Two-component phase diagrams I

Monday, September 14, 2020 17:19

Time on task: 2 hours (material posted on Oct 19th, Student hour: Monday Nov 2nd and Wednesday Nov 4th)

Goals:

Upon completion of lecture 11 you should be able to

- read a 2 components phase diagram with a single eutectic
- describe the melting and crystallization history
- determine the phase proportions and compositions at a given temperature and for a given composition.
- Link your calculations to your thin section observations

This lecture is complemented with your PS4 (due on Nov 27th)

1. Definitions.

- **Phase (Φ)**= a **physically separable** part of the system with distinct physical and chemical properties. A system must consist of one or more phases.
- **Component (c):** Each phase in the system may be considered to be composed of one or more components. The number of components (i.e., **chemical formula**) in the system must be the minimum required to define all of the phases.
  (see lecture 10)
- **Liquidus:** The curve separating the field of **all liquid** from that of **liquid + crystals**.
- **Solidus:** The line separating the field of **all solid** from that of **liquid + crystals.**
- **Eutectic point:** the point on a phase diagram where the maximum number of allowable phases are in equilibrium. When this point is reached, the temperature must remain constant until one of the phases disappears. A eutectic is an invariant point.
- **Congruent melting** - melting wherein a phase melts to a liquid with the same composition as the solid: in one component system, at the eutectic
  e.g., when ice melt, the composition of the water is the same than the composition of the ice, i.e., H2O
- **Incongruent melting:** melting wherein a phase melts to a liquid with a composition different from the solid and produces a solid of different composition to the original solid.
  e.g., when a peridotite melts, the composition of the magma (i.e., basalt with >45% SiO2) is different form the composition of the peridotite (i.e., an ultramafic rock: SiO2<45 wt%).

In this lecture we will go over three types of two-component phase diagrams:

- **Eutectic system**
- **Solid solution system**
- **Peritectic system**

We will only look at the case of equilibrium melting.

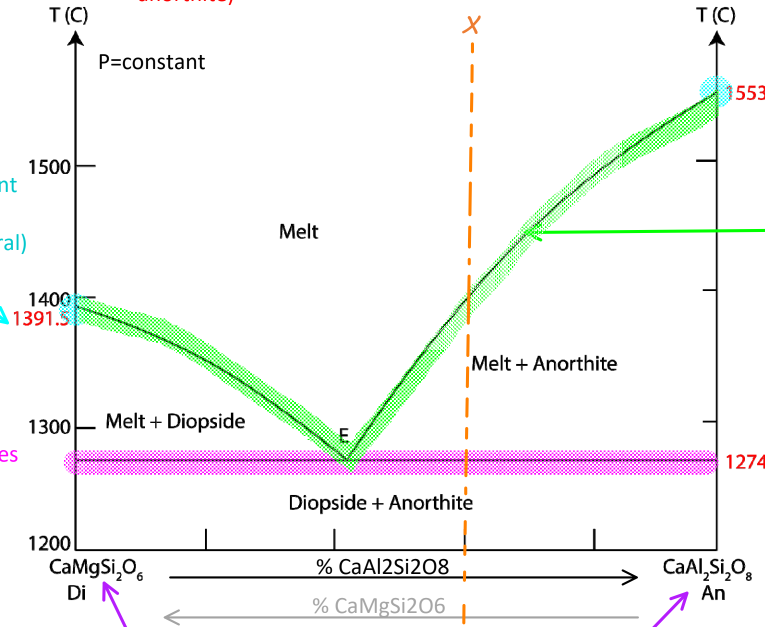
2. Two component eutectic system

2.1. Description of the phase diagram

In the previous lecture, we have been looking mostly at one component system and we look for the phase equilibria at different pressure and temperature conditions. We now have two components and we want to determine the phase equilibra for various proportions of component A and B from 100% A-0%B to 0%A-100%B.
Hence, we now have 3 changing parameters: P, T and X (composition) that would requires to work in 3D. This is not practical. Hence, we fix one parameter (usually Pressure) and work in 2D.

