Phase Diagrams
C:\Courses\320\fall2007\in class\1810-PhaseDiagrams.wpd; November 6, 2007 (5:00pm)

<u>Example #1: Graphite-Diamond</u>

If you Google for graphite-diamond, and click so you only search images, you will find this diagram:

> *phase*: A substance that has distinct physical and chemical properties. Minerals, and other compounds are phases. In addition, we may consider a molten phase or a fluid phase containing, for example H_2O or CO_2.
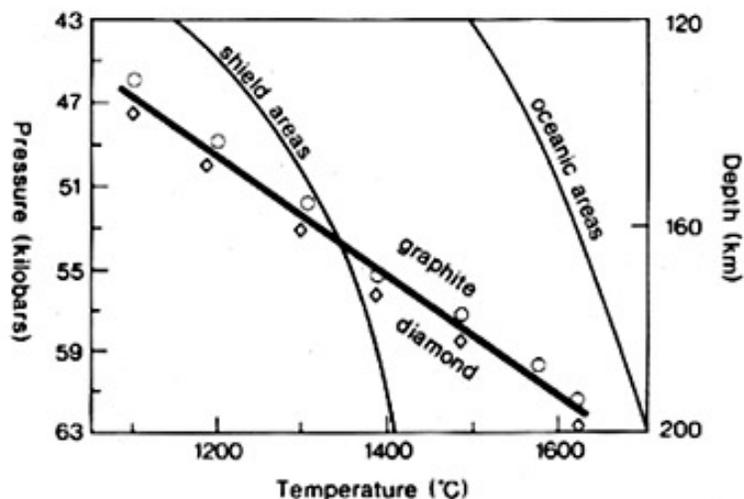

Figure 1. From http://www.canadianrockhound.ca/2002/01/diamonds_fig_12.jpg

This diagram shows the results of some experiments on pure carbon. Carbon was allowed to react at various temperatures and pressures, and graphite grew under some conditions (open circles) while diamond grew under other conditions (diamond symbols).

Also shown are typical geotherms for continental (shield) and oceanic regions. Carbon may exist as graphite or as diamond. Graphite is stable at low pressure – at shallow depths. Diamond becomes stable at higher pressure - deeper in the Earth. The transition from graphite to diamond takes place at around 170 km depth in shield regions. In oceanic areas, which are hotter, the transition takes place at depth greater than 200 km.

Because pressure increases down into the Earth, many people like to show diagrams as in Figure 1, with an upside-down Y-axis. Often, too, the range of axes values is truncated to show only conditions of interest – in this case the conditions of the experiments. If we are interested in the big picture, and if we want to plot things using a normal plot where Y-axis values increase upwards, we can flip the diagram and expand it and get something like this:
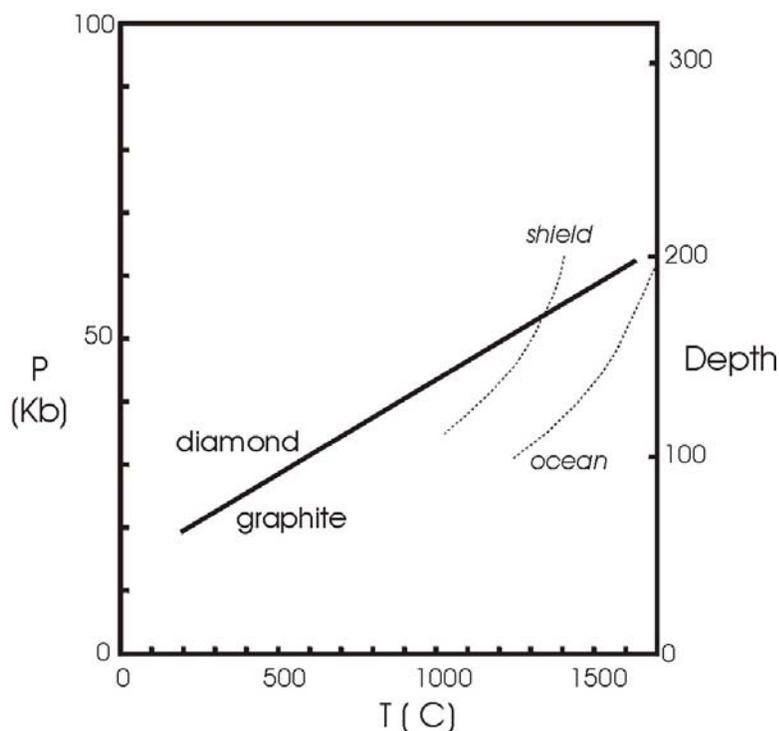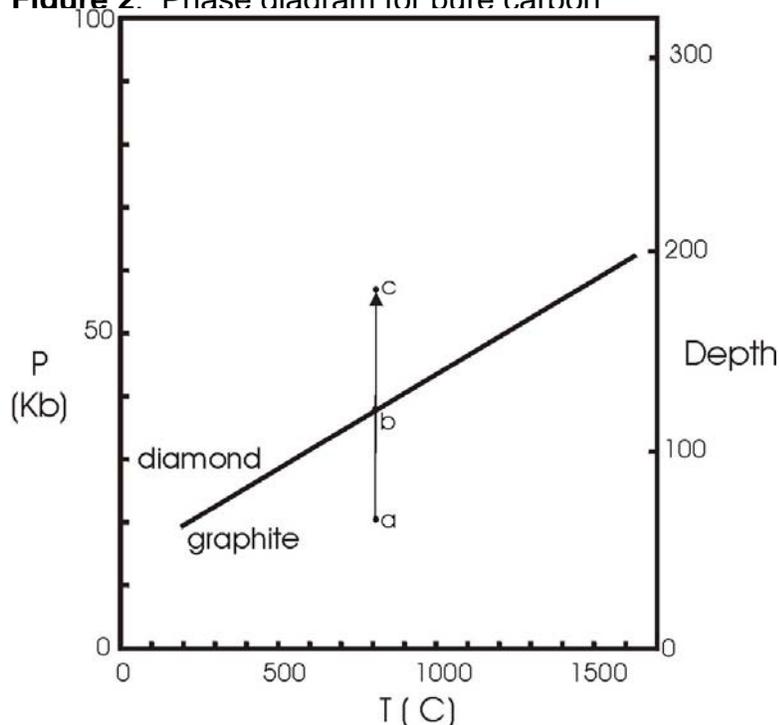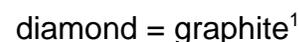
Figure 2. Phase diagram for pure carbon

