

The use of visualization and sketches of thin sections to encourage a better understanding of phase diagrams: Binary and ternary phase diagram exercises

Jennifer M. Wenner University of Wisconsin Oshkosh, Geology Department, 800 Algoma Blvd. Oshkosh, Wisconsin 54901

Drew S. Coleman Department of Geological Sciences, University of North Carolina, CB #3315, Chapel Hill, NC 27599

Instructors Notes:

We developed these exercises to put the concepts of igneous phase diagrams into practical context. Our objective was to relate phase diagrams that students manipulated for homework to things that they were seeing in lab. And, not coincidentally, igneous phase diagrams pop up in lab exercises; students are asked to relate what they are seeing in the rocks to a phase diagram. By making the students think about what is actually happening with the magma/crystals, they seem to make connections better and to understand why a basic comprehension of phase diagrams is crucial to our understanding of igneous rocks.

In total, there are 10 exercises included. Four exercises deal with binary phase diagrams (one eutectic (Di-An), one peritectic (Fo-En-Q) and two alkali feldspar) and all questions relate to equilibrium crystallization. Four different ternary phase diagrams are included (Q-Ab-Or @ both low and high P_{H_2O} , Fo-An-Q, and Di-Ab-An). Four exercises address equilibrium crystallization of compositions on each of these diagrams. Two other ternary phase diagram exercises address the fractional crystallization and/or partial melting of compositions in the Fo-An-Q and high P_{H_2O} Q-Ab-Or systems. Each exercise is 1-3 pages long and is completely self-contained (bold title separates individual exercises). None builds on any other; thus, an instructor may pick and choose the exercises that she/he feels are appropriate to his/her course. Graphics files (in .PDF format) are included so that an instructor may change the compositions involved in a given exercise. All graphics files are modified from phase diagrams found in Chapter 10 of Philpotts (1990).

An introduction to thermodynamics and phase diagrams in general is crucial to the success of these exercises. Many textbooks [Best (2002); Winter (2001) and Philpotts (1990) are three that come to mind] provide excellent introductions to thermodynamics and phase diagrams. Below is a handout that we have used in the past to introduce phase diagrams. In different semesters, this handout has been introduced in Mineralogy or early in Petrology; it condenses the general concepts behind phase diagrams into a few pages and provides the students with something tangible to take home for reference when completing homework exercises. When we have used it in Mineralogy, it has been as a part of a laboratory exercise. In Petrology, we have used worked through it as an in-class exercise (or at least started it in class).

Also included here, is an overhead that we put up at the beginning of every class in which we discuss phase diagrams: "Easy Rules for Phase Diagram Interpretation". It outlines 5 easy rules that students need to remember to interpret any phase diagram. Students seem to respond to this and have an easier time working with phase diagrams in the homework when they keep these rules in mind.

Although not included, a discussion of the lever rule is also essential in order for students to successfully complete these exercises. Students need to know how to use the lever rule for both binary and ternary phase diagrams. In each of the exercises, they are asked to calculate

proportions (or percentages) of solid to liquid and proportions of different solid phases. In some cases for ternary phase diagrams, they are asked to use the lever rule to calculate instantaneous compositions (using the tangent to the cotectic) of crystallizing solids. In most cases, it is not necessary for a student to use a ruler to get actual numbers; instead we feel that it is enough to show that they can set the problem up. The assumption is that they could “plug and chug” if they were asked.

References cited

- Best, M.G. (2002) *Igneous and Metamorphic Petrology*. 756 p. Blackwell Publishing, Malden, MA.
- Philpotts, A.R. (1990) *Principles of Igneous and Metamorphic Petrology*. 498 p. Prentice Hall, Englewood Cliffs, NJ.
- Winter, J.D. (2001) *Introduction to Igneous and Metamorphic Petrology*. 697 p. Prentice Hall, Upper Saddle River, NJ.

