

Physical Chemistry and Physical Properties of the Synthetic Magmas

Phase Rule

To understand or to read any phase diagram, it is necessary to understand the ***phase rule*** or ***Gibbs phase rule***, which is given in the following equation :

$$F + P = C + 2$$

Where, **P = number of phases**, **C = number of components**, **F = the degree of freedom** that shows the factors governing the crystallization system such as pressure, temperature and composition used in the phase diagram and can be changed freely without destroying the phase or creating new phase. The **2** comes from the two extensive variables, pressure and temperature.

Here, it is very important to understand some terms related to the phase equilibrium such as systems, phases and components in order to understand the methods used in graphical representation termed "Chemography" of the geochemical data.

System : is any part of the universe could be studied. The system is either homogeneous (i.e. composes of one phase only) or heterogeneous (i.e. composes of two phases or more). System are classified to ***closed*** or ***open*** systems.

Phase : is any part of the system has physical properties and chemical composition and can be separated from other parts. Mineral is an example of phase in the rock, which can be separated from other minerals present in the rock.

Component: represents the chemical formula units that necessary to describe the identified phases in a system. For easy clarification, we have chosen the minimum components that describe all phases. As example, if we have acidic igneous rock, we see that it composes simply of three phases of quartz (SiO_2), albite ($\text{NaAlSi}_3\text{O}_8$), and orthoclase (KAlSi_3O_8). The components of this system are three, they are represented the minimum number of components, not $\text{SiO}_2 + \text{Na}_2\text{O} + \text{Al}_2\text{O}_3 + \text{K}_2\text{O}$ (4 components) or $\text{Si} + \text{Na} + \text{Al} + \text{K} + \text{O}$ (5 components).

Phase diagram

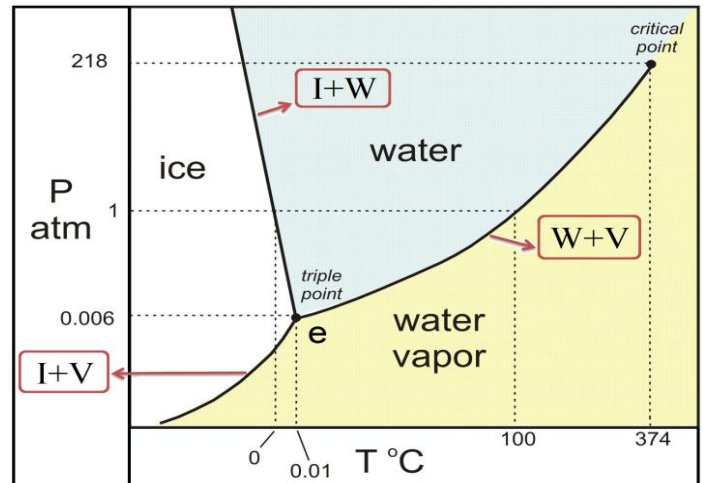
Equilibrium phase diagrams represent the relationships between temperature, compositions, and the quantities of phases at equilibrium. A phase diagram is actually a collection of solubility limit curves. Set of solubility curves that represent the locus of temperatures ***above*** which all compositions are ***liquid*** are called liquidus, while ***solidus*** represents a set of solubility curves that denote the locus of temperatures ***below*** which all compositions are ***solid***. Phase diagrams are classified based on the number of components in the system. Single component systems have ***unary diagrams***, two-component systems have ***binary diagrams***, three-component systems are represented by ***ternary diagrams***, and four-component systems are represented by ***Quaternary diagrams***.

(i) One Component (Unary) Systems

They are the systems which compose of one component only ($C = 1$). An example of the unary systems and the simplest application of the Gibbs phase rule are water system (H_2O) and quartz system (SiO_2).

1) H_2O System

The figure display three fields of stability of water (ice = I, liquid water = W, and vapor = V). In each field, only one phase is stable either (I) or (W) or (V), each in its own determinants of the two variable of diagram (Pressure and Temperature). This means that the number of phases in each stability field is one ($P = 1$). And as the system compose of only one component (H_2O) (i.e. $C = 1$), we will obtain form the equation of Gibbs phase rule



$$F = C + 2 - P = 1 + 2 - 1 = 2 \text{ (divariant field)}$$

that $F = 2$ (divariant field), which means that there are two variables (Pressure and Temperature) govern the field of stability, that we can freely change one of them or both to transfer to another field.

