Phase diagrams II

Monday, October 5, 2020 11:50

Time on task: 2 hours (material posted on Oct 26th, Student hour: Monday Nov 9th and Wednesday Nov 11th)

Goals:

Upon completion of lecture 12 you should be able to

- read a 2 components phase diagram with a solid solution or a peritectic
- Read a ternary diagram with a eutectic

1. Two component diagram with a solid solution

1.1. Description of the phase diagram and Gibbs phase rule

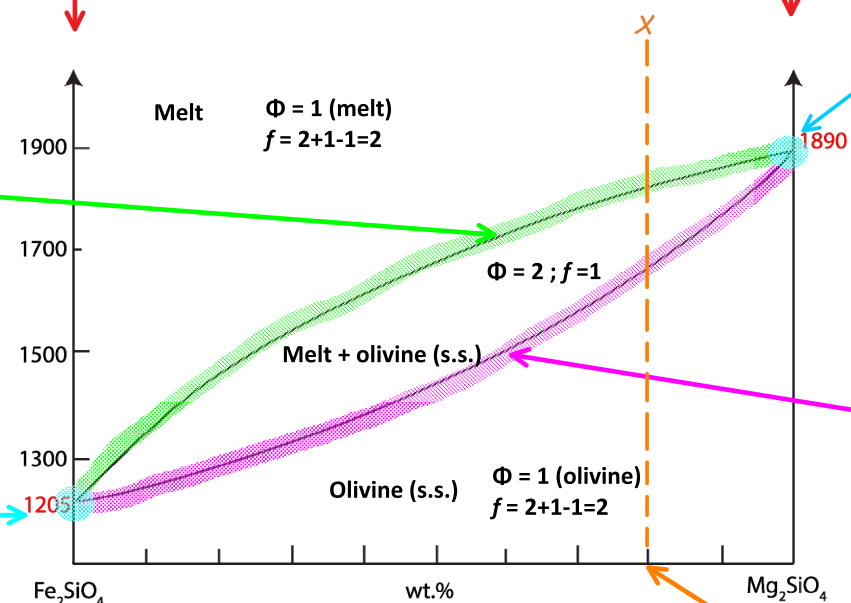
In the previous lecture, we have been looking at a two-component system for which the mineral phases were exclusively pure end-member. Here we are looking at the case where the two components define the end-member of one complete solid solution.

The figure below show a two component diagrams for a system Mg2SiO4 - Fe2SiO4. These two components are the end-members (forsterite and fayalite, respectively) of the solid solution olivine.

If you are looking at a system with a composition Mg2SiO4 (i.e, composition of pure forsterite), then it must be treated as a one component system (same thing for the composition Fe2SiO4, i.e., pure fayalite)

Liquidus: above this curve, the system is completely liquid (=state) and contains only melt (1 phase)

Invariant point: at 1890 °C, crystals of forsterite are in equilibrium with a liquid of composition Mg2SiO4. If the temperature changes, one of these two faces disappear.
Φ = 2 (melt & forsterite)
f = 1+1-2=0



Φ = 2 (melt & fayalite)
f = 1+1-2=0

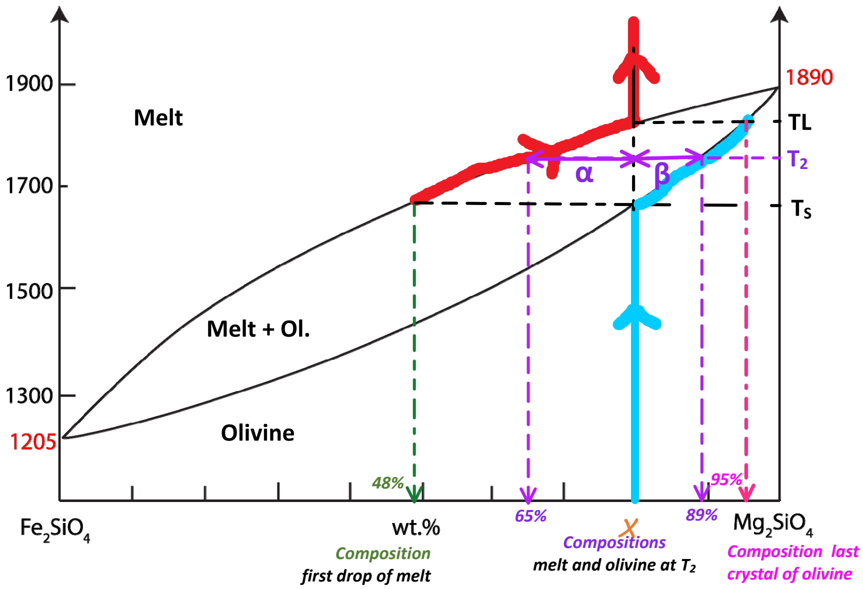
Solidus: Below this curve, the system is completely solid (=state) and contains only olivine (1 phase)

A system with a composition X is composed of 80% Mg2SiO4 and 20% Fe2SiO4. It's bulk composition is:
$(Mg_{1.6}Fe_{0.4})SiO_4$
This is a mineral formula (the parentheses indicates it's a solid solution).

