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POLYMORPHIC TRANSITIONS

Background Paper

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## MINERAL POLYMORPHISM AND ONE-COMPONENT SYSTEMS

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### I - MINERAL POLYMORPHS IN NATURE

A number of minerals have several polymorphs which occur in rocks. If they can be identified easily and their P-T stabilities are known, they can be used as crude geobarometers and thermometers. Common examples include:

SiO <sub>2</sub>	-quartz, tridymite, cristobalite, coesite, stishovite,
CaCO <sub>3</sub>	-calcite, aragonite.
H <sub>2</sub> O	-ice, (steam and water are common non-mineral polymorphs)
KAlSi <sub>3</sub> O <sub>8</sub>	-microcline, sanidine (and other feldspars).
Al <sub>2</sub> SiO <sub>5</sub>	-andalusite, sillimanite, kyanite.

To better understand how their stabilities depend upon pressure and temperature we need to consider the variation of  $\Delta G^0_f$  (Gibbs energy (free enthalpy) of formation) with P and T.

### II - EQUILIBRIA AND THE CHANGE OF G WITH T AT CONSTANT PRESSURE

The curves in Figure 1 show the variation of  $\Delta G^0_f$  (here simply G), and entropy, S, as a function of increasing T at constant P. The slopes  $(\partial G/\partial T)_P$  for solid, liquid and gas are all negative, as S must be positive.  $(\partial G/\partial T)_P$  is largest for the gas, as it has the largest molar entropy. Because the more stable form has the lowest molar free-enthalpy, the stable segments of the G-T curves are therefore shown with heavy lines. The intersection of the G-T curves for solid-liquid is the melting point ( $T_m$ ), and that of liquid-gas is the boiling point ( $T_b$ ). Reactions such as melting or boiling are called "first-order reactions", because the first derivatives of G, i.e.  $(\partial G/\partial T)_P = -S$  and  $(\partial G/\partial P)_T = +V$ , are discontinuous, with an abrupt change in value at  $T_m(P_m)$ ,  $T_b(P_b)$ . Because many mineral reactions show a great dependence upon pressure, we should consider how  $\Delta G^0_f$  varies with pressure for liquid, solid and gas equilibria.

## POLYMORPHIC TRANSITIONS : Background Paper

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### III - EQUILIBRIA AND THE CHANGE OF G WITH P

We may construct polybaric G-T curves if we know the change in free enthalpy with pressure,  $(\partial G/\partial P)_T = +V$ . The relative positions of G-T curves, for two pressures ( $P_b > P_a$ ) are shown for each of gas, liquid and solid in Figure 2. The displacement of the intersections causes the shift of the melting point and boiling point curves recorded in the P-T diagram beneath. Because the gas is the most compressible, the  $dP/dT$  of the liquid-gas curve is much less than the  $dP/dT$  of the solid-liquid curve.

It is necessary to consider how such two-phase curves in P-T space terminate. One possibility is a triple point and another is a critical point.

### IV - THE CHANGE OF G WITH T AND P AND THE OCCURRENCE OF A CRITICAL POINT

Consider an isobaric G-T section at  $P = P_a$  for gas and liquid. At sufficiently high temperature the slope of the liquid free energy curve will equal that of the gas (Figure 3a), because the second derivative  $(\partial^2 G/\partial T^2)_P = -(\partial S/\partial T)_P = -C_p/T$ , and the heat capacity,  $C_p$ , of a liquid, is greater than that of a gas with which it is in equilibrium.

At a temperature  $T_c$  for  $P = P_a$ , because the G-T curves for liquid and gas will have the same slope,  $(\partial G/\partial T)_P = -S$ , they will have the same molar entropies (Figure 3a).

If the pressure is raised, G for the gas will increase faster than for the liquid, because  $(\partial G/\partial P)_T = +V$ . At some pressure at temperature  $T_c$ , the molar volumes of gas and liquid will be equal and both the slopes and absolute values of the G-T curves will coincide (Figure 3b). At the critical point (Figure 3c), at  $P_c = T_c$ ; G; S; V and H will be identical in gas and liquid. Thus the critical point is a termination of the liquid-gas curve after which (in P-T space) neither phase is distinguishable and therefore appropriately we should deal with a "supercritical fluid".