Figure 3. The graphite-diamond transition

Figure 2 is a typical *phase diagram* showing two phases (in this case they are minerals), each having its own stability field.

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field: A portion of a phase diagram bounded by at least one reaction line.

The line that separates the diamond and graphite fields represents a *reaction*:

diamond = graphite[1]

which we might abbreviate:
Di = Graph

Above this line, graphite cannot exist – only diamond is stable. Below the line, diamond cannot exist and graphite is stable.

Consider a piece of graphite at 800° and 20 Kb pressure (condition *a* in Fig 3). If pressure is increased, the graphite will be stable until point *b* is reached. Then it will react to form diamond, continuing on to higher pressure at point *c* only after the reaction goes to completion.

So, under most conditions, only one phase will be stable. Two phases will be stable only if conditions fall on the reaction line.

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[1]By convention, we write reactions with the high-temperature mineral or assemblage on the right hand side.

Heterogeneous Phase Equilibria Involving One Component

The graphite-diamond system is an example of a *heterogeneous*, meaning it involves more than one phase. But, it is a *one component system*, because all the possible phases in the system have the same composition.

We refer to reactions such as diamond = graphite as being *univariant*. Univariant means that, in order to stay on the reaction line, we can only change one variable independently. If we increase T, we must increase P proportionally or we will no longer be on the line.
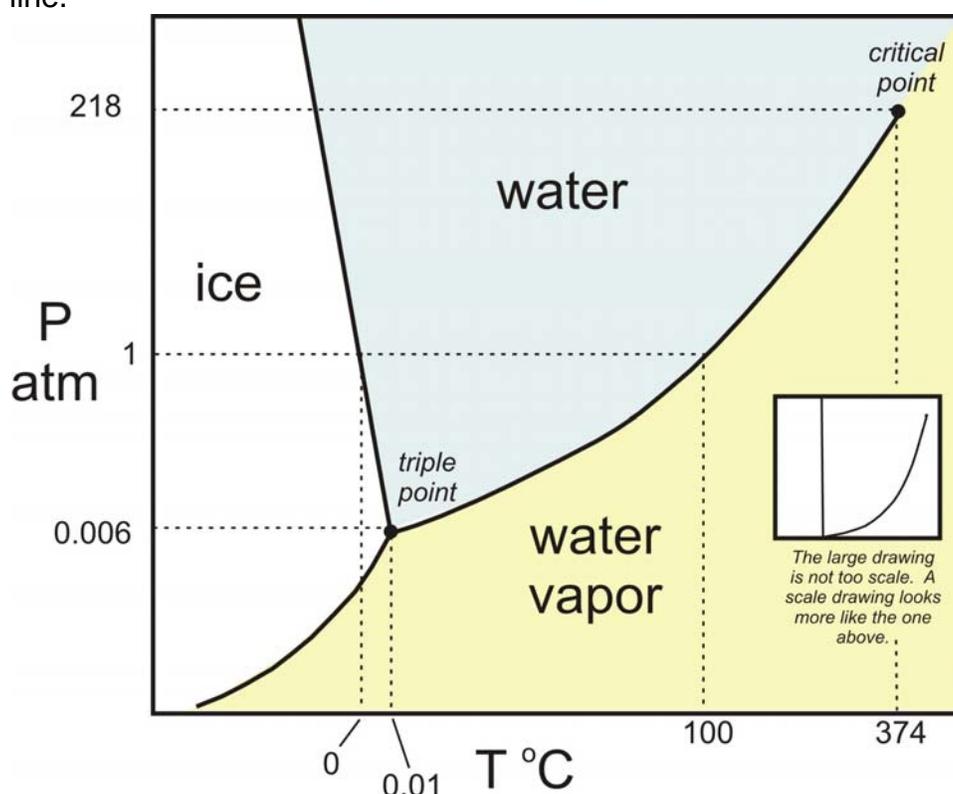