At the lines or curves that separate the fields, the number of phases is 2 ($P = 2$) instead of 1. i.e. on the line between ice and water, the two phases coexist ($I + W$); consequently, $F = 1$ as follows :

$$F = C + 2 - P = 1 + 2 - 2 = 1 \text{ (univariant line or curve)}$$

That means we have only one variable (either pressure and temperature) we can change to transfer to one of the stability fields (ice or water).

At the eutectic point (e), where the three phases ($I+W+V$) coexist, the number of phases is 3 ($P = 3$); and the value of degree of freedom will be zero ($F = 0$) as follows :

$$F = C + 2 - P = 1 + 2 - 3 = 0 \text{ (invariant point)}$$

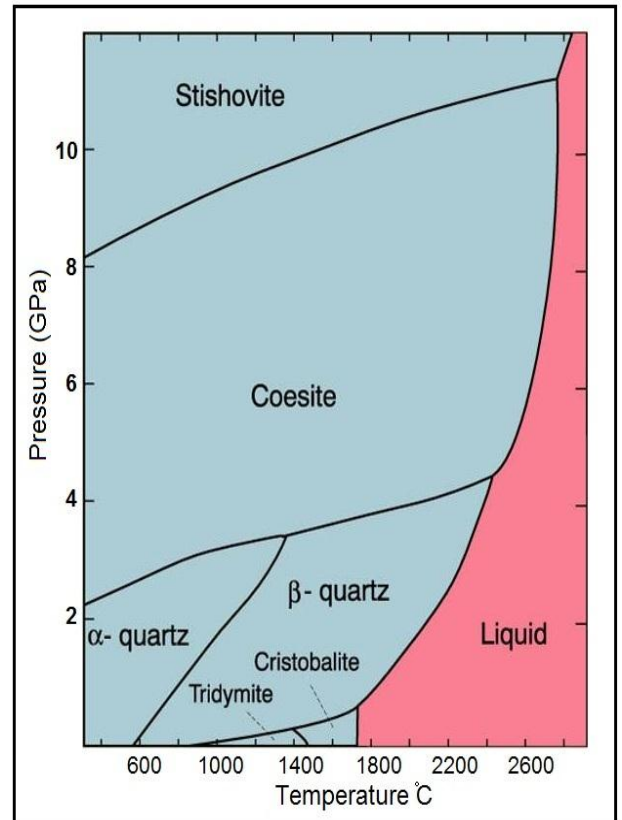
This means that there is no degree of freedom, i.e. at eutectic point we cannot change neither pressure or temperature unless one or two phases exhaust together. In other words, the eutectic point (e) at which the three lines or curves meet is called invariant point.

2) SiO₂ System

Another important one component phase diagram is the quartz system which composes of silica (SiO₂). Six stability fields are shown in this diagram below, alpha (α) and (β) quartz are stable at lower and higher temperature respectively with low pressure when compared with coesite and stishovite. The tridymite and cristobalite are both stable at high temperature and very low pressure. Coesite is stable at higher pressure than α and β quartz with wide temperature range. While stishovite is stable at highest pressure with wide temperature range also. All these six mineral phases are chemically composed of silica (SiO₂).

It is evident that the system is **divariant** when one phase is stable, i.e. $F = C - P + 2$; $F = 1 - 1 + 2 = 2$.

The system is **univariant** along the boundary curves where two phases can coexist stably, i.e. $F = 1 - 2 + 2 = 1$, and **invariant** at the junctions, known as triple points, where three phases can exist (tridymite, cristobalite, and β – quartz) in equilibrium, i.e. $F = 1 - 3 + 2 = 0$.

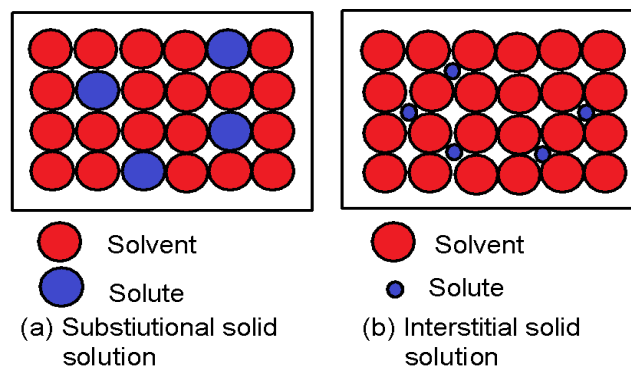


(ii) Two Components (Binary) Systems

They are the systems which compose of two components ($C = 2$). They are two types :

- 1) without solid solution
- 2) with solid solution

The solid solution consists of atoms of at least two different types where solute atoms occupy either substitutional or interstitial positions in the solvent lattice and the crystal structure of the solvent is maintained.