The figure below show a two component diagrams for a system $CaMgSi_2O_6$-$CaAl_2Si_2O_8$. Any other 2-component diagrams with a simple eutectic look similar:

If you are looking at a system with a composition CaMgSi2O6 (i.e, composition of pure diopside), then it must be treated as a once component system (same thing for the composition CaAl2Si2O8, i.e., pure anorthite)



The intersection of the liquidus curve and the Temperature axis gives the melting temperature of the corresponding one-component system.
e.g., - at 1553°C, anorthite (mineral) → anorthite (melt)
- at 1391.5°C, diopside (mineral) → diopside(melt)

At T_E = 1274 °C, all three phases are in equilibrium: Diopside, anorthite and melt

For any composition between CaMgSi2O6 and CaAl2Si2O8, the liquidus curve intersects the solidus at the **Eutectic point.**
Above this curve, the system is completely liquid (=state) and contains only melt (1 phase)

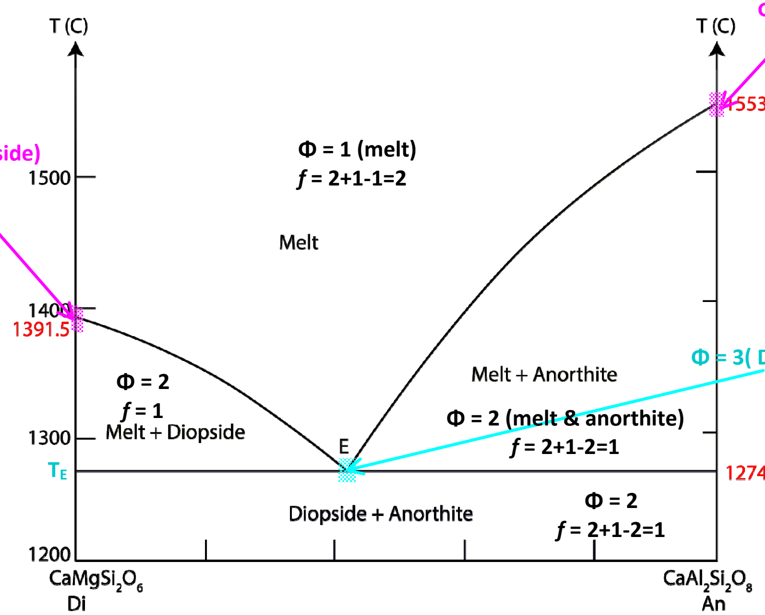
For any composition between CaMgSi2O6 and CaAl2Si2O8, the solidus is a horizontal line.
Use a ruler when you draw it!
Below 1274°C, the system is completely solid (=state) and contains 2 phases (i.e., diopside and anorthite)

You need two components (i.e., two chemical formula) to describe the all the phases that can be present in this system (ie, diopside, anorthite and melt).
In a simple eutectic phase diagram, the two components are always the chemical formula of the two solid phases than can be present in the system.

A system with a composition X is composed of 60% CaAl2Si2O8 and 40% CaMgSi2O6.
It's bulk composition is:
$CaMg_{.4}Al_{1.2}Si_2O_{7.2}$
2+0.4+1.2*3+2*4=14.4+ vs 7.2*2=14.4-
This is not a mineral formula, this is just the chemical formula of the bulk composition. I could also have asked to express the formula in wt.% of oxide as you learned to do in Lecture 8 and PS3.

2.2. Application of the Gibbs phase rule

Phase rule: $f = c + n - \Phi$
We work at constant pressure, hence n = 1 (i.e. temperature): $f = c + 1 - \Phi$