Figure 4. Phase diagram for H_2O

Example #2: Water-Ice-Steam

Another example of one component phase equilibria is shown in Figure 4, a phase diagram for H_2O. In this case, however, there are three possible phases (water, ice and steam), and three reactions. At the *triple point*, all three phases may coexist. Along either of the three univariant reaction curves, two phases may coexist. In any of the three open areas between curves (*divariant fields*), only one phase may exist (either water, ice or steam).

For the H_2O system, we can expect to find one phase under most conditions. If we are lucky and are at a P and T that falls on a reaction curve we may find one of the following two-phase *assemblages*:

     water-ice
     ice-steam
     water-steam

assemblage: Any specific collection of phases that can coexist. The amounts of each phase are not important; all that matters is that they exist together.

If we have some sophisticated equipment and can create conditions exactly on the triple point – at about 6 millibars pressure (well below 1 atmosphere) and 0.01 °C (just slightly over normal water freezing temperature) – we may get a three-phase assemblage:

     water-ice-steam

Figure 5. Heating H_2O at a constant rate causes temperature to increase except when melting or vaporization are taking place. The slopes of the heating curves are different in the ice, water and steam fields because ice, water and steam have different heat capacities.

Consider a mind experiment: Suppose we start with a piece of ice at low temperature, and a pressure above the triple point. If we add heat at a constant rate, the ice temperature will increase until the ice begins to melt. When we reach the melting/freezing curve, additional heat will cause the ice to melt without further increase in temperature (Figure 5). After all ice is melted, temperature will increase again as we add heat. When we reach the vaporization/condensation curve, heating will stop until all the water has vaporized. Then it will continue to increase until we stop our experiment.

Ice has a lower heat capacity than water, which in turn has a lower heat capacity than steam. So, as we add heat, ice will not warm as quickly as water, and water will not warm as quickly as steam. Consequently, the slopes of the heating curves are different in all three fields in Figure 5.

Heterogeneous Equilibria

Example #3: Diaspore-Corundum-Water

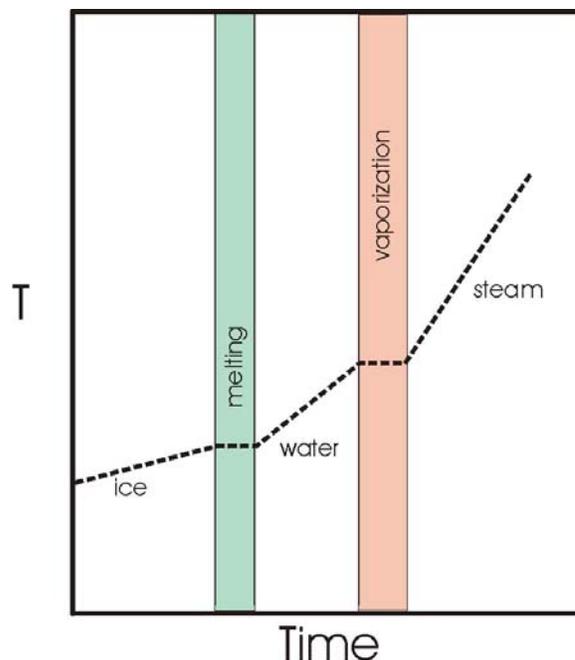Most mineral equilibria are heterogeneous, and most involve more than a single

component. Consider, for example, the three phases:

     diaspore AlO(OH)
     corundum Al_2O_3
     water H_2O

(We refer to H_2O as *water* in this example but acknowledge that we are above the critical point, so a better phrase might be *water vapor*.)