1.2. Equilibrium melting of a rock composed of olivines with a composition X

A rock composed of 100% olivine is called a dunite.

In equilibrium processes, the final composition of the system will be identical to the initial composition of the system.



- If T> T_S: all solid (e.g, at T_1 = 1500°C) the system is all solid and composed of 100% olivine.
- At T_S: the rock starts to melt. The liquid path (red) starts on the liquidus curve
- At T_S<T<T_L: 2 phases: Melt and olivine. *Composition of the solid (i.e, the olivine) can be read on the solid path (blue, that follows the solidus curve), the composition of the melt is read on the liquid path (red, that follows the liquidus curve).*
  During melting both the liquid and the olivine becomes more enriched in forsterite component.
- At T=T_L: the melt reaches the same composition than the initial olivine, which means that the olivine is completely melted. That also marks the end of the solid path.
- At T>T_L: the system is and the temperature of the system can increase while keeping a constant composition.

Let's make this a bit more quantitative.

- **Compositions of the phases:**

The composition of the solid solution is read on the solid path, the composition of the melt is read on the liquid path.
At a given temperature, the composition of the liquid is read directly on the liquid path.
e.g., - at T1=1500°C, the system is all solid and the composition of the olivine is X: 80% Mg_2SiO_4 and 20% Fe_2SiO_4. This is a solid-solution, so that correspond to a mineral formula: $(Mg_{1.6}Fe_{0.4})SiO_4$

- at T_S, the olivine just starts to melt. The composition of the olivine is still $(Mg_{1.6}Fe_{0.4})SiO_4$, the composition of the melt in equilibrium is read on the liquidus path at the same temperature (i.e, on the same horizontal line): 48% Mg2SiO4-52%FeSiO4 = $(Mg_{.96}Fe_{1.04})SiO_4$

- at T_2, the system is composed of olivine and melt. The composition of the olivine is $(Mg_{1.78}Fe_{0.22})SiO_4$, the composition of the melt in equilibrium is read on the liquidus path at the same temperature $(Mg_{1.3}Fe_{0.7})SiO_4$

- at T_L, the composition of the melt now has the same composition than the initial olivine: $(Mg_{1.6}Fe_{0.4})SiO_4$. The composition of the last crystal of olivine in equilibrium with this melt is read on the solidus path at the same temperature (i.e, on the same horizontal line): $(Mg_{1.9}Fe_{0.1})SiO_4$.

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

At a temperature below the solidus (i.e., T < T_S), the system is composed of 100% olivine.

At T2, we can use the **lever rule**:
At T_2, the system is composed of olivine and melt => I'm using the lever rule between the olivine composition (read on the solid path) and the melt composition (read on the liquid path).
%olivine = α/(α+β) *100 = 15/(15+9)*100=62.5%
%melt = 100-%olivine = 37.5%
(I found more olivine than melt, so I double check my result by making sure my bulk composition, X, is closer to the solid path than to the liquid path at T_2: I'm good)