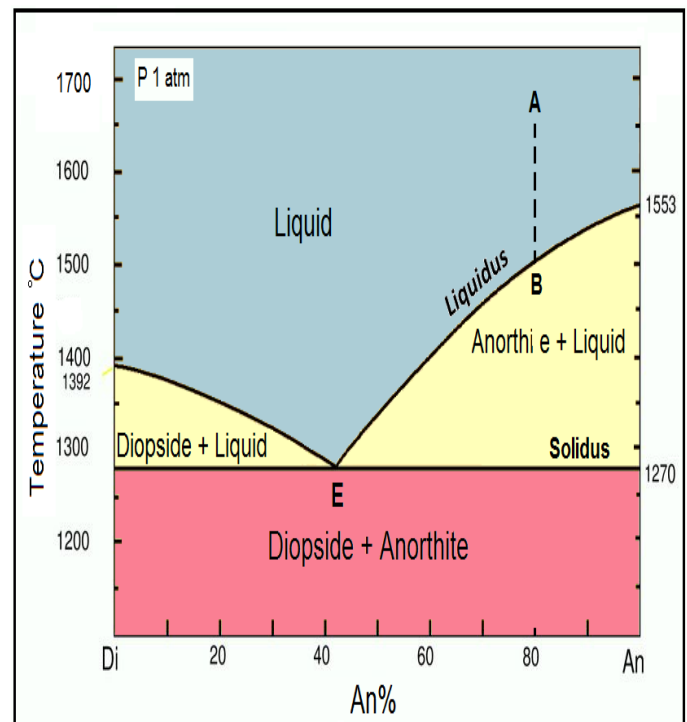


Two types of solution (a) substitution solid in which particles of the solute replace interstitial solid, solution in which the solute particles fit in spaces between particles of the host lattice (the solvent)

1) Binary System without solid solution (with Eutectic relation) : example :

Diopside – anorthite system

An example of the condensed systems (at constant pressure $P = 1 \text{ atm}$) is the (diopside – anorthite) system represented by temperature (in degree Celsius) on y-axis, and composition on x-axis (Di 100% "An 0%" to the left, and An 100% "Di 0%" to the right); where Di = diopside, An = Ca-plagioclase. The field over liquidus line represents the liquid magma, whereas the two fields beneath liquidus line represent (Di+L) to the left, and (An+L) to the right. Below solidus line (at about 1270°C , the field of the two solid minerals (Di+An) occurs. **The eutectic point (E)** is the lowest melting point of liquidus line at which cooling possibly occurs.



Suppose in this phase diagram that we have liquid magma at the point (A) at about 1650°C . To begin and continue crystallization, cooling must occur and the line drops downward to reach the point (B) at which anorthite crystallizes with liquid rest (An+L). The cooling continues along the liquidus line to the direction of point (E) resulting in crystallization of more anorthite.

At the eutectic point (E), the two minerals (An+Di) crystallize together at $T = 1270^\circ\text{C}$.

This system of crystallization is special for crystallization of basaltic magma to produce gabbro (coarse-grained) and its volcanic equivalent basalt (fine-grained).