A phase diagram involving these three phases shows one reaction (Figure 6).

We can balance and write this reaction as:

     2 Dsp = Co + H_2O
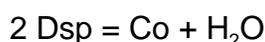
There are several things that set this reaction apart from ones discussed earlier.

First, it is heterogeneous. That is, the compositions of the phases involved are all different.

Figure 6. Phase diagram showing the reaction 2 diaspore = corundum + H_2O.

Second, the reaction line curves and become tangential to the temperature axis at low temperature. The curvature, as we shall see later, is because the thermodynamic properties of H_2O vary greatly with pressure and temperature, and because phases containing H_2O, such as diaspore, cannot be stable in a complete vacuum.

Third, it appears superficially that the number of phases is not as predictable or as regular as in the previous examples. We apparently see that to the left of the reaction (point *a*) only one phase (diaspore) is stable. To the right of the reaction (point *c*), two phases (corundum + H_2O) are stable together. On the reaction, all three phases can be stable. I have used the words *superficially* and *apparently* because, as you may surmise, things are not quite as they seem.

Note that in Example #1 (graphite - diamond), we needed only one chemical component to describe the compositions of the phases (C= carbon). So, too in Example #2 (water-steam-ice). Everything is made of H_2O. In the third example, however, we need two components. Generally, as we shall see, we choose oxide components when practical. So, Al_2O_3 and H_2O are the standard choices. Diaspore, corundum and water are all made of Al_2O_3 or H_2O, or a combination.
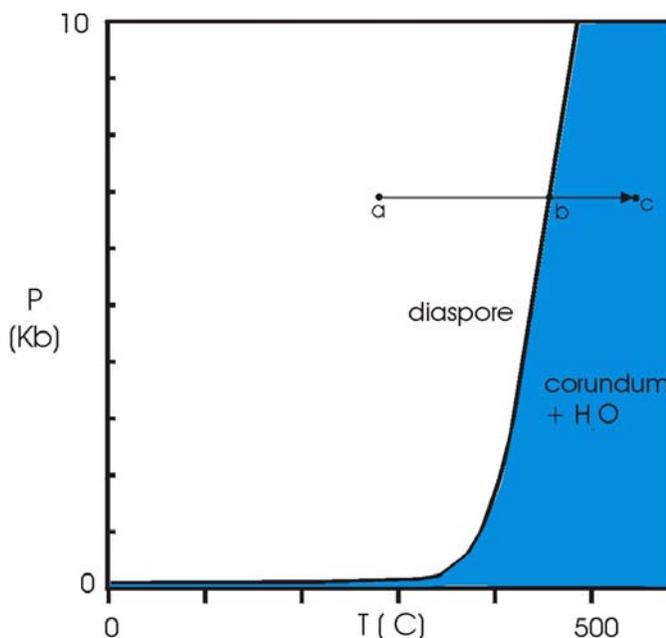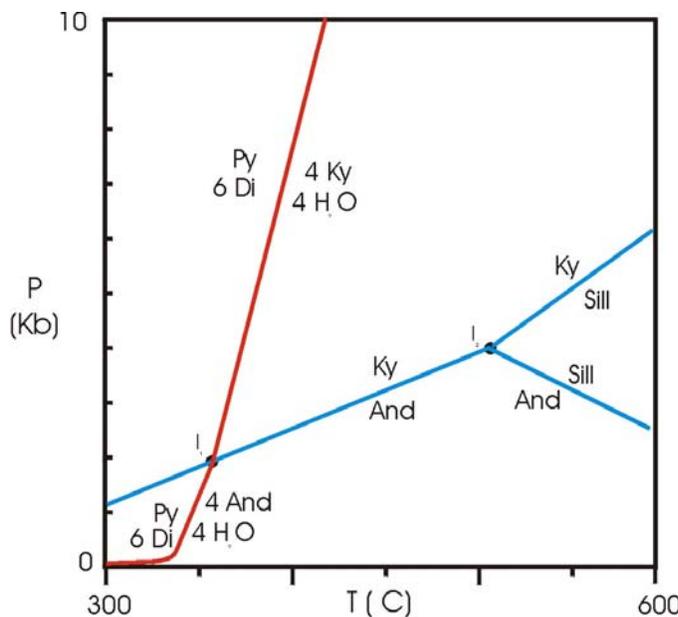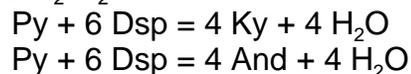
Adding Another Component

Figure 7. Some reactions in the system Al_2O_3-SiO_2-H_2O

Example #4: Pyrophyllite-Kyanite-Sillimanite-Andalusite-Quartz-Water

Figure 7 shows some reactions involving phases whose compositions fall into the three component system Al_2O_3-SiO_2-H_2O. These reactions are:

$$Py + 6\ Dsp = 4\ Ky + 4\ H_2O$$
$$Py + 6\ Dsp = 4\ And + 4\ H_2O$$

On these reaction curves, four phases can coexist. In space to either side of the curves, the labels only show two phases but, as we will see, this is misleading.