### V - FREE ENTHALPY-PRESSURE CURVES FOR A ONE-COMPONENT SYSTEM

To emphasize that  $(\partial G/\partial P)$  in nature is just as important as  $(\partial G/\partial T)$ , schematic isothermal G-P diagrams are shown (Figure 4) for  $T_5 > T_4 > T_3 > T_2 > T_1$ . Because the phase with the lowest G in any P range is the stablest one, these are shown by heavy lines. The resulting P-T diagrams is shown at the bottom right. Note at  $T_4$  the three G-P curves intersect at a triple point. In the P-T diagram, full lines show stable equilibria and dashed lines show metastable equilibria. This diagram applies for a system in which  $V^L > V^G > V^S$  and  $S^L > S^G > S^S$ .

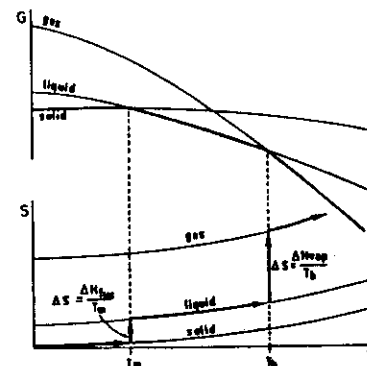


Figure 1 : Variation of G (free enthalpy) and S (entropy) with temperature (T) at constant pressure for these phases (gas, liquid, solid in a one-component system. From Dickerson, (1969, p.224).

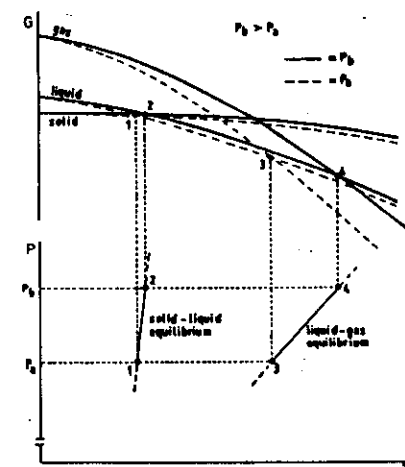


Figure 2 : Relation between G-T (free enthalpy-temperature) curves at pressures  $P_b > P_a$  and the P-T diagram (from Dickerson, 1969, p.226).

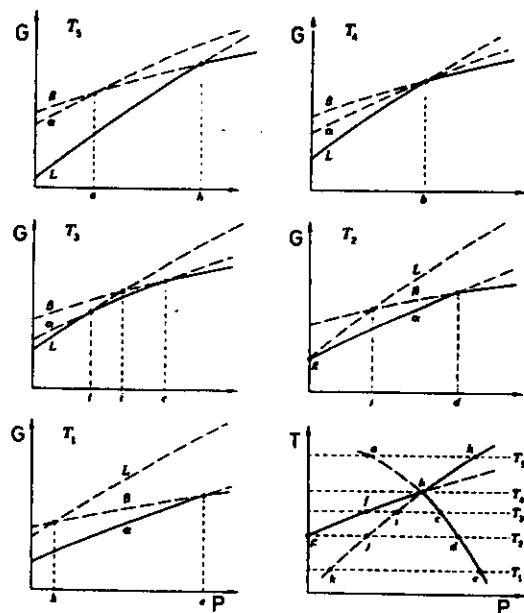


Figure 4 : G-P (free enthalpy-pressure) diagrams at different temperatures ( $T_4 > T_3 > T_2 > T_1$ ) and the formation of a triple point in the P-T diagram (from Gordon, 1968, p.33).

