Phase Diagrams and Chemographic Diagrams

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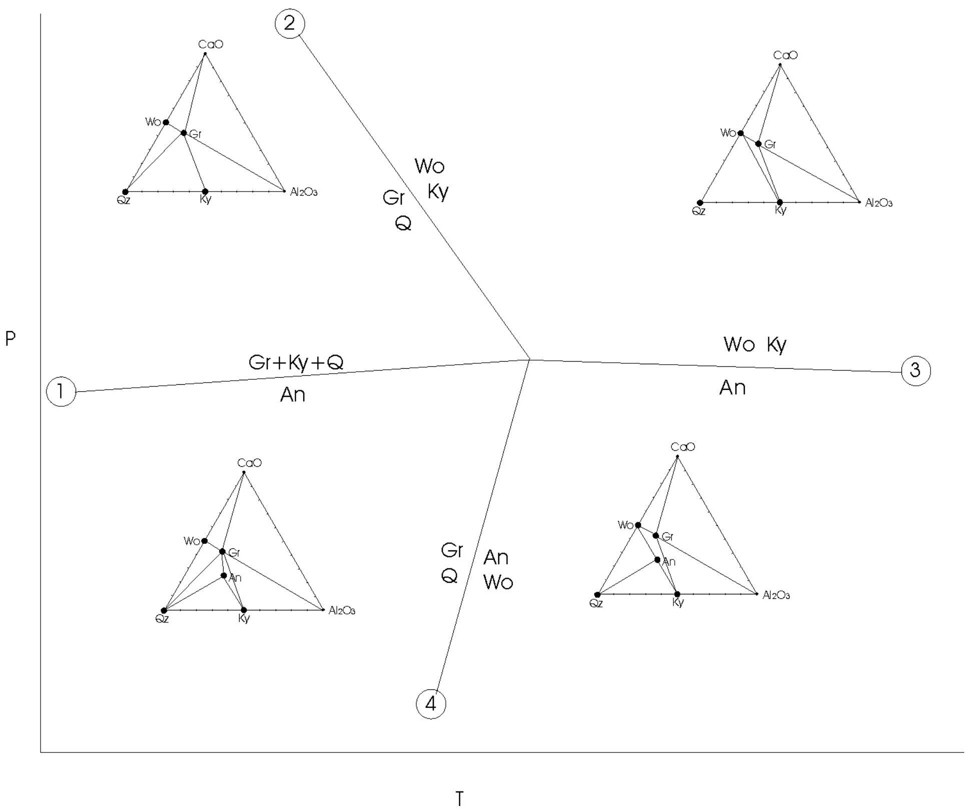
Recall the phase rule: C + 2 = P + F.

At a point on a phase diagram where two reactions intersect, P and T are specified and F =1. We call such points **invariant** points. F=0.

Reactions are **univariant** because along a reaction line F=1.   The space between reactions is divariant (F=2) because both P and T can be varied **independently**.

Referring back to the phase rule again, we see that at an invariant point we can have a bunch of phases coexisting stably. Along a reaction line there will be one less stable phase. And, in a divariant field there will be one less again.

Below is a schematic diagram showing four reactions in P-T space. At the invariant point (F=0, P=5) five minerals can be stable together: grossular, quartz, wollastonite, kyanite, and anorthite.



Along any reaction (F=1, P=4) four minerals can be stable together.

In space between reactions, only three can be stable together (F=2, P=3).

The three phase assemblages are shown as little triangles within the larger CaO-Qz-Al_2O_3 triangles.

The triangles used to depict stable mineral assemblages above are one example of a type of **chemographic** diagram.

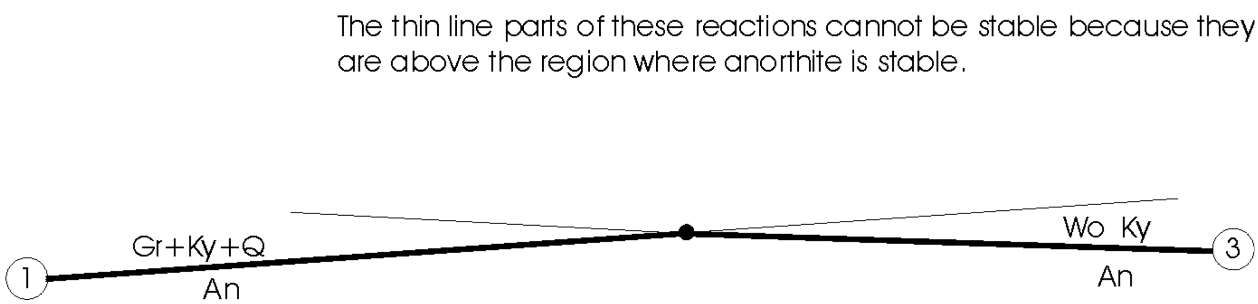
Metastability

There is one other important thing to point out about the diagram on the previous page. Note that none of the reactions pass through the invariant point. This is because they become **metastable**.