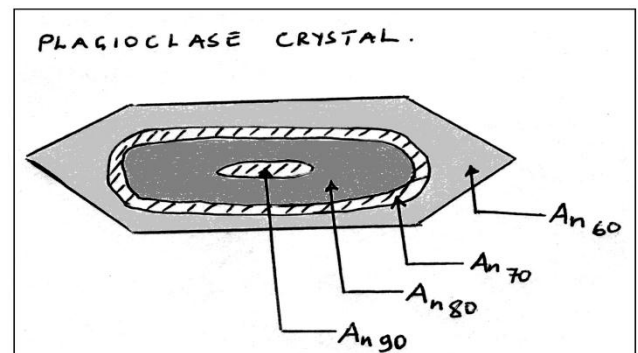
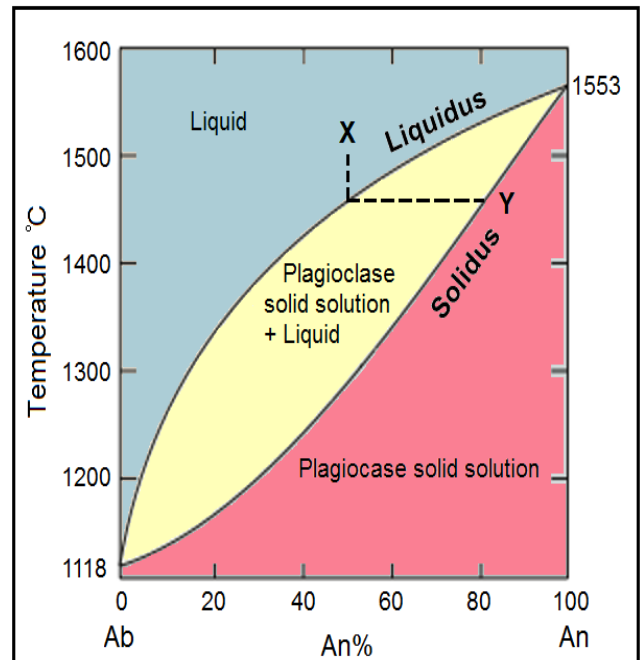
2) Binary System with solid solution (without Eutectic point)

(i) Anorthite – Albite System (Plagioclase End Members)

The albite ($\text{NaAlSi}_3\text{O}_8$) – anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) solid-solution diagram is the best-known system in silicate petrology.

For this system, different rates of cooling of a melt may lead to the formation of different end products: quenching (or rapid cooling) will yield a glass; slow cooling will result in the formation of homogeneous crystals; and intermediate rates of cooling should lead to the formation of zoned crystals.

When crystals are formed, the first-formed crystals are more calcic than the melt. For example, a melt with the composition An_{50} , X on figure, would first yield crystals of $\text{An}_{\sim 85}$, Y. Theoretically, during slow cooling, the first formed and subsequently formed crystals would react continuously with the remaining liquid, thus maintaining equilibrium until all of the melt had been used up, and the system would then consist wholly of homogeneous crystals with the composition An_{50} . (This situation is seldom achieved either in nature or in the laboratory). During more rapid (i.e., "intermediate rate") crystallization, equilibrium between already formed crystals and the remaining liquid is not maintained; consequently, the crystals are commonly zoned, with for example, their outer zones being more sodium-rich than the original

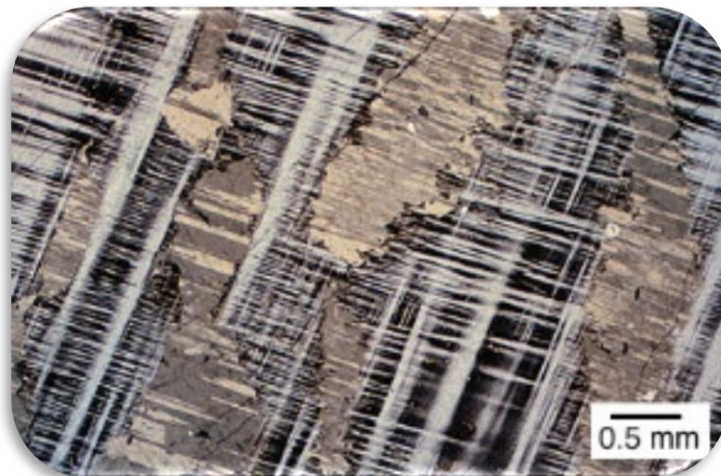
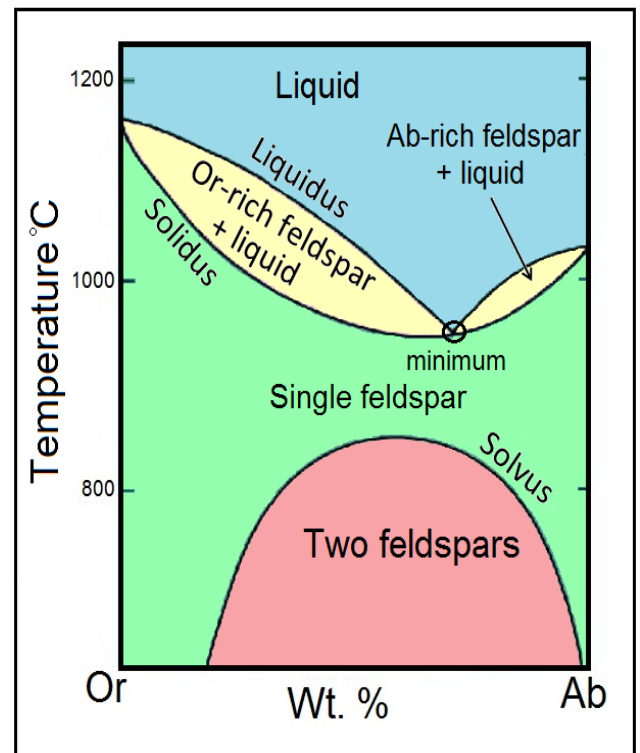