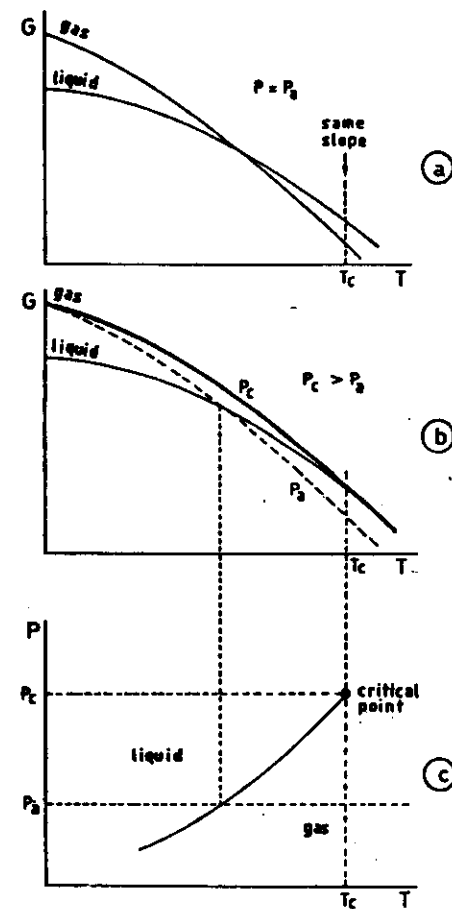


Figure 3 : G-T (free enthalpy-temperature) diagrams at different pressures ( $P_0 > P_a$ ) and the explanation for a liquid-gas critical point (from Dickerson, 1969, p.237).

That such P-T diagrams are not the same in all cases may be seen by comparing phase relations for "normal" substances and the "common" substance-H<sub>2</sub>O.

#### VI - PRESSURE-TEMPERATURE AND VOLUME-ENTROPY DIAGRAMS FOR "NORMAL" SUBSTANCES AND FOR H<sub>2</sub>O

The P-T diagram deduced from the G-P diagrams for the case  $V^L > V^S > V^G$  and  $S^L > S^S > S^G$  is typical (normal) for most substances (Figure 5a,b). For H<sub>2</sub>O, because the ice-I structure collapses on melting and the molar volume decreases, the solid-liquid line has a negative dP/dT (Figure 5c,d). It should be noted that the other ice polymorphs are denser than liquid-H<sub>2</sub>O and their melting curves show positive dP/dT (Figure 6).

V-S diagrams show the same relations as P-T diagrams (Figure 5). In both cases,  $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$ . For H<sub>2</sub>O,  $V_{\text{gas}} > V_{\text{ice-I}} > V_{\text{liquid}}$ , whereas for normal substances  $V_{\text{gas}} > V_{\text{liquid}} > V_{\text{solid}}$ .

#### VII - THE PHASE RULE AND ONE-COMPONENT SYSTEMS IN NATURE

In a one-component system, by definition C=1. Some oxide components occur as phases in nature, H<sub>2</sub>O, SiO<sub>2</sub>, etc. For other minerals, e.g. Al<sub>2</sub>SiO<sub>5</sub>, the mineral formula clearly represents the best choice of component for the polymorphic reactions. Three polymorphic (two-phase) transformations meet at a triple point in P-T space.

The number of coexisting phases:  $\Phi = 3$  at the triple point (invariant).  
may be determined by inspection:  $\Phi = 2$  along the lines (univariant).  
of the phase diagram. :  $\Phi = 1$  in the fields (divariant).

The number of independent :  $v = 0$  at the triple point, P-T fixed (inv.)  
variables:  
(variance = v) may also be :  $v = 1$  along the lines, P or T fixed (univ.)  
evaluated from the equilibrium :  $v = 2$  in the fields, P and T variable (div.)  
phase diagram.

Thus an examination of the equilibrium phase relation for a one-component system, where P and T are the intensive variables, reveals one formulation for the "phase-rule".

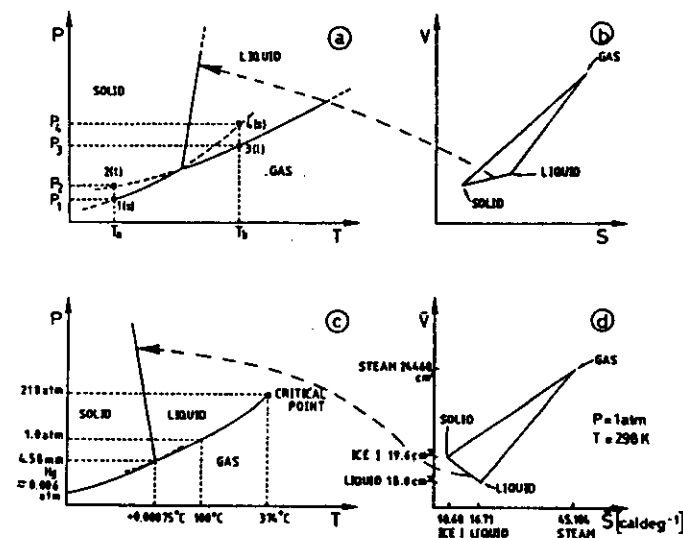


Figure 5 : Relation between P-T (pressure-temperature) diagrams (from Dickerson, 1969, p.233) and VS (volume-entropy) diagrams at the triple points for a "normal" substance (a,b) and for H<sub>2</sub>O (c,d, where in fact volume-entropy data for H<sub>2</sub>O at 1 atmosphere and 298 K are plotted).