Consider the Reaction #1, An = Gr+Ky+Q. This reaction cannot pass Reaction #3 (An = Wo+Ky) because An is not stable past reaction #3. (See diagram below.)

A **metastable extension** of Reaction #1 continues past the invariant point, but it will never take place as long as the system maintains thermodynamic equilibrium.

Don't get misled – sometimes reactions do pass through invariant points. Just not in this case.



A More Complicated Example: Equilibrium in a Metamorphosed Bauxite

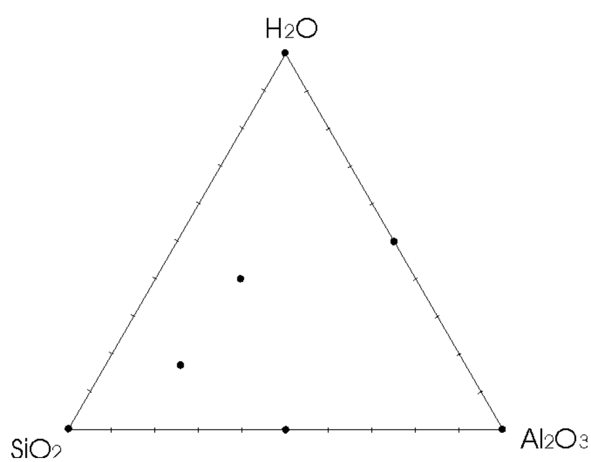
To describe important equilibrium in a metamorphosed bauxite, we need only consider minerals composed of Al, Si, H and O. (Although other components may be present, they are minor and do not affect mineralogy to a significant extent.)

Stable minerals that we must consider are listed in the table below, along with their compositions expressed as % Al_2O_3, % SiO_2, and % H_2O.

mineral	**formula**	**abbreviation**	**% Al_2O_3**	**% SiO_2**	**% H_2O**
quartz	SiO_2	Qz		100%	
corundum	Al_2O_3	Cor	100%		
andalusite	Al_2SiO_5	And	50%	50%	
kyanite	Al_2SiO_5	Ky	50%	50%	
sillimanite	Al_2SiO_5	Sil	50%	50%	
diaspore	AlO(OH)	Ds	50%		50%
kaolinite	$Al_4Si_4O_{10}(OH)_8$	Ka	20%	40%	40%
pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	Py	17%	66%	17%
H_2O (vapor)	H_2O	H_2O			100%

All minerals are in the system Al_2O_3-SiO_2-H_2O, a three component system. So, we can plot them on a triangular diagram.

Question #1. Here is the diagram with the minerals plotted. Put the mineral abbreviations (above table) next to the correct dots in the diagram.



<u>What Reactions Occur?</u>

We have a three component system. So, according to the phase rule:

$C + 2 = P + F$ or

$5 = P + F$

This means that for a normal univariant reaction (a line on a phase diagram), F = 1 and therefore P = 4.