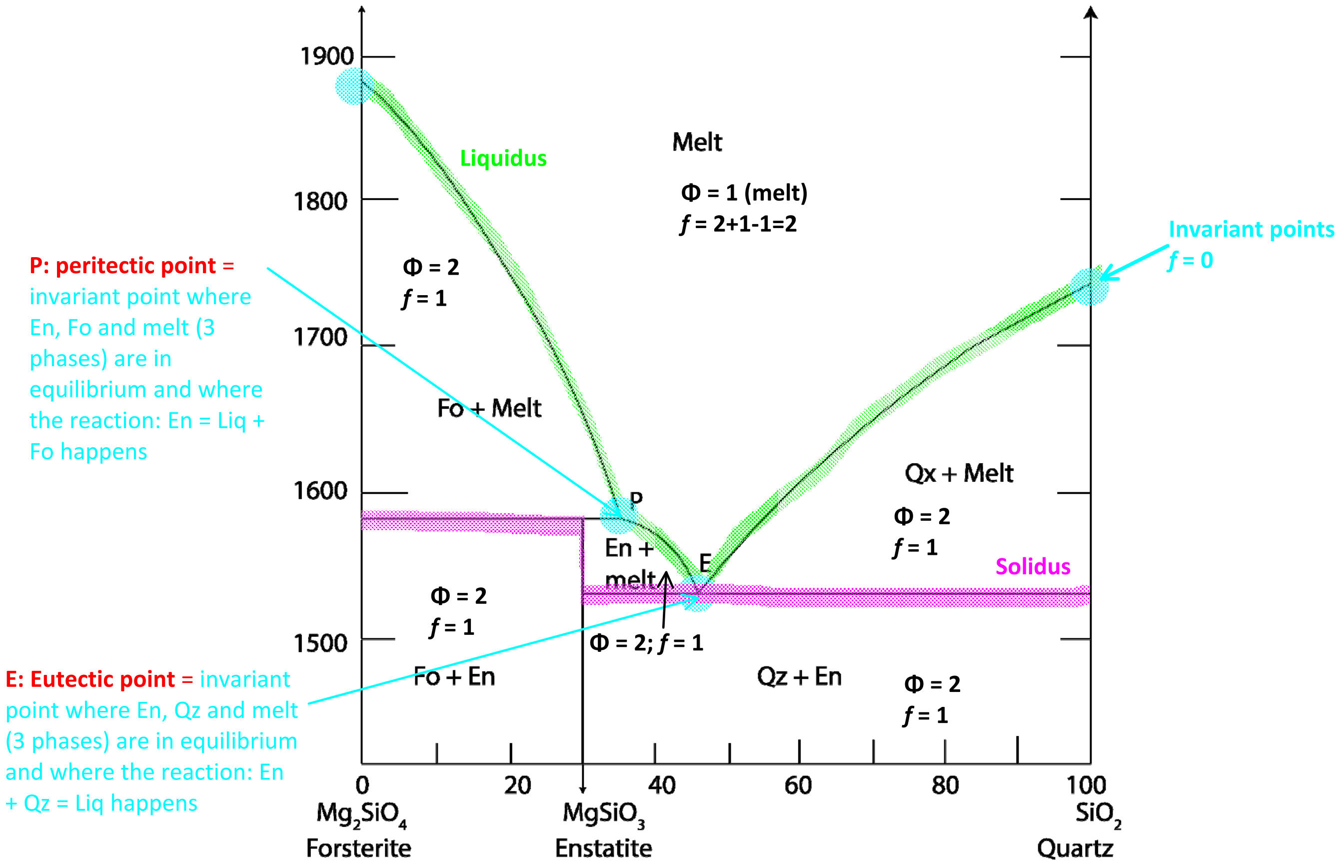
At a temperature above the liquidus (i.e., T > T_L), the system is composed of 100% melt.

Peritectic

2. Two component diagram with an intermediate unstable phase.

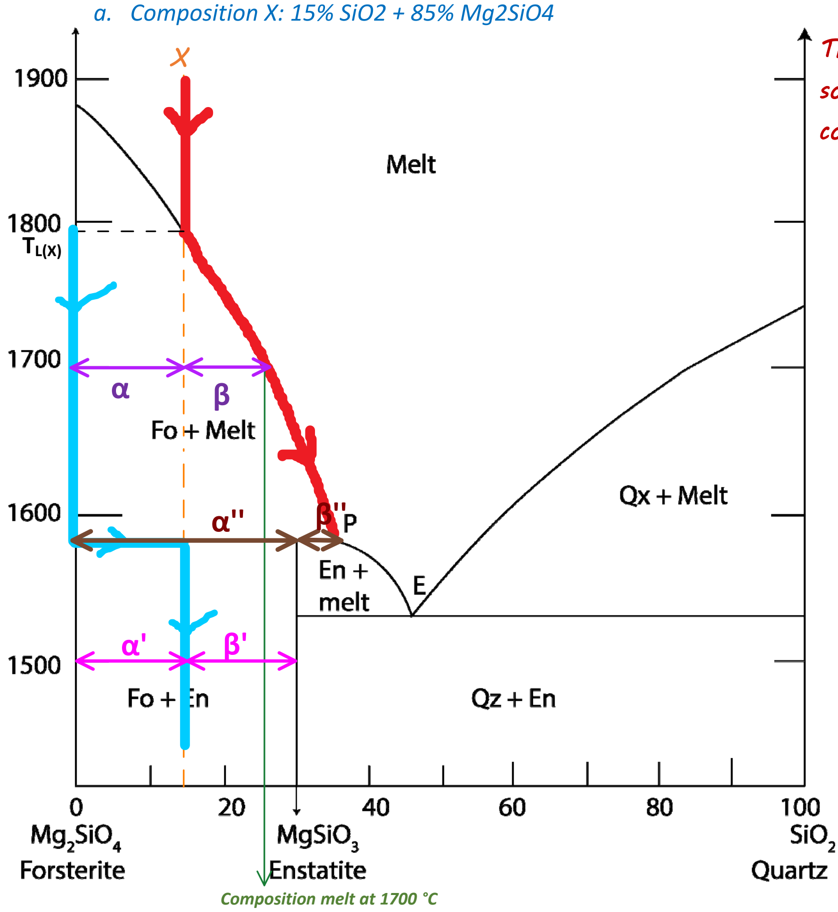
2.1. Description of the phase diagram and Gibbs phase rule