Φ = 2 (melt & anorthite)
f = 1+1-2=0

Φ = 2 (melt & diopside)
f = 1+1-2=0

Φ = 3(Diopside, anorthite, and melt)
f = 2+1-3=0

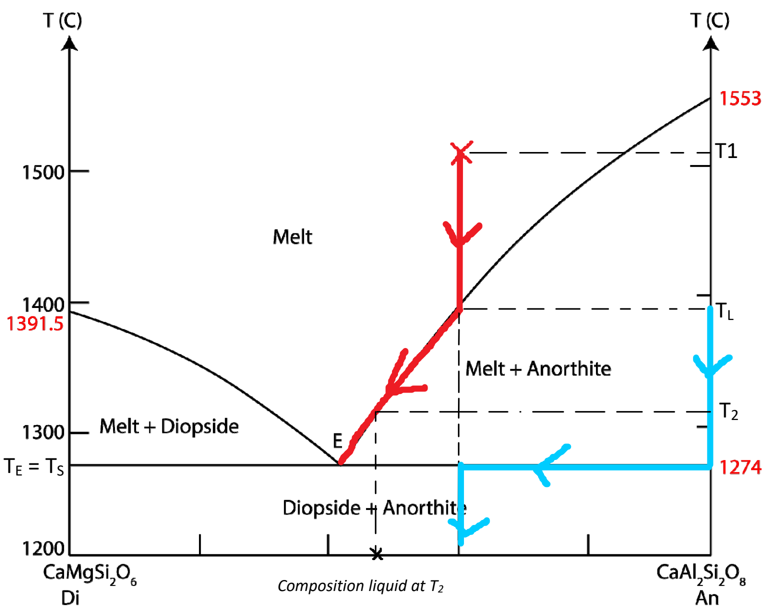
$CaMgSi_2O_6$ Di $CaAl_2Si_2O_8$ An

For any compositions intermediate between $CaMgSi_2O_6$ and $CaAl_2Si_2O_8$, this phase diagram shows 1 divariant field (*f*=2), 3 univariant fields (*f*=1) and 1 invariant point (*f*=0).
Additionally, for pure $CaMgSi_2O_6$ and pure $CaAl_2Si_2O_8$ composition (i.e., the Y-axes), we treat them as one-component diagrams: on each Y-axis, there are one invariant point (*f*=0) and two univariant field (*f* = 1. In other words, for a given pressure, diopside melts at one single temperature (1391.5°C at 1 atm). Similarly pure anorthite melts at 1553°C.

For any other compositions, melting starts at T_E = 1274°C.
If X ≠ E: melting is incongruent and happened on a range of temperature.
If X = E: melting is congruent and happens at one single temperature, T_E

2.3. Equilibrium crystallization of a liquid with the composition X.

In equilibrium crystallization or melting, the final composition of the system will be identical to the initial composition of the system.
=> The liquid X has a composition corresponding to a mixture of 60% Anorthite and 40% diopside => the final product of crystallization of this liquid will be composed of 60% Anorthite and 40% Diopside.



- **If T> T_L**: all liquid (e.g, at T_1 = 1508°C, the system is all liquid)
- **At T_L:** first crystal of Anorthite
- **At T_E<T<T_L:** 2 phases: Melt and Anorthite. *Composition of the solid is read on the solid path, composition of the liquid is read on the liquid path.*
- The liquid composition follows the liquidus curve: during the crystallization (ie, temperture decreases), the system crystallizes more and more anorthite, hence the liquid becomes progressively more enriched in Diopside to preserve a constant bulk composition.
- **At T=T_E:** the first crystal of Di crystallizes, 3 phases are present: melt, anorthite and diopside. It's an invariant point: the system will stays at T_E until one phase, the melt, disappears.
- **At T<T_E:** the system is solid and composed of 60% anorthite and 40% diopside.

Let's make this a bit more quantitative.