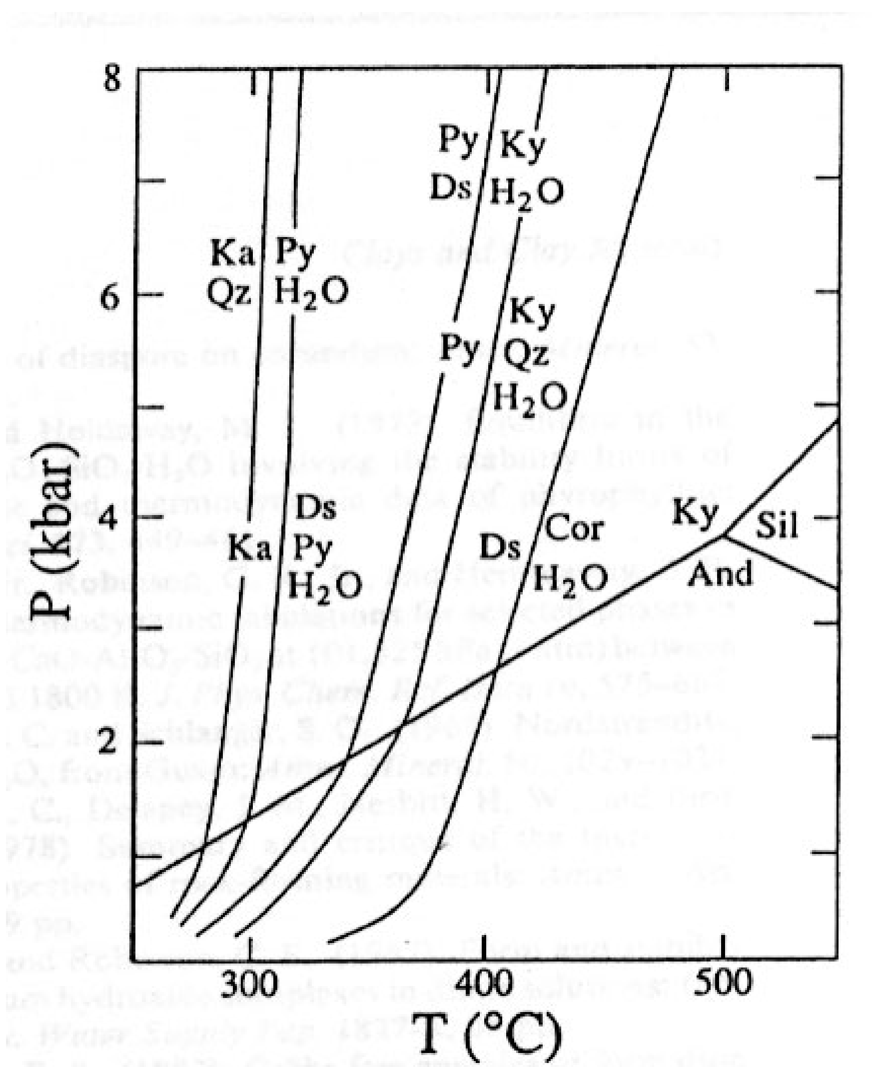
Even if we consider kyanite-andalusite-sillimanite all to be the same, there are over 25 possible reactions in this system.

We could go through a painstaking exercise and list them all, but we won't. Several investigators have found that the only reactions that actually are stable (more on this later) are:

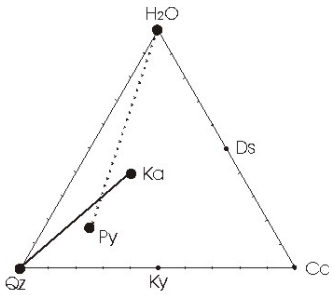
1. Ka + Q = Py + H_2O
2. Ka = Ds + Py + H_2O
3. Py + Ds = Ky + H_2O
4. Py = Ky + Q + H_2O
5. Ds = Cor + H_2O

Note, we can substitute Sil or And for Ky in any of the above reactions: the total is 15 possible reactions.

Here is a phase diagram showing where these reaction plot on a P-T diagram. See Anovitz et al. (1991, Am. Mineralogist 39, 225-233) if you want to know where this diagram comes from.

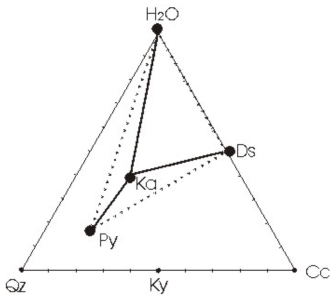


Showing Reactions on Triangular Diagrams

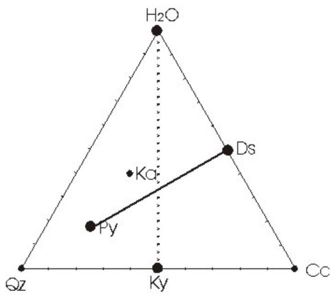


We will only consider the kyanite (not andalusite or sillimanite reactions). We can depict these reactions on triangular diagrams. In the drawings on this page, the high temperature side of the reaction is shown as a dashed line.

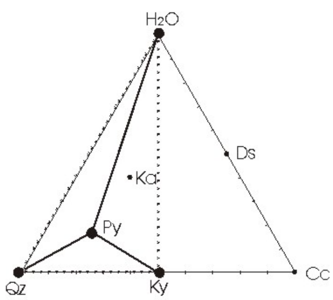
Reaction #1: This reaction limits the stability of kaolinite + quartz together. Many sediments contain these minerals, but only slight metamorphism makes them react to produce pyrophyllite.



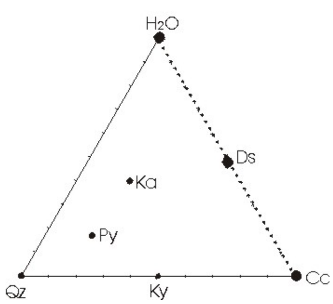
Reaction #2: This reaction provides an upper temperature limit for kaolinite. Below this temperature, assemblages of Py+Ka, Di+Ka, or Ka+H_2O are stable. Above this temperature, kaolinite is absent and the stable mineral assemblage is Py+Di+H_2O.