Also shown in Figure 7 are three reactions that belong to a 1 component system, a system that is really part of the larger Al_2O_3-SiO_2-H_2O system. The one component is Al_2SiO_5 and the system is homogeneous (all phases have the same composition)[2]. The reactions are:

kyanite = andalusite
kyanite = sillimanite
andalusite = sillimanite
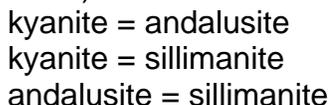
Along these reaction curves, it appears that only two phases can coexist. In the space to either side, it appears that only one phase can exist. However, this is not really the case, as we shall see.

There are two *invariant points* shown in Figure 7. At point I_1, five phases can coexist (Py, Dsp, Ky, And, H_2O). At point I_2, five phases can coexist also, but it is not obvious from this diagram.

invariant point. A point on a phase diagram at which two reaction curves intersect

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[2]We could also describe the compositions of these minerals using oxide components: Al_2O_3 and SiO_2. But, and this is important, when counting components, we must always choose the smallest number of components possible. In this case one, Al_2SiO_5, does the trick.

Example #5: A Four Component Reaction

Figure 8 is a schematic diagram showing two reactions that occur in aluminous schists. The first involves three components, the second involves four:

$$Py = Ky + 3Q + H_2O \qquad (1)$$
$$Ms + Q = Ksp + Ky + H_2O \quad (2)$$
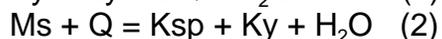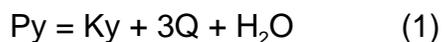
Note that the first reaction involves one fewer phase than the second.

The two reactions divide PT space into three regions, labeled A, B, and C.

Let's start by considering the stability of single phases by themselves. This diagram shows that pyrophyllite is only stable in region A or on reaction (1). At higher temperatures it would break down to Ky-Q-H_2O. The diagram does not, however, limit the stability of any of the other phases if they are by themselves.

Figure 8. Reactions in aluminous schists. Reactions (1) and (2) divide PT space into three regions.

If we consider phases in pairs, things are more restrictive. Any pair of minerals that includes pyrophyllite is stable, as in the last paragraph, on or to the left of reaction (1). If muscovite and quartz, coexist, conditions must be to the left of reaction (2). All other pairs of minerals are stable everywhere!

As you should have figured out by now, the more phases in a mineral assemblage, the smaller its stability field. In this example, we are considering six phases: pyrophyllite, kyanite, quartz, water, muscovite, and K-feldspar.

What happens when we have lots of minerals together? Where on the diagram are all six stable together? Nowhere! Pyrophyllite is only stable in region A, but Ksp-Ky-H_2O is only stable in region C. So, the six cannot coexist.

What about five-phase assemblages. Consider, for example Py-Ky-Q-H_2O-Ms. The reaction involving the first four is labeled (1). The four can only be found together along this line. Ms is stable everywhere. So, the answer is that Py-Ky-Q-H_2O-Ms is stable along reaction (1).

However, not all five phase assemblages are stable. Consider, for example, Py-Q-Ksp-Ky-H_2O. It has no stability field. In fact, any assemblage containing Py-Ksp-Ky-H_2O
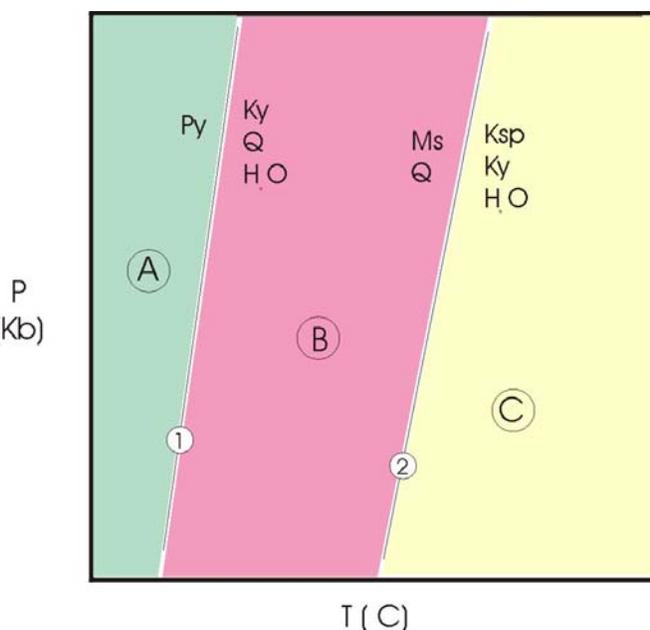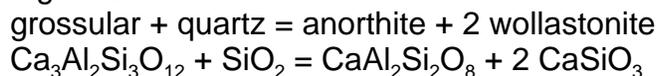
has no stability field. Do you see why?