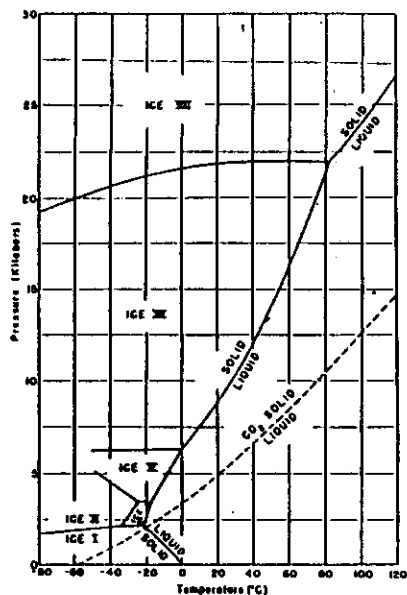


Figure 6a : P-T diagram for  $H_2O$  (from G.C. Kennedy and W.T. Holser, in Clark, 1966, p.373). The  $CO_2$  solidus is included in the original figure but is not discussed here.

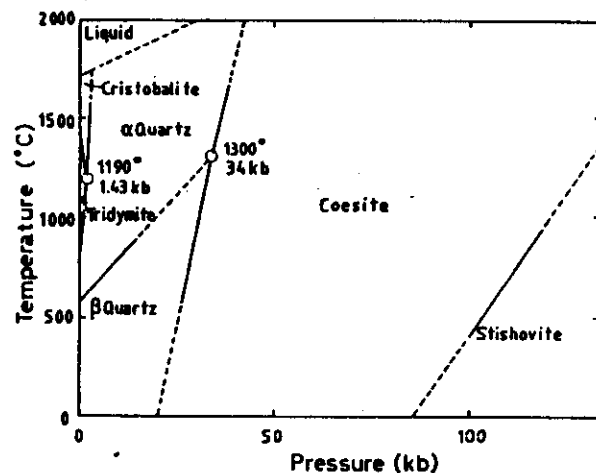


Figure 6b : P-T diagram for  $SiO_2$  (from Ehlers, 1972, p.157).

$$v = c - \Phi + 2$$

variance = number of components - number of phases + 2

#### VIII - EXERCISE TO CALCULATE THE $Al_2SiO_5$ PHASE DIAGRAM

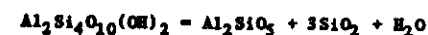
a) From the following thermodynamic data determine the relative stability of kyanite-andalusite-sillimanite (data from Robie et al., U.S.G.S Bull. 1452, (1978) p.339-343)

	Kyanite (p.339)	Andalusite (p.341)	Sillimanite (p.343)
$AG_f^0(298,1)$	-2441'276+/-1920	-2439'892+/-2100	-2438'988+/-1750 $J \text{ mol}^{-1}$
$S^0(298,1)$	83.76+/-0.34	93.22+/-0.42	96.11+/-0.42 $J \text{ mol}^{-1} K^{-1}$
$V^0(298,1)$	4.409+/-0.007	5.153+/-0.004	4.99+/-0.004 $J \text{ bar}^{-1}$

b) Use the approximations  $AG_T \sim +\Delta VAP$  and  $AG_P \sim -\Delta SAT$  and the Clapeyron equation ( $dP/dT = \Delta S/\Delta V$ ) to calculate a P-T diagram. We will call this approximation the "affinity-displacement" method.