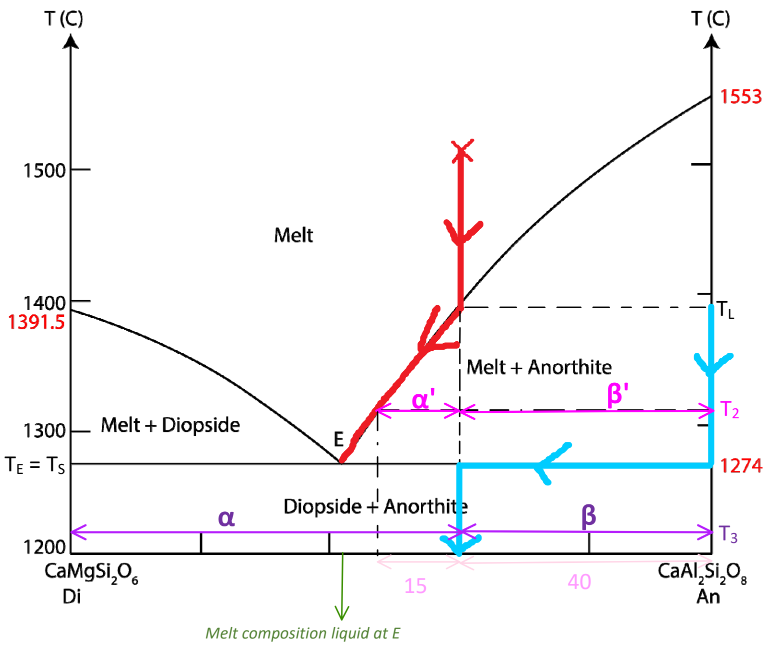
- **Compositions of the phases:**

In a simple eutectic phase diagram, the solid phase (i.e., the minerals) are pure "end-member". Hence, the composition of the minerals correspond to the components:
Diopside: CaMgSi2O6
Anorthite: CaAl2Si2O8
At a given temperature, the composition of the liquid is read directly on the liquid path.
e.g., - at T1, the system is all liquid and the composition of the liquid is X: 60% CaAl2Si2O8 and 40% CaMgSi2O6 (or $CaMg_{.4}Al_{1.2}Si_2O_{7.2}$, see section 2.1).
 - at T2, the system is composed of pure anorthite and melt. The composition of the melt can be read direction on the liquidus curve, i.e., 47% CaAl2Si2O8 + 53% CaMgSi2O6

- **Proportion of the phases (= mode = amount of each phases):**

At a temperature below the solidus (i.e., T < T_E = 1274°C), the system is composed of pure anorthite and pure diopside in proportions such as the bulk composition of the system is equal to X.
As we already said that the composition of the system (X) is 60% CaAl2Si2O8 (ie the formula of anorthite) and 40% CaMgSi2O6 (ie, the formula of diopside), you can intuitively find that the phase proportions below the solidus are **60% anorthite and 40% diopside.**

But this result can also be found by using the **lever rule**: The lever rule must be applied between the composition of the phases present *at given T* and relative to the bulk composition of the system:



At T_2, the system is composed of pure crystals of An and of melt => I'm using the lever rule between An and the melt composition (read on the liquid path).
%An = α'/(α'+β') *100 = 15/(15+40)*100=27.3%
%Di = β'/(β'+α')*100 = 100-%An = 72.7%

At T_3, the system is composed of pure crystal of An and pure crystal of Di => I'm using the lever rule between An and Di.
%An = α/(α+β) *100 = 60/(60+40)*100=60%
%Di = β/(β+α)*100 = 100-%An = 40%

- **What does happen at the eutectic?**

The Eutectic is an invariant point (f = 0): at the eutectic temperature, 3 phases are present: melt, diopside and anorthite. For the composition X, the eutectic is the temperature at which Di starts to crystallizes. The system is going to stays at this temperature until all the melt has crystallize. Hence, we can determine the phase composition when the system 1) reaches the eutectic and when the system 2) leaves the eutectic. We can also determine what 3) crystallization reaction happens at the eutectic.

1) *Phase compositions and proportions when t**he system reaches the eutectic**.*

Phases present: melt + anorthite
Phase compositions: Anorthite: CaAl2Si2O8
Melt (read on the liquid path <=> composition at E: 42% CaAl2Si2O8 + 58% CaMgSi2O6
Phase proportions (I apply the lever rule between E and An): %An = 18/(18+40)*100 = 31%
%Melt = 100-31 = 69 %

2) *Phase compositions and proportions when t**he system leaves the eutectic**.*

Phases present: Diopside + Anorthite
Phase compositions: Anorthite: CaAl2Si2O8
Diopside: CaMgSi2O6
Phase proportions: 60% An and 40% Di

3) *Crystallization reaction at t**he Eutectic***

At the eutectic, we have a crystallization reaction such as: 100%Melt → aDi% + bAn% (with a+b=100%)
The coefficients a and b are simply the proportions of Di and An for the composition E: 100 Melt = 58% Di + 42% An.

2.4. Equilibrium melting of a rock with the bulk composition X.

It is the exact same path than the crystallization path, but this time, we starts below the solidus and the temperature increases!

