in SiO<sub>2</sub>) since it has to be of eutectic composition.

#### 4- Ternary systems with solid solution

##### A- The system Ab - An - Di

The joins Ab - Di and An - Di are both binary eutectics, whereas the subsystem Ab - An is characterized by complete solid solution. The ternary phase diagram Di - An - Ab will therefore appear rather simple, with one subtraction curve (cotectic curve) joining the two binary eutectics E<sub>1</sub> and E<sub>2</sub> (Fig. 15). Two phases: Di and a plagioclase (solid solution) will precipitate continuously along this cotectic. The direction of migration of the liquid composition along the cotectic is determined experimentally (the alkemade theorem does not help in this case). Nevertheless, if we are familiar with the binary solid solution system, we can probably predict this direction (as it is usually the same as that for the binary).

Another problem with this system is our inability to figure out the composition of plagioclase feldspar crystallizing in equilibrium along the cotectic with diopside from the principles we learned earlier. In fact, the only proper way for determining the composition of the solid plagioclase is through experiment. Nevertheless, familiarity with the binary for plagioclases (Fig. 15, lower diagram) can be helpful in this regard. This is simply because the composition of the liquid along the eutectic can be easily determined from the ternary. If we then project this composition down onto the binary diagram (assuming that the presence of Di has no effect on the shapes of the liquidus and solidus curves of coexisting plagioclase, an assumption which is not strictly correct), we can immediately figure out the

composition of the solid phase in equilibrium with this liquid. Therefore, on Fig. 15, at point A, a liquid of composition  $P_1$  coexists with Di and a solid plagioclase, the composition of which is "approximated" by  $P_2$  as determined from the binary Ab - An. Note that the "exact" composition of the solid plagioclase can only be determined experimentally, since the presence of Di "distorts" the shapes of the liquidus and solidus for the system Ab - An.

**Sequence of equilibrium crystallization of a melt of composition "X" (Fig. 15):**

A melt of composition X has to end up crystallizing Di + a plagioclase of composition  $P_1$  in percentages given by the lever rule ( $\% \text{ Plag} = X - \text{Di} / \text{Di} - P_1$ ;  $\% \text{ Di} = P_1 - X / P_1 - \text{Di}$ ). The sequence of crystallization is:

Liquid  $\rightarrow$  L + Di until  $T \sim 1240^\circ\text{C}$ , when a plagioclase solid solution begins to crystallize along the cotectic. The first crystal to form will have the composition  $P_2$ . As the T drops, plagioclase  $P_2$  reacts with the liquid to crystallize more Plag which will also be more Ab - rich, and the liquid changes its composition by migrating down the cotectic. This process continues until the last drop of liquid (which will have a composition B) is used up to crystallize Plag of composition  $P_1$ .

**Sequence of equilibrium crystallization of a melt of composition "D" (Fig. 16):**

A melt of composition D has to crystallize Di + Plag of composition " $P_1$ " (Fig. 16). However, the liquid path at temperatures above those of cotectic crystallization will not be a straight line drawn from one of the apices of the ternary, but will be curved (Fig. 16). This curve will be constrained by the composition of the Plag crystallizing, and the bulk composition of the melt. Once more, the liquid path of evolution can only be determined experimentally.

**B- The system Qz - Ab - K-spar**

This system is very important for understanding the crystallization of granites, and partial melting in the lower crust to form granitic melts. It is also often referred to as petrogeny's residua system. At low pressures, the system consists of two binary eutectics along the joins Qz - K-spar and Qz - Ab (Fig. 17a). The cotectic line joining these two binary eutectics will be one along which Qz and an alkali feldspar solid solution coprecipitate. However, unlike in the Di - An - Ab system, this system has a minimum melting point ( $720^\circ\text{C}$  at 1 kbar) at an intermediate composition "M" ( $\sim 35\%$  Qz,  $50\%$  Ab,  $15\%$  K-spar). This composition is remarkably similar to the compositions of many granites (Fig. 18), which in turn suggests that such granites may have indeed formed by partial melting of crustal material (at T of  $700^\circ\text{C}$  or less). At higher fluid pressures ( $P_{\text{H}_2\text{O}}$ ), as the solidus (and eventually the liquidus) of the binary K-spar - Ab intersect the solvus, two feldspars (one Ab - rich, the other K-spar rich) form instead of one, and the ternary system changes to one with a ternary eutectic where two feldspars and Qz precipitate (Fig. 17b). It should also be noted that at low pressures, the system has a small primary field for leucite (Fig. 17a), even though Lc was not one of the components. This is simply because K-spar melts incongruently.