PHASE DIAGRAMS AND THE PHASE RULE

PART I: Definitions and some basic thermodynamics

Definitions

System: a portion of the universe separated from the rest of the observable universe by well-defined boundaries.

Phase: a part of the system that is physically separable and spatially uniform in its properties. (Remember -- phase is a subjective term -- greater resolution often changes one's opinion. Remember too that more than one phase can have the same composition.)

Components: *minimum* number of chemically distinct constituents needed to *describe* the composition of each phase in the system. As you will see, it is not possible to have more components than phases for a given system.

Examples: Water + ice = H_2O

NaCl-brine = H_2O and NaCl (Not Na^+ , Cl^- , H^+ , OH^- . These are not physically separable phases.)

Rock with jadeite ($\text{NaAlSi}_2\text{O}_6$) and nepheline ($\text{NaAlSi}_3\text{O}_8$) = NaAlO_2 and SiO_2

Equilibrium: The condition of minimum energy for a system. The lowest possible free energy (G).

Instability: A condition of a system where energy is not at a minimum. There is another configuration of the system with lower energy.

Degrees of freedom: The number of intensive variables that must be specified arbitrarily before a system is defined.

Intensive variables: Variables whose value does not change as the amount of the material in the system increases or decreases. Temperature, pressure and chemical potential (μ) of each component.

“Ambient variables”: Temperature and pressure. In some systems either T or P is fixed and the number of ambient variables is reduced from 2 to 1.

Basic thermodynamics

Equilibrium state = state of an isolated system in which there is no change throughout the system as a function of time or position in the system (intensive variables would be identical throughout the system). Must specify time frame.

Gibbs Phase Rule (There are no known exceptions to the phase rule. Should perhaps be called the Gibbs Phase Law.) If you want to see a derivation of the phase rule, please see me and we can go over it.

$$F = c - p + 2$$

where,

F = degrees of freedom

c = components

p = phases

When:

F < 0; unstable

F = 0; invariant point (e.g. for a two component system: eutectics are invariant points)

F = 1; univariant (e.g. for a three component system: cotectics are univariant lines)

F = 2; divariant (e.g. for a two component system: plot as regions)

Note: For geological applications (particularly igneous petrology), we are often examining phase equilibria at a constant pressure. This reduces the degrees of freedom and results in the **condensed phase rule**:

$$F = c - p + 1$$

Still, when:

F < 0; unstable

F = 0; invariant point (e.g. for a two component system: eutectics are invariant points)

F = 1; univariant (e.g. for a three component system: cotectics are univariant lines)

F = 2; divariant (e.g. for a two component system: plot as regions)

Most important thing to remember:

The phase rule applies only to the number of phases and not the quantity of phases. For example, a large pool of water in equilibrium with a single ice cube is no different than a small tub of water in equilibrium with a big block of ice. Therefore, it's more important to recognize the complete range of phases present than it is to recognize their quantity.