Reaction #3: This reaction represents the first appearance of kyanite (or andalusite or sillimanite). At temperatures below this reaction, Py+Dii are found instead. (This assumes H_2O is present – in general a good assumption.) So, the aluminosilicates are generally absent in low temperature rocks.



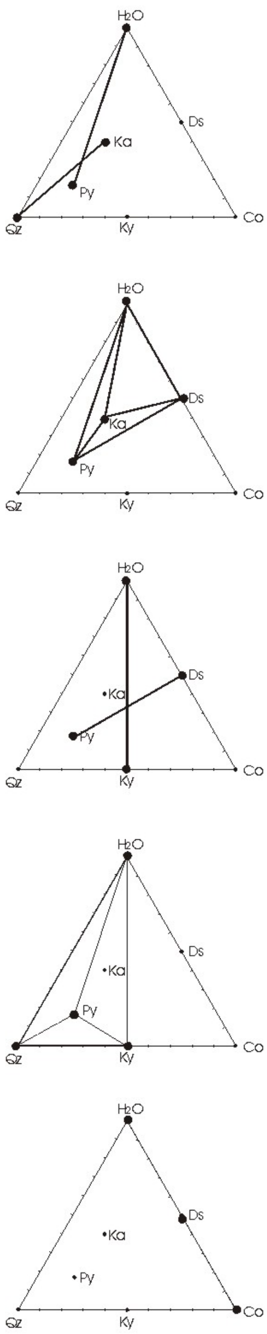
Reaction #4: This reaction represents the upper temperature limit for pyrophyllite. As with most micas and mica-like minerals, pyrophyllite dehydrates when heated above a certain temperature. It is replaced by anhydrous phases. Below that temperature, assemlabes of Py-Qz, Py-Ky, and Py-H_2O are stable. Above that temperature we get Qz-Ky-H_2O instead.

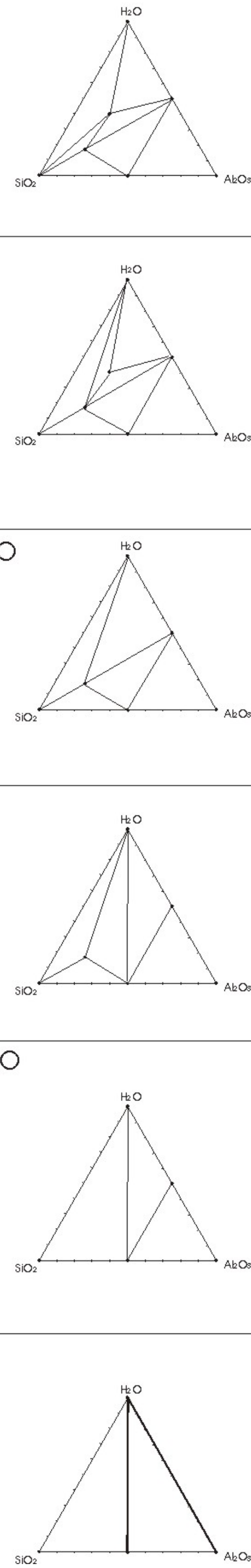


Reaction #5: This is a degenerate reaction. It represents the upper temperature limit of diaspore. Above this temperature, diaspore breaks down to form Co+H_2O.

Stable Mineral Assemblages

Reactions





Ka + Qz
———
Py + H_2O

Ka
———
Py + Ds + H_2O

Py + Ds
———
Ky + H_2O

Py
———
Ky + Qz + H_2O

Ds
———
Co + H_2O

Compatibility Diagrams

Between the 5 reactions, divariant mineral assemblages are stable, shown at left.

The diagrams showing the stable assemblages are called are called **compatibility diagrams.**

Rotate this page 90E counter clockwise and compare with the phase diagram on page 4.

Why Are Some Reactions Metastable?

I said before that many of the reactions that could possibly take place were metastable. Why?
The answer can be seen by considering an example:

Look at the diagram and try to figure out where the reaction

Co + Ka = Ds + Py

could occur.

It can only occur if Co + Ka are stable together. But there is no place where that happens. This is why the reaction Co + Ka = Ds + Py is always metastable.

Question #2. Use only the information on the phase diagram below (same as the one on page 4) to answer the following for each of the assemblages listed below: Where in P-T space, if anywhere, is it stable? (Use the numbered reactions and the labeled regions of PT space to answer the question.)

a. Ds

b. Ka

c. Ka + Q

d. Py + Q

e. Ds + H_2O

f. Ds + Q

g. Ka + Q + And

h. Ka + Ky + And

i. Cor + Ky + And + H_2O

j. Py + Ds + Ky + Qz

k. Py + Qz +Ky + H_2O

l. Ky + And + Ds + Cor + H_2O