- c) Draw schematic G-T diagrams for the 3 cases:
- a fixed pressure higher than the triple point
  - at the pressure of the triple point
  - a fixed pressure lower than the triple point

d) To consider how the preservation of mineral polymorphs may be influenced by other components in nature, we will consider a few reactions in the system  $Al_2O_3-SiO_2-H_2O$ . In the presence of quartz and  $H_2O$ , the  $Al_2SiO_5$  polymorphs can form the hydrates pyrophyllite and kaolinite at temperatures below about 400°C. With the help of the mol. percent triangle  $Al_2O_3 + SiO_2 + H_2O$  and the G-T diagrams in (c) draw the phase-relationships between pyrophyllite, kyanite or andalusite, quartz and  $H_2O$  on the P-T diagram:



and between kaolinite, pyrophyllite, quartz and  $H_2O$ .



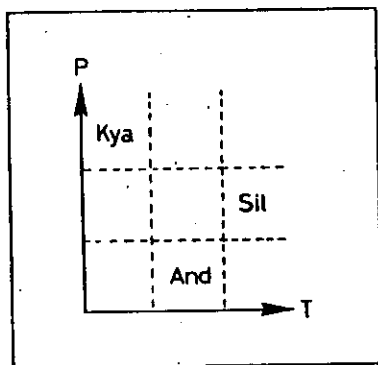


Figure 7 : Relative P-T stability of  $\text{Al}_2\text{SiO}_5$  polymorphs based on entropy and volume data.

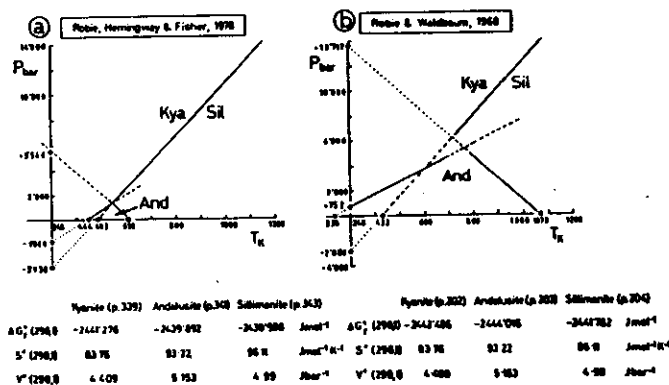


Figure 8 : Calculated P-T stability diagram for  $\text{Al}_2\text{SiO}_5$  polymorphs using data from two different thermodynamic tabulations and the "affinity displacement" method.

## IX - SOLUTION OF THE $\text{Al}_2\text{SiO}_5$ PHASE DIAGRAM PROBLEM

a) Because kyanite has the most negative  $\Delta G_f^\circ (298.1)$  it will be the stable phase at (298,1) for these values. The relative P-T stabilities deduced from V-S values are as shown in Figure 7.

b) It is clear that we have neglected the error limits on G, S and V data and not corrected for changing G and S with T (i.e. assumed  $\Delta C_p = 0$ ). The following values are obtained, neglecting errors:

	$\Delta G_{298}$	$\Delta S$	$\Delta V$	$dP/dT$
And-Kya	+1384	+ 9.46	+0.744	12.72
Sil-And	+ 904	+ 2.89	-0.163	-17.73
Sil-Kya	+2288	+12.35	+0.581	21.26
	$\text{J mol}^{-1}$	$\text{J mol}^{-1} \text{K}^{-1}$	$\text{J bar}^{-1}$	$\text{bar K}^{-1}$

Using  $\Delta G \sim -\Delta SAT$  at 1 bar pressure we obtain,

$$\text{And-Kya } \Delta T \sim -1384 / -9.46 = 146 + 298 = 444 \text{ K} : dP = 146 \times 12.72 = -1857$$

$$\text{Sil-And } \Delta T \sim -904 / -2.89 = 312 + 298 = 610 \text{ K} : dP = 312 \times 17.73 = +5531$$

$$\text{Sil-Kya } \Delta T \sim -2288 / -12.35 = 185 + 298 = 483 \text{ K} : dP = 185 \times 21.26 = -3933.$$