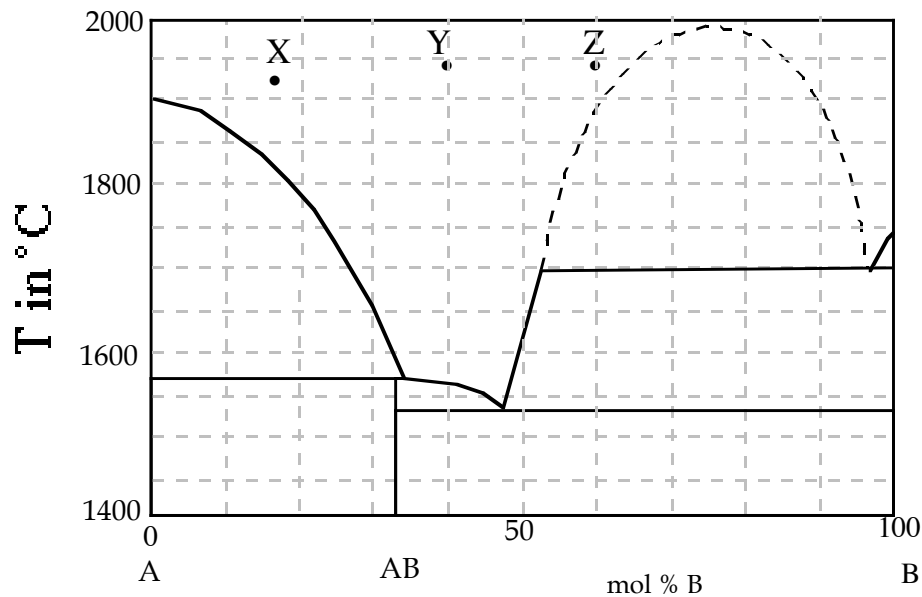
PART II: Application of the phase rule

1. Determine and list the minimum number of chemical components for a system with the phases:
 - a) pyrite (FeS_2) + marcasite (FeS_2)
 - b) quartz (SiO_2) + cristobalite (SiO_2) + tridymite (SiO_2)
 - c) sillimanite (Al_2SiO_5) + mullite ($\text{Al}_6\text{Si}_3\text{O}_{15}$) + quartz (SiO_2) + corundum (Al_2O_3) + kyanite (Al_2SiO_5)
 - d) spinel (MgAl_2O_4) + olivine (Mg_2SiO_4) + enstatite (MgSiO_3)
 - e) calcite (CaCO_3) + lime (CaO) + vapor (CO_2)
2. In the above sets of minerals, list the groups of minerals that are examples of polymorphism?
3. Determine the variance (# of degrees of freedom) for each system above using the phase rule, and comment on the viability of the assemblage (assuming equilibrium, of course). Determine if the assemblage represents a divariant field, a univariant line, or an invariant point.

Part III: Interpretation of phase diagrams

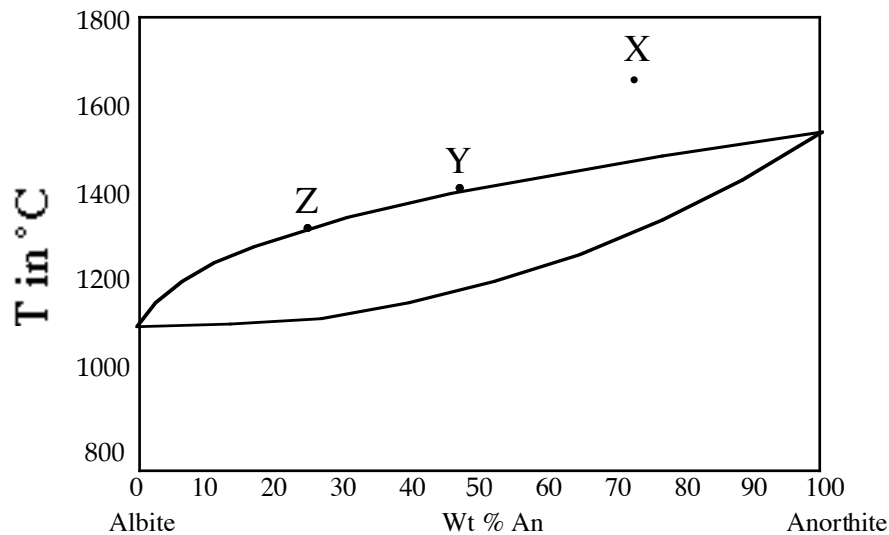
A. Binary eutectic system

All of the systems use the condensed phase rule because pressure is held constant ($P = 1 \text{ atm}$) for each of them. So for each of these phase diagrams we do not consider pressure. These diagrams would change if the pressure changed.



1. Label the fields on this phase diagram (i.e. which phases are stable in each of the T-composition regions). Label any peritectics (P) or eutectics (E).
2. Interpret the binary phase diagram shown below by describing the crystallization history of three different melts (X, Y, and Z). (Use different colors for each crystallization sequence.)
3. Under what conditions would it be possible for phases A and B to occur in the same rock? What is an example of an actual mineralogical system that behaves in this way?