Example #6: Grossular-Quartz-Anorthite-Wollastonite

Figure 9 shows the reaction:
grossular + quartz = anorthite + 2 wollastonite
$Ca_3Al_2Si_3O_{12} + SiO_2 = CaAl_2Si_2O_8 + 2 CaSiO_3$

This reaction involves four minerals that fall
into the three-component system: CaO-Al_2O_3-
SiO_2.

Let's start with 1 mole of anorthite and 2
moles of wollastonite at conditions shown by
point *a*. An increase in pressure gets us to
point *b*, at which point all the anorthite and
wollastonite will be replaced by grossular and
quartz. While at point *b*, all four phases may
coexist. If we continue to increase pressure
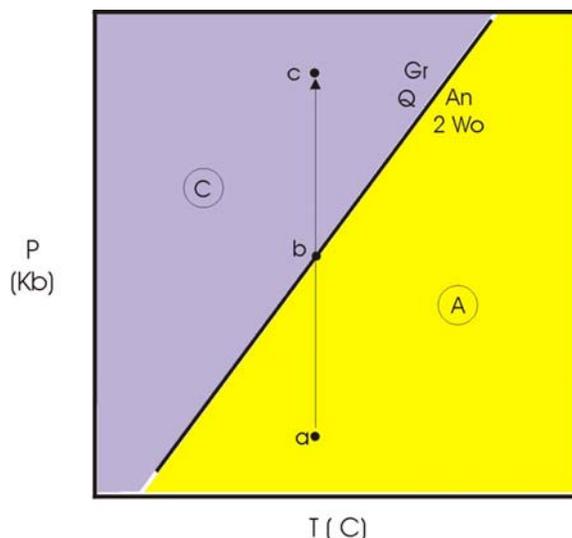toward *c*, only the two-phase assemblage
grossular-quartz may exist.

Figure 9. Anorthite and wollastonite
react to produce grossular and quartz
when pressure is increased.

The above seems straightforward, but consider what happens if we do the same mind
experiment, but start with 2 moles of anorthite and 2 moles of wollastonite. In this case,
anorthite and wollastonite will react at point *b*, as before. But, the wollastonite will be
exhausted before all the anorthite is used up. Consequently, as we move from point *b*
to point *c*, we will have left over anorthite. A three-phase assemblage will be stable:
grossular-quartz-anorthite. Similarly, if we start with excess wollastonite, we will have
wollastonite left over, and grossular-quartz-wollastonite will be stable.

Let's consider all possible mineral assemblages. Where are they stable? The table
below shows that, in general, the more minerals in an assemblage, the more restricted
its stability field.

assemblage	# of phases	In which fields is the assemblage stable?
Gr	1	C and A
Q	1	C and A
An	1	C and A
Wo	1	C and A
Gr-An	2	C and A
Gr-Wo	2	C and A
Q-An	2	C and A
Q-Wo	2	C and A
Gr-Q	2	C

An-Wo	2	A
Q-An-Wo	3	A
Gr-An-Wo	3	A
Gr-Q-Wo	3	C
Gr-Q-An	3	C
Gr-Q-An-Wo	4	on reaction line only

Chemical Systems

We often talk about chemical systems, designated by their components. If, for example, we were talking about the system Mg-O, we would be considering any composition from pure magnesium to

> *chemical system*: End-member chemical components and all compositions that fall between them.

pure oxygen. (This system contains one mineral, *periclase*, MgO.) If we talk about the system $NaAlSi_3O_8$-$KAlSi_3O_8$, we are talking about all compositions that correspond to *alkali feldspar*. (This system, too, contains only one mineral, but the composition of that mineral is not fixed.)

As the above examples make clear, the more components in a system, the more phases that can coexist. We use the letter *C* to designate the number of components, and the letter *P* to designate the number of phases that can coexist.