Using  $\Delta G \sim \Delta V \Delta P$  at 298 K we obtain,

$$\text{And-Kya } \Delta P \sim -1384 / +0.744 = -1860 \text{ bar}$$

$$\text{Sil-And } \Delta P \sim -904 / -0.163 = +5546 \text{ bar}$$

$$\text{Sil-Kya } \Delta P \sim -2288 / +0.581 = -3938 \text{ bar.}$$

It is useful to compare the calculated diagrams (Figure 8) for two sets of G data (S and V the same). The differences principally arise from  $\Delta H_f^\circ$  values which are very difficult to obtain by calorimetric methods. They do not dissolve easily in HF for acid-solution calorimetry and the uncertainties are large when they are dissolved in  $\text{Pb}_2\text{B}_2\text{O}_4$  melts in molten-salt calorimetry. The geological interpretation will be clearly different depending upon which values are used. The choice is left to the reader as it is necessary to consider the errors and assumptions in the calculations as well as the method used.

Figure 9 shows a variety of published  $\text{Al}_2\text{SiO}_5$  phase relations (Zen, 1969). More recent studies have shown much greater agreements between Kya-Sil and Kya-And phase relations. Most of the discrepancies result from And-Sil

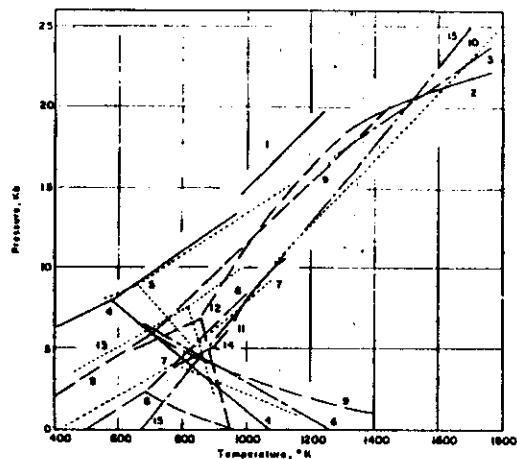


Figure 9 : A selection of experimental data on  $\text{Al}_2\text{SiO}_5$  phase relations (from Zen, 1969, p.298).

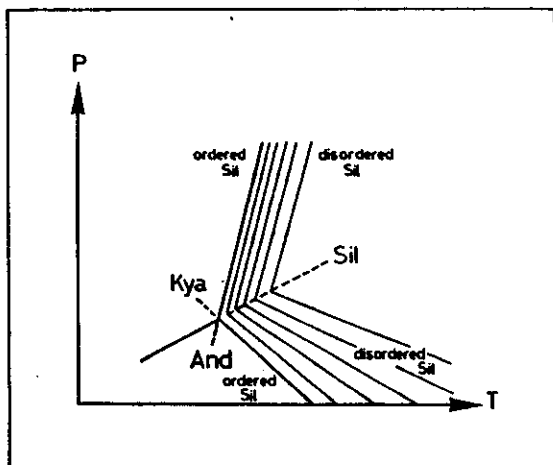


Figure 10 : A schematic illustration of how Al/Si disorder in Sil, could displace And-Sil and Kya-Sil phase boundaries.

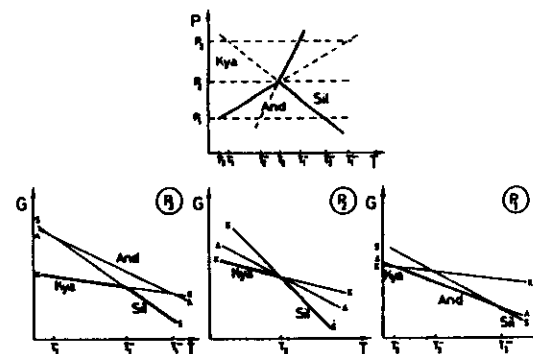


Figure 11 : Schematic G-T diagrams for three pressures ( $P_3 > P_2 > P_1$ ) showing the relative stability of  $\text{Al}_2\text{SiO}_5$  polymorphs. The actual lines should be slightly curved (Figure 1).