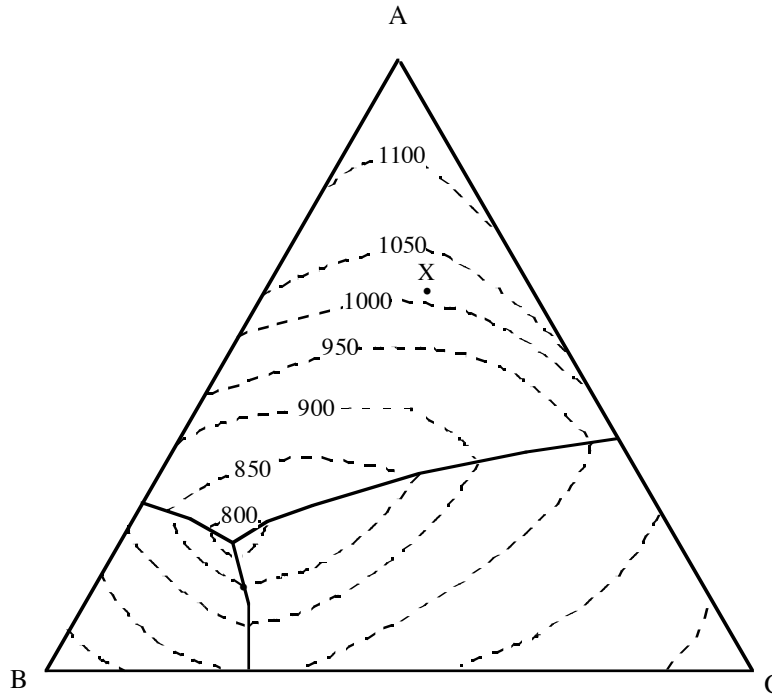
B. Binary solid solution system



1. Label the fields on this diagram as you did in part A.
2. Interpret the plagioclase diagram by following the crystallization history of melt “X” under equilibrium conditions.
3. Using the lever rule, determine the relative quantities of melt and solid at point Y. What is the composition of melt at this point? What is the composition of the solid at this point? Answer the same questions for point Z.
4. Now melt a plagioclase. At which temperature does a plagioclase with 60 wt% anorthite begin melting? What is the first or initial composition of this melt? At 1400°C, what are the proportions of liquid and solid for a bulk composition of 60 wt% anorthite? What is the composition of the liquid at 1800°C?

Extra Credit: What would a grain of plagioclase that formed under disequilibrium conditions look like in thin section?

C. Ternary phase diagram



1. Label the fields on the diagram below. Remember that you need to visualize a third dimension on these types of phase diagrams. Temperature axis is coming out of the page and the liquid field is “hovering above the page”.
2. What is the first phase to crystallize from a liquid of composition X?
3. What is the approximate composition of liquid X in terms of percentages of the components A, B, and C?
4. For bulk composition X, what phases are at equilibrium when $T = 900^{\circ}\text{C}$? Give compositions of the phases by means of letters or numbers placed on the diagram. What are the proportions of the phases?
5. For composition X, what phases are at equilibrium when $T = 850^{\circ}\text{C}$? Give compositions of phases by means of letters or numbers placed on the diagram and state the proportions of:
 - a. Liquids to solids
 - b. solid phases.
6. Draw a picture of the thin section as you might see it in your microscope if it were frozen at 850°C .
7. What phases are present in the final crystalline product?

EASY RULES FOR PHASE DIAGRAM INTERPRETATION

1. Label all fields, cotectics, eutectics and/or peritectics.
2. When you find yourself in a field, determine what phases are in equilibrium.
3. Draw a horizontal tie line at the appropriate T until you reach phase boundaries (for binary diagrams); or draw a tie line from liquid composition through bulk composition to solid phase boundary (for ternary diagrams).
4. Determine proportions of each phase using the lever rule.
5. Decide which phases need to be added or subtracted to move into next field.