Here is what we have seen so far:

example #	Chemical system	$C =$ # of Components	$P =$ Maximum number of phases that can coexist <u>in our examples</u>
1	C	1	2
2	H_2O	1	3
3	Al_2O_3-H_2O	2	3
4	Al_2O_3-SiO_2-H_2O	3	5
5	K_2O-Al_2O_3-SiO_2-H_2O	4	5
6	CaO-Al_2O_3-SiO_2	3	4

Degrees of Freedom (*F*)

There is one other thing that affects the number of phases we can have: the *degrees of freedom*. In Example #1, we had two minerals with stability fields separated by a

reaction. In Example #2, however, we not only had reactions but we had an invariant point. In Example #3, we had three minerals and stability fields separated by a reaction. Example four contained two invariant points and six minerals. Example 5 involved two reactions and no invariant points. Example 6, only one reaction.

The key idea behind the degrees of freedom is to ask: what can be changed without changing the mineral or assemblage? In the case of an invariant point, the answer is <u>nothing</u>. If P or T change, the conditions no longer fall on the invariant point. There are no degrees of freedom ($F = 0$). In the case of a reaction, we can change P and T, but we must change them together or we will no longer be on the reaction line. So, there is one degree of freedom ($F = 1$). If we are out in some general regions of PT space, we can change (within some limits) both P and T in arbitrary ways without crossing a reaction and changing the assemblage. So, the degrees of freedom is 2 ($F = 2$). To summarize:

<u>where on the diagram?</u>	<u>degrees of freedom</u>
at an invariant point	$F = 0$
along a reaction line	$F = 1$
in general PT space	$F = 2$

The Phase Rule

Goldschmidt and other have derived what is called the *Phase Rule*. The Phase Rule relates *C*, *P* and *F* as follows: the maximum number of phases that can coexist (*P*) is equal to the number of components (*C*) plus 2, less the degrees of freedom (*F*). More often it is written:

$$C + 2 = P + F$$

Summarizing, for our examples:

example #	$C =$	# of phases at invariant point ($F=0$)	# of phase on a reaction line ($F=1$)	# of phases in general PT space ($F=2$)
1	1		2	1
2	1	3	2	1
3	2		3	2
4	3	5	4	3
5	4		5	4
6	3		4	3

In all cases, our examples follow the phase rule.

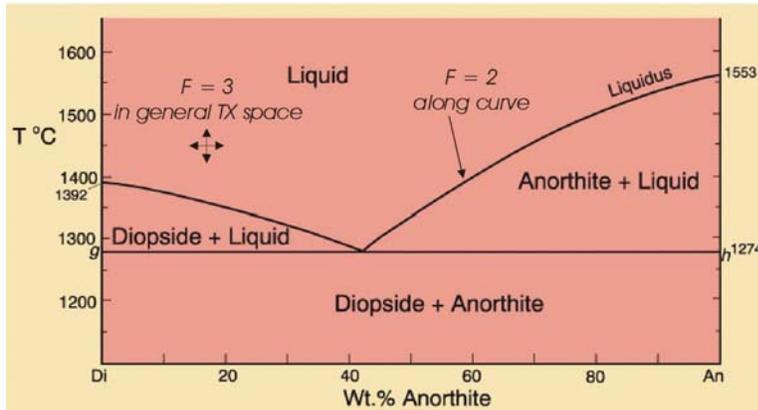## What Variables Can We Use On the Axes?

Figure 10. Melting relationships for diopside-anorthite at 1 atmosphere pressure.

All the above examples are examples of PT diagrams, but we could have plotted other kinds of phase diagrams. For example, Figure 10 shows melting relationships for mixtures of diopside + anorthite, a two-component system ($C = 2$). This diagram is for 1 atm. pressure; the diagram changes if pressure changes. So, this is really a projection from 3D space to two dimensions. Or, you can think of this diagram as a slice through a three dimensional diagram.

There are two possible variables in this diagram: temperature and melt composition. In general, we use the variable X to designate composition. So, this is an example of a *TX diagram*. Note that pressure may also vary, so there are three potential variables: T, X and P. In a general portion of TX space, we can vary all three ($F = 3$) and we have one phase, the melt, and $P = 1$. Along a reaction curve, we have one less degree of freedom ($F = 2$) and one more phase ($P = 2$). In all cases, $P + F = C + 2 = 4$.