The figure below show a two component diagrams for a system Mg2SiO4 - SiO2. These two components correspond to the chemical formula of two different minerals: forsterite and quartz.



2.2. Equilibrium crystallization

a. Composition X: 15% SiO2 + 85% Mg2SiO4



The composition X is in the solid field of En and Fo, so I know that my final product is going to be composed of Enstatite and forsterite.

- **If T> $T_{L(x)}$**: all liquid (e.g, at T_1 = 1850°C, the system is all liquid)
- **At T_L:** first crystal of Forsterite
- **At T_P<T<$T_{L(x)}$:** 2 phases: Melt and Forsterite. *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 SiO2 to preserve a constant bulk composition.
- **At T=T_P:** the first crystal of Enstatite crystallizes, 3 phases are present: melt, Fo and En. The reaction is Fo + melt → En (both Fo and melt are consumed during the reaction). It's an invariant point: the system will stays at T_P until one phase disappears. I know that I have forsterite in my final solid, so the reaction will stop when all the melt is consumed. **P is the end of the liquid path**
- **At T<T_P:** the system is solid and composed of 50% forsterite and 50% enstatite.

Let's make this a bit more quantitative.

- **Compositions of the phases:**

The solid phase (i.e., the minerals) are pure "end-member".
Forsterite: Mg2SiO4
Enstatite: MgSiO3
Quartz: SiO2
At a given temperature, the composition of the liquid is read directly on the liquid path.
e.g., - at T = 1700, the composition of the melt is 25% SiO2 + 75% Mg2SiO4 (*compositions are always expressed in % of components, you should not use the intermediate phase*)

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

- At 1700 °C, the system is composed of 2 phases: Forsterite and melt. I use the lever rule between the forsterite composition and the liquid composition:

%forsterite= β/(α+β) *100 = 10/(10+15)*100=40%
%melt = 60%

(Once again, I double-check: I found more melt than forsterite, my bulk composition, X, is closer to the solid liquid than to the solid path at 1700°C: I'm good)

- At 1500 °C, the system is composed of 2 phases: Forsterite and Enstatite. I use the lever rule between the forsterite composition and the enstatite composition:

%forsterite= β'/(α'+β') *100 = 15/(15+15)*100=50%
%enstatite= 50%

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

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

1) *Phase compositions and proportions when t**he system reaches the peritectic**.*
   Phases present: melt + forsterite
   Phase compositions: forterite: Mg_2SiO_4
   Melt (read on the liquid path <=> composition at P: 35% SiO_2+ 65% Mg_2SiO_4
   Phase proportions (I apply the lever rule between P and Fo): %Fo = 20/(20+15)*100 = 57%
   %Melt = 100-57 = 43 %

2) *Phase compositions and proportions when t**he system leaves the peritectic**.*
   Phases present: forsterite+ enstatite
   Phase compositions: Forsterite: Mg_2SiO_4
   Enstatite: $MgSiO_3$
   Phase proportions: 50% Fo and 50% En

3) *Crystallization reaction at t**he Peritectic***
   At the peritectic, we have a crystallization reaction such as: a %Fo + b %melt → 100% En (with a+b=100%)
   To find the coefficients, you must apply the lever rule between Fo and melt, and the composition of the intermediate phase (Enstatite): a = $\beta''/(\alpha''+\beta'')*100$ = 5/(5+30)*100=14.3%, b=100-14.3=85.7%.
   The peritectic reaction is 14.3% Fo + 85.7% melt → 100% En.