(ii) Orthoclase – Albite System

It contains two series of solid solution meet at point called (minimum); in addition to a lower curve called (solvus).

The point (minimum) is a point that represents the lowest temperature on the solidus curve at which the orthoclase solid solution series to the left sides and the plagioclase solid solution series meet together.

The solvus curve represents low temperatures (around 800 °C), and represents also (miscibility gap) above which one kind of feldspar forms, and under which the two series of orthoclase and albite are mixed together, then they crystallize in one mineral known as perthite at these relatively low temperatures (near or less than 800 °C). Perthite is in fact an orthoclase grain or crystal contains fine and small threads of white albite.



3) Three Components (Ternary) Systems

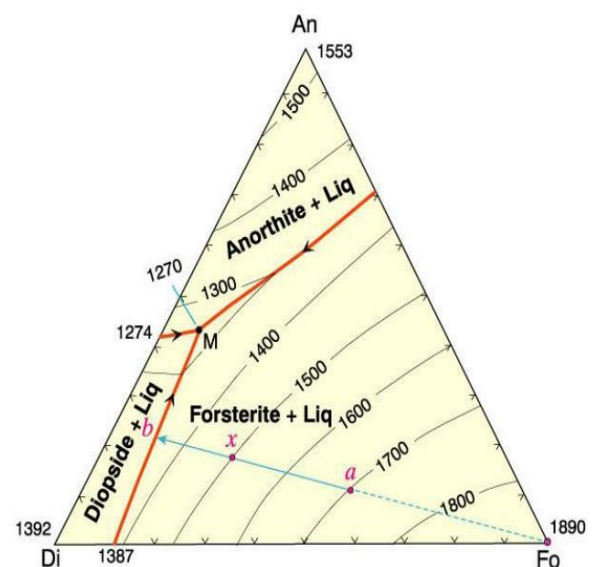
The system that contains three components ($C = 3$) as for example (Di-An-Fo) below is called three components system or ternary system. The binary eutectics are where two solid phases coexist. The ternary eutectic, where three solid phases are stable, is usually just referred to as the cotectic.

Diopside-Anorthite-Forsterite System with cotectic point

The two dimensions of the triangle projectile in the figure below are temperature (T) and composition (X), therefore, it is called (T - X projection, or T - X diagram). The cotectic point has an estimated $T = 1270^\circ\text{C}$. The figure contains three fields : (1) Forsterite+Liquid, (2) Diopside+Liquid, and (3) Anorthite+Liquid.

To read this ternary phase diagram for understanding the mutual phase relationships between the three components (An-Di-Fo), suppose we have a melt (liquid) at a temperature $T=1700^\circ\text{C}$ to be the point (a) of starting crystallization (the figure below).

To determine the direction of propagation in this system, we draw a straight line from (Fo) to the point (a), then to point (x) at 1500°C , this means that the temperature of the melt has been decreased 200°C . The continuous decrease in temperature until reaching point (b), at which diopside begins to crystallize beside olivine, and the propagation will not continue in a straight line, but will deviate to move on the liquidus curve that separates between the two fields (Forsterite+Liquid) and (Diopside+Liquid) to the direction of the cotectic point (M). At (M), the behavior of the system is similar to the eutectic point of the binary systems.



3) Four Components (Quaternary) Systems

These systems contains of course four components ($C = 4$). For example the system (An-Ab-Di-Fo) as shown below is represented by a pyramid of three dimensions; each component is at one of the four solid angles of the pyramid. Note that the fields of the coexisting minerals are clear such as (Di+Fo), (Pl+Di), and (Fo+Pl). In addition, the temperatures of crystallization of each mineral are written beside each one.