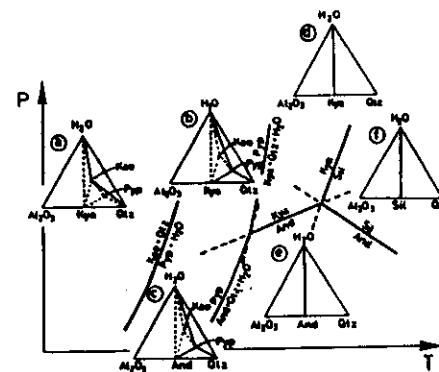


Figure 12 : The relationship of the stability fields of pyrophyllite and kaolinite to the  $\text{Al}_2\text{SiO}_5$  polymorphs, with excess quartz and  $\text{H}_2\text{O}$ . Near the triple point each polymorph is shown stable with  $\text{H}_2\text{O}$  and quartz. At lower T, the hydrate pyrophyllite will form permitting the assemblages  $\text{Al}_2\text{SiO}_5 + \text{Pyp} + \text{Qtz}$ ;  $\text{Al}_2\text{SiO}_5 + \text{Pyp} + \text{H}_2\text{O}$ ;  $\text{Pyp} + \text{Qtz} + \text{H}_2\text{O}$ . At still lower T,  $\text{Kao} + \text{Qtz}$  replaces  $\text{Pyp} + \text{H}_2\text{O}$  permitting these mineral assemblages in the  $\text{H}_2\text{O}$ -deficient region;  $\text{Kao} + \text{Pyp} + \text{Al}_2\text{SiO}_5$ ;  $\text{Pyp} + \text{Al}_2\text{SiO}_5 + \text{Qtz}$ ;  $\text{Kao} + \text{Pyp} + \text{Qtz}$ . It will be noticed that the three-mineral assemblages are stable without  $\text{H}_2\text{O}$  at temperatures below the dehydration boundaries.



boundaries. In our calculations we also neglected Al-Si disorder in sillimanite; this could result in a diagram like Figure 10.

Figure 11 shows the schematic G-P-T relations among  $\text{Al}_2\text{SiO}_5$  polymorphs and Figure 12 shows some lower-T transformations with presence of quartz and water. (Figure 12, a, b, c).

## I - USE OF MINERAL POLYMORPHS IN GEOSBAROMETRY-GEOTHERMOMETRY

It is common practice in the geological literatures to use the relative stability of mineral polymorphs as pressure-temperature indicators. The finding of an "abnormal" polymorph means either that the mineral crystallized outside of its stability field or that it crystallized within its stability field but was preserved by kinetic factors.

The occurrence of aragonite in some blueschists has been considered diagnostic of high-P metamorphism. The fact that some marine organisms build their skeletons from aragonite, and others from calcite, has been explained because of chemical impurities (e.g.  $\text{SrCO}_3$  has the aragonite structure at room P and T) or because of kinetic factors. So clearly there are some chemical constraints for polymorphic reactions.

The finding of stishovite and coesite in meteoritic impact craters supports their high pressure origin. At low pressures, however, tridymite and cristobalite can grow in the quartz stability field.

The preservation of sanidine in volcanic rocks and in metasediments in contact aureoles around intrusions, is related to kinetic factors which inhibit transformation to microcline during cooling.

The regional distribution of the  $\text{Al}_2\text{SiO}_5$  polymorphs, Kya, And, Sil is often considered diagnostic of different metamorphic regimes following tectonic processes. To understand to what extent the  $\text{Al}_2\text{SiO}_5$  polymorphs may be used to assign P-T conditions we will examine some aspects of the  $\text{Al}_2\text{SiO}_5$  polymorphs in terms of stability, chemical impurities and mineral kinetics.

From the form of the  $\text{Al}_2\text{SiO}_5$  phase diagram calculated above, it is clear that the occurrence of one polymorph only limits P-T equilibration conditions in a very broad way relative to a triple point. If we find two- or three  $\text{Al}_2\text{SiO}_5$  polymorphs in a single specimen or across a large regional metamorphic terrain what does this tell us about equilibration conditions?

### 1 - $\text{Al}_2\text{SiO}_5$ phase diagrams

The variations in the available phase diagrams reflects the fact that because the  $\Delta G^\circ_f$  differences are so small it is very hard to locate the equilibrium boundaries experimentally (Figure 9). Indirect calculations are

equally as unreliable as the uncertainties on each  $\Delta G^\circ_f$  is greater than the maximum difference between them over the whole P-T range of interest. It is extremely difficult to measure  $\Delta H^\circ_f$  for  $\text{Al}_2\text{SiO}_5$  by calorimetric methods (see above). Experimental studies based upon growth or disappearance of polymorphs are made difficult by kinetic problems (see below) and the difficulties of distinguishing them by X-ray powder methods.