Note that the presence of a peritectic point where a phase is consumed is consumed in addition to melt during crystallization, or inversely, a phase is produced in addition to melt during melting is very common.
The most famous example is the melting of the mantle. The mantle is dominated by peridotite, a rock composed of olivine (Ol), orthopyroxene (Opx), clinopyroxene (Cpx) and a aluminous phase (Al-p: plagioclase/spinel/garnet, depending on the pressure).
The typical melting reaction for a peridotite at P<3 Gpa is:
a Opx + b Cpx + c Al-p = d melt + e Ol
The values of the coefficients a-e depend on composition and pressure-temperature conditions. (At P>3GPa, olivine is consumed and opx is produced during the melting reaction)

b. Composition Y: 32% SiO_2 + 68% Mg_2SiO_4

Your turn! Write the crystallization history of the composition Y, give the phases compositions and proportions at 1700°C, 1600°C, 1575°C and 1500°C, and describe what happened at the invariant point(s). (keys are on the next page)

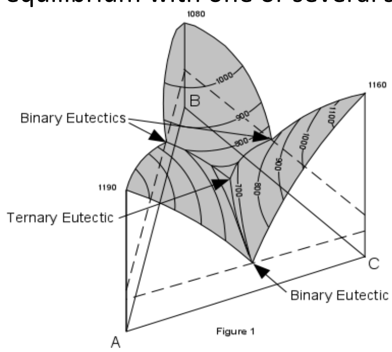
Introduction to ternary phase diagrams (c = 3)

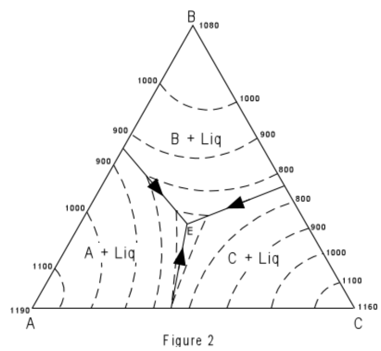
Friday, October 9, 2020 11:59

3. Ternary diagram

Studying in details ternary diagrams is beyond the scope of this class, but because ternary diagrams are extensively used in the igneous petrology literature, I want to introduce a few notions here (you will study ternary diagrams in petrology class). Here we are only going to introduce the simple case of a ternary diagram with a single eutectic point.

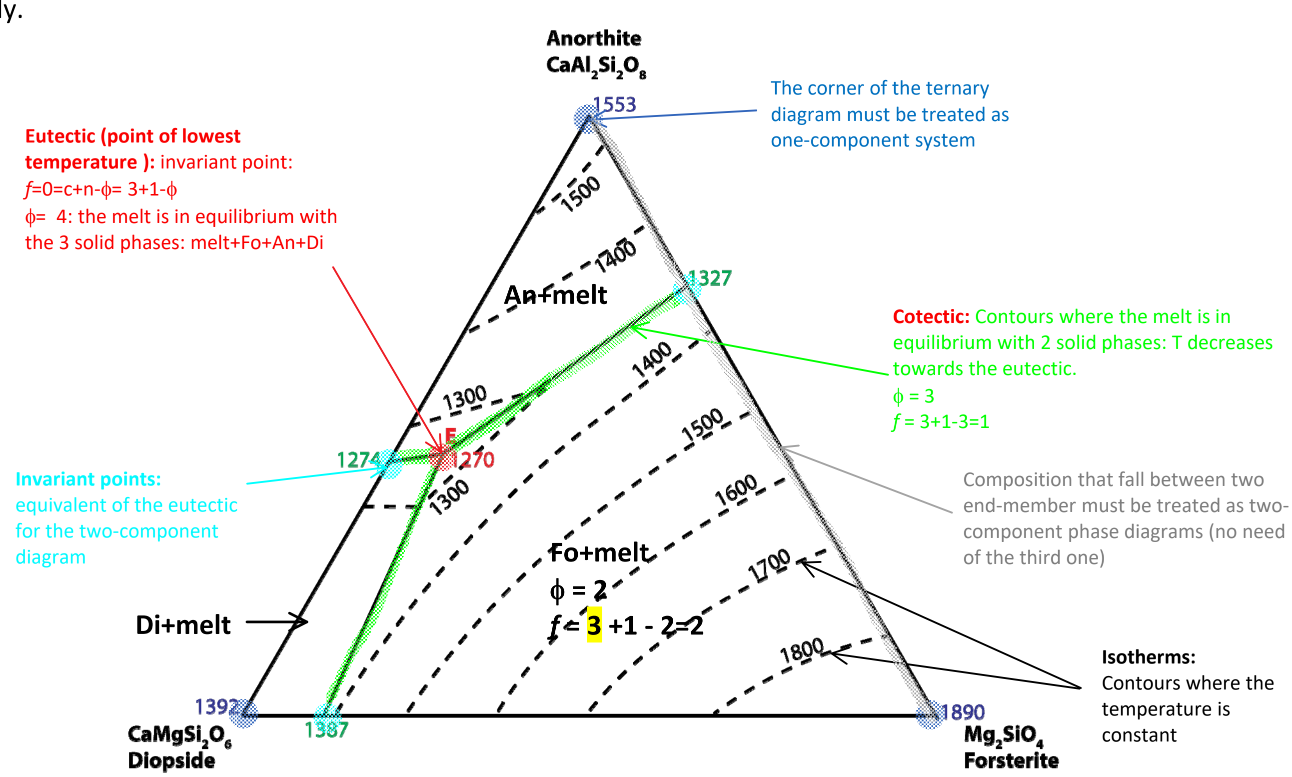
A ternary diagram is the projection of the liquidus surface (think about it as a topography map where the elevation contour lines are replaced by isotherms, i.e., contour where the temperature is constant, where the melt is in equilibrium with one or several solid phases)