Minerals, Abbreviations, Formulae

mineral	abbreviation	formula
diamond	Di	C
graphite	Graph	C
diaspore	Dsp	AlO(OH)
corundum	Co	Al_2O_3
water	H2O(s)	H_2O
pyrophyllite	Py	$Al_2Si_4O_{10}(OH)_2$
kyanite	Ky	Al_2SiO_5
sillimanite	Si	Al_2SiO_5
andalusite	And	Al_2SiO_5
muscovite	Ms	$KAl_2(AlSi_3O_{10})(OH)_2$
K-felspar	Ksp	$KAlSi_3O_8$
grossular	Gr	$Ca_3Al_2Si_3O_{12}$

quartz	Q	SiO_2
anorthite	An	$CaAl_2Si_2O_8$
wollastonite	Wo	$CaSiO_3$
periclase	Pe	MgO
kaolnite	Ka	$Al_2Si_2O_5(OH)_4$
zoisite	Zo	$Ca_2Al_3Si_3O_{12}(OH)$
gehlenite	Ge	$Ca_2Al_2SiO_7$

Questions

1. Figure 3 shows that diamond is not stable under normal Earth surface conditions. Yet, there are many examples of diamond at the Earth's surface. Similarly, Figure 7 shows that sillimanite is not stable under normal Earth surface conditions, yet I have a lot of it in my mineral collection. Explain these apparent contradictions.

2. Consider Figure 6. Possible phase assemblages are

assemblage	# of minerals in assemblage
diaspore	1
corundum	1
H_2O	1
diaspore-corundum	2
diaspore-H_2O	2
corundum-H_2O	2
diaspore-corundum-H_2O	3

Make a sketch of the phase diagram and show where each of these assemblages is stable.

3. Figure 7 involves six minerals. In all, there are 63 possible assemblages. List all 63. Which of them are stable <u>nowhere</u> on this diagram?[3]

4. Consider Figure 8. Suppose we start with a mineral assemblage at conditions at some point in field *a*. Then we heat it, it crosses into field *b*, and eventually into field *c*. The question is, how will the assemblage change? The answer depends on what we started with.

For each of the five assemblages listed below, describe what happens as it is heated. Will it change when reactions 1 or 2 are crossed? What minerals will be present in each field in each case? The simplest way to show your answers is to fill out the table rather than to use words. Note that I have specified the number of moles of each mineral present. That is important information!

Assemblage #	Minerals (and amounts) in Field A	Minerals (and amounts) in Field B	Minerals (and amounts) in Field C
1	3 moles of pyrophyllite		

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[3]I was just kidding about listing all 63. But I do want to see the list of those that are unstable everywhere on this diagram.

2	2 moles of pyrophyllite 3 moles of quartz		
3	1 mole of pyrophyllite 1 mole of muscovite		
4	1 mole of pyrophyllite 3 moles of muscovite		
5	1 mole of pyrophyllite 5 moles of muscovite		

5. Consider these two reactions in the system Al_2O_3-SiO_2-H_2O:
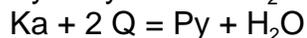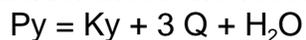
$Py = Ky + 3 Q + H_2O$
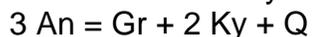$Ka + 2 Q = Py + H_2O$

This is a 3 component system ($C = 3$) and according to the phase rule each reaction will involve 4 phases ($F = 1$, $P = 4$).

We are considering five phases total (Py, Q, H_2O, Ka, Ky). If each reaction involves 4 phases, how many independent univariant reactions do you think there are? List and balance them.

6. Figure 9 shows one reaction involving minerals in the system CaO-Al_2O_3-SiO_2:

$Gr + Q = An + 2 Wo$

Another reaction in this system is

$3 An = Gr + 2 Ky + Q$

This is a 3 component system ($C = 3$) and according to the phase rule each reaction will involve 4 phases ($F = 1$, $P = 4$).

We are considering five phases total (Gr, Q, An, Wo, Ky). If each reaction involves 4 phases, how many univariant reactions do you think there are? List them.

Oops! If you do this correctly, something goofy happens. You don't get as many reactions as you expected. Explain what happens and explain why.

7. Figure shows a phase diagram involving minerals in the CASH $(CaO-Al_2O_3-SiO_2-H_2O)$ system.

There are six reactions (numbered 1 through 6) which divide PT space into seven fields (A through G).

7a Write all reactions with the correct mineral formulas and balance them.

7b. For each of the following 15 assemblages, tell in what zones or on what reactions it is stable:

Co
Zo
Ge
Zo-An
An-Ge
Zo-An-Ge
Gr-An-H_2O
An-Wo-Q
Gr-Co-An-Ge
Gr-An-Co-H_2O
An-Ge-Wo-Zo
Zo-Ky-Co-Gr-H_2O
Gr-An-Zo-Q-H_2O
An-Co-Gr-Ge-H_2O
An-Co-Gr-Q-H_2O