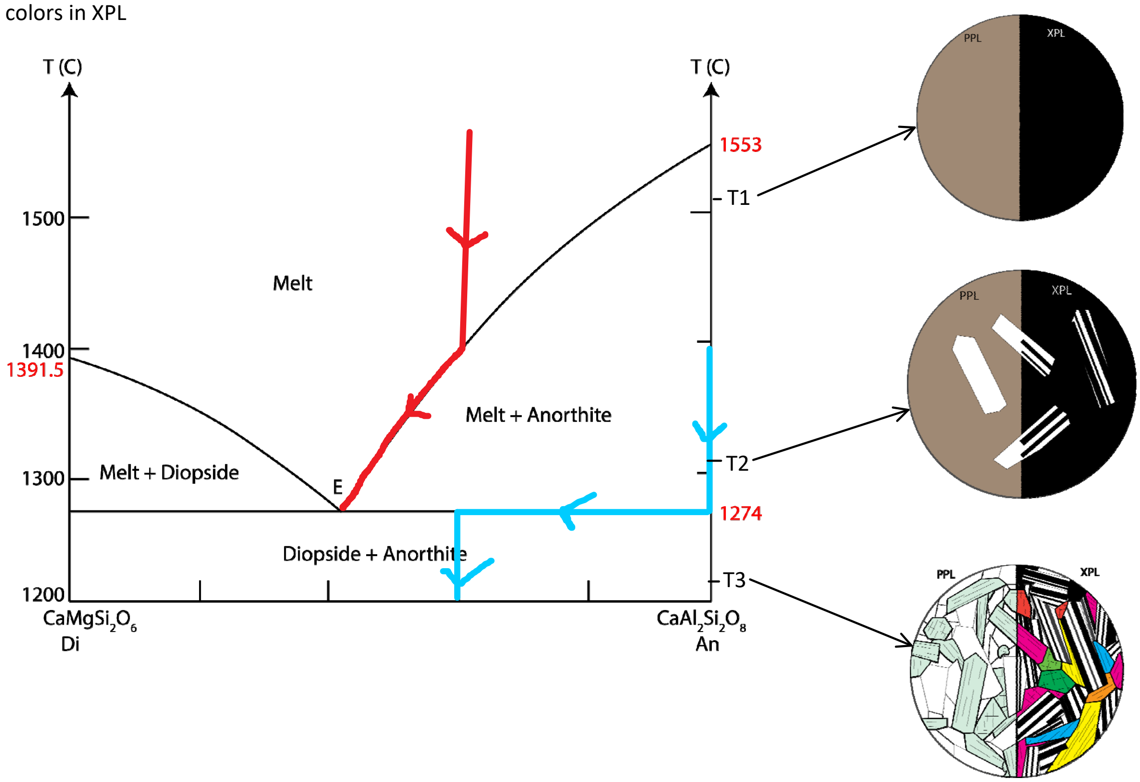
2.5. Thin section observations.

Imagine now that you could collect a series of rock that illustrate the crystallization of a magma X (this could happens for instance if the magma stays in a magma chamber and starts to crystallize, but episodically, an eruption happens and some of this magma reaches the surface. Because the temperature contrast is huge, the magma is "quenched", ie, the melt is instantaneously converted into glass and the rock preserve the melt/glass, and mineral proportions it had at the time of the eruption).

How will look a rock that erupted at 1500°C, at T2 and at T3 and was quenched instantaneously?
At T1: the magma is above its liquidus temperature. Hence, it's composed of 100% melt. Once quenched, it makes 100% glass. Volcanic glass brown in PPL and is isotropic.

At T2, the magma is composed of 27.3% anorthite and 72.7% melt. There is a lot of space for these crystal to grow, so they will present euhedral shapes. An is colorless in PPL with a low relief and often shows polynthetic twins in XPL.

At T3, the magma is completely crystallized and is composed of 60% anorthite and 40% diospide. Diospide has a high relief, can be colorless to light green in PPL, 90° cleavges on the basal section, and show vivid second order interference colors in XPL



Personal assessment.

Monday, October 5, 2020 9:24

Write the melting history of the composition Y (20%CaAl2Si2O8 - 80%CaMgSi2O6):

- Identify the critical stages (i.e., when a phase appear or disappear)
- Determine the phase compositions and proportion at each critical stages and for a couple of intermediate temperatures