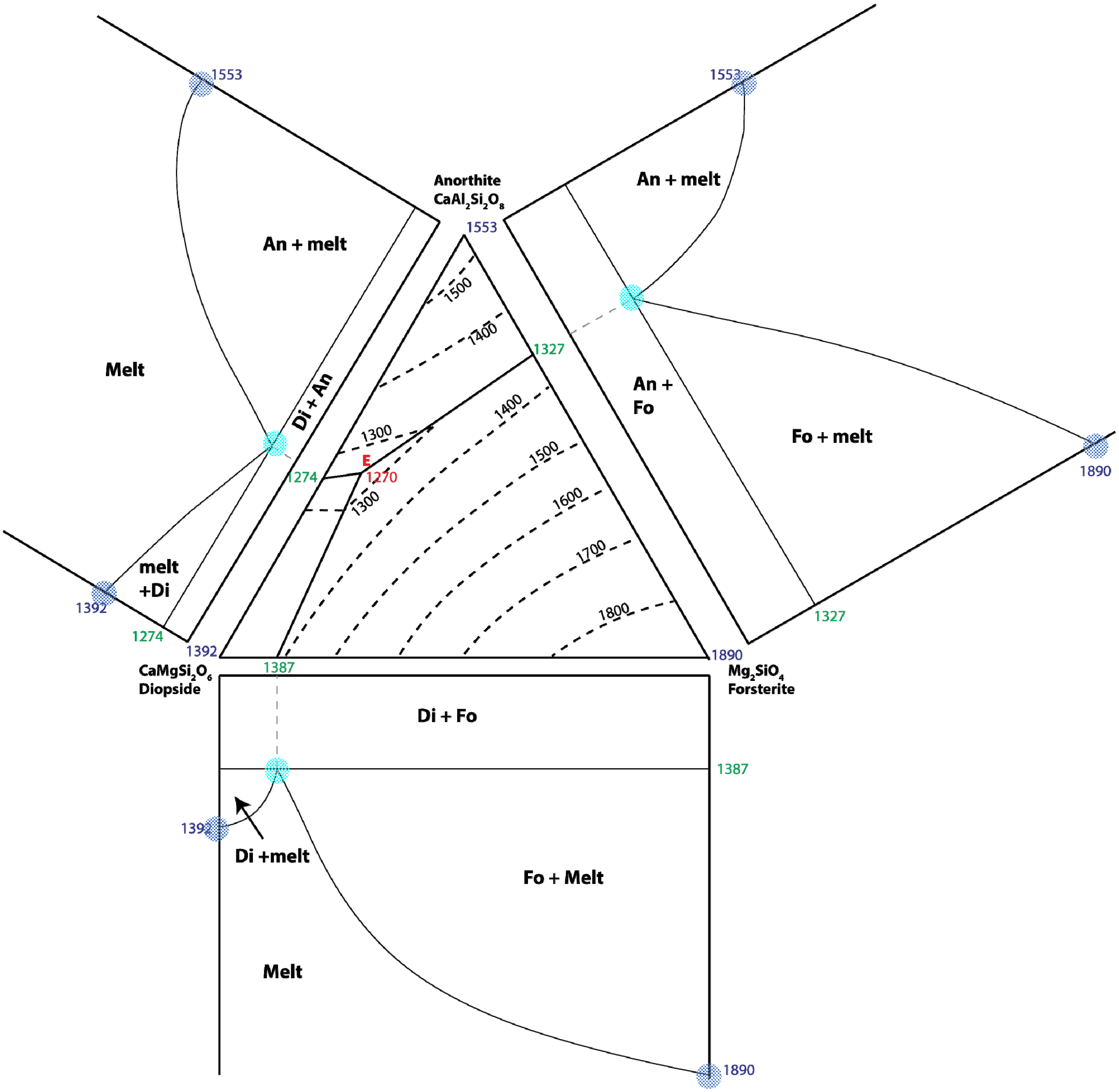
Credits: Tulane University: https://www.tulane.edu/~sanelson/eens212/ternaryphdiag.htm

The figure below show a three component diagrams for a system Mg2SiO4 -CaMgSi2O6-CaAl2Si2O8. These three components are the formula of the pure minerals forsterite, diopside and anorthite, respectively.



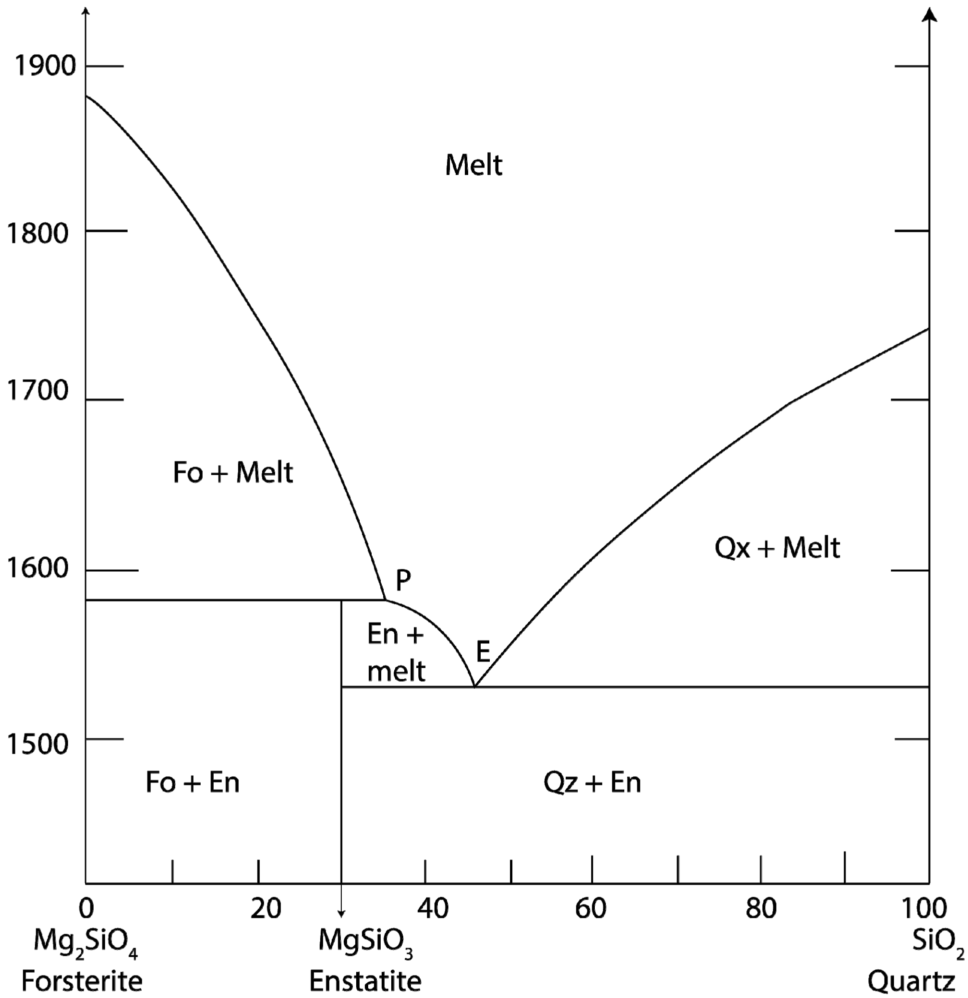
A three component diagram is the intersection of three 2-component diagrams.

To visualize a this ternary diagram in 3D, open **ternary.html** posted with the lecture file on Canvas.

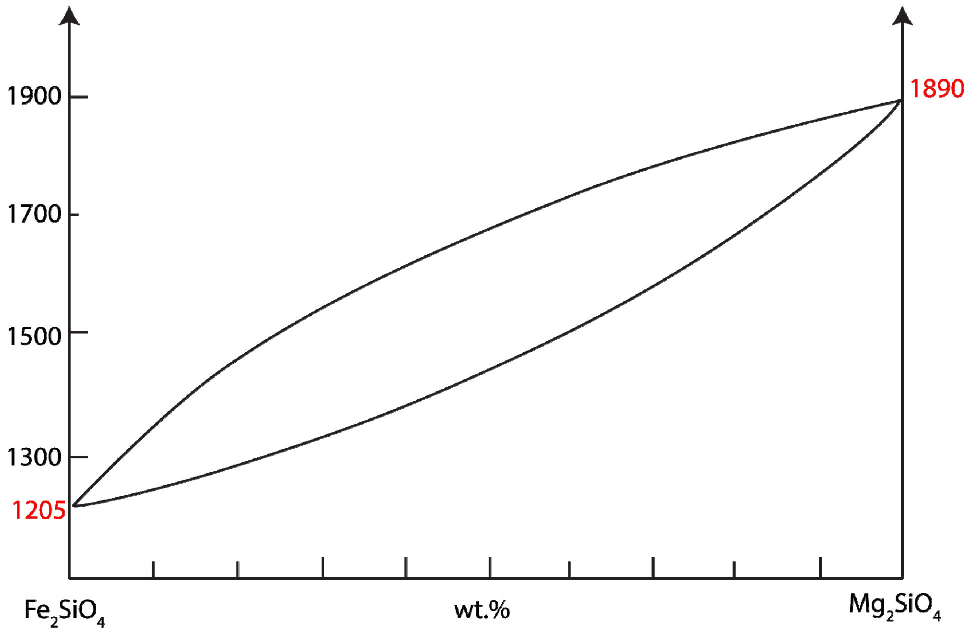


Personnel assessment.

Sunday, October 11, 2020 13:08



1) **Write the crystallization history of the composition Z (MgSiO3)**



2) **What is the composition of the last drop of melt during equilibrium crystallization of a liquid of composition Y: 50% Mg2SiO4 - 50% Fe2SiO4?**

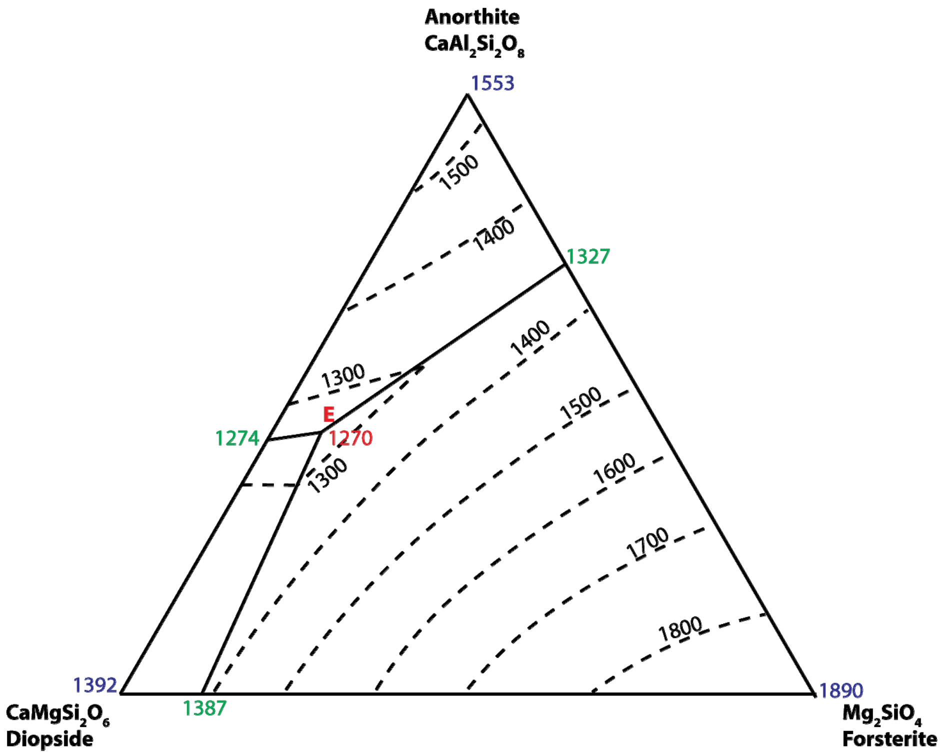
A – 50% Mg2SiO4
B – 18% Mg2SiO4
C – 18% Fe2SiO4 same
D – 0% Mg2SiO4

3) **What is the liquidus temperature of the composition Mg2SiO4?**

A – 1890°C
B – 1205°C
C – between 1890°C and 1205°C

4) **What is the solidus temperature of the composition Mg2SiO4?**

A – 1890°C
B – 1205°C
C – between 1890°C and 1205°C



3) What is the solidus temperature of a system composed of 10% CaAl2Si2O8, 30% CaMgSi2O6, 60% Mg2SiO4?

A – 1700°C
B – 1890°C
C – 1270°C
D – We don't know

4) What is the liquidus temperature of a system composed of 10% CaAl2Si2O8, 30% CaMgSi2O6, 60% Mg2SiO4?

A – 1700°C
B – 1890°C
C – 1270°C
D – We don't know