Chemical impurities such as  $\text{Fe}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Cr}^{3+}$  shift the phase boundaries considerably due to unequal solution in the three polymorphs, and Al/Si disorder in sillimanite means that the And-Sil and Kya-Sil boundaries can easily vary from experiment to experiment.

### 2 - Kinetics of $\text{Al}_2\text{SiO}_5$ transformations

Because it is not uncommon to find a coexistence of  $\text{Al}_2\text{SiO}_5$  polymorphs in metamorphic rocks, it is necessary to determine if univariant or invariant conditions are commonly achieved or whether kinetic factors control the natural coexistence? The kinetic details of the  $\text{Al}_2\text{SiO}_5$  transformations are not well known, but we can illustrate the problems with some simple diagrams. Figure 13 shows a schematic isobaric Ttr (TTT) diagram. Temperature (T) is plotted against  $\log t$  (time) relative to an equilibrium boundary (e.g. Kya-Sil) where the equilibrium temperature is  $T_0$ . The C-shaped curves below  $T_0$  for the Sil-Kya transformations show schematic values of  $\tau$  (amount of transformation, 5 % just after the start of transformation and 95 %, close to the finish). The C-shape results from the different temperature dependence of nucleation and diffusion-controlled growth (Putnis and McConnell, (1980), p. 145). The curves above  $T_0$  for the Kya-Sil transformations show only the lower part of the Ttr curve.

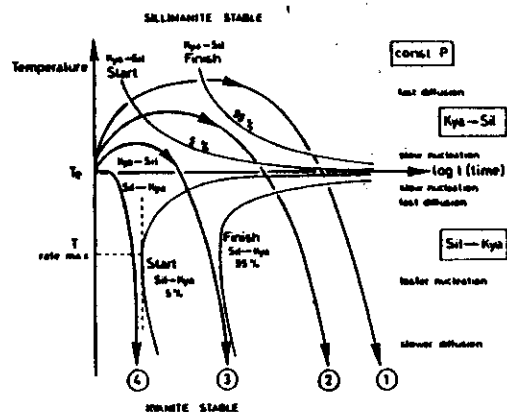
We will consider some CCT (constant cooling rate transformation) paths for the Kya-Sil transformation. Beginning at  $T_0$ , path 1 passes through the Kya-Sil transformation such that all Kya is converted to Sil. On passing  $T_0$ , because of slow nucleation rates for Sil, the kyanite may remain although unstable.

Along path 2 the Kya-Sil transformation begins but does not go to completion. On passing through  $T_0$ , as with path 1 the kyanite may remain although sillimanite is stable.

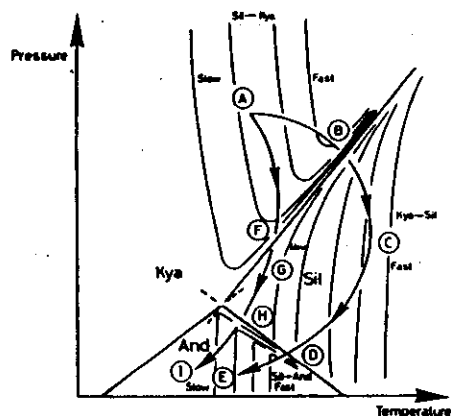
Along path 3, the Kya-Sil transformations will not start. If Sil was present it would certainly convert to Kya on cooling.

Along path 4, no transformation occurs.

We may extend our CCT diagrams to elevated pressures and consider some schematic P-T paths (Figure 14). The lines of constant transformation rate (isokines) are as yet relatively schematic. The P-T paths refer to the uplift



**Figure 13 :** Schematic isobaric T-t diagram for Kfs-Sil transformations. Schematic T-t paths 1,2,3, and 4 are shown relative to the 5 % (start) and 95 % (finish) transformation curves (drawn by analogy with Putnis and McConnell, 1980, Figures 6:13, 6:14). Although most T-t diagrams are determined isothermally, the curves shown here are intended to represent continuous cooling transformation (CCT) curves determined at constant cooling rate.



**Figure 14 :** Schematic P-T diagram showing  $\text{Al}_2\text{SiO}_5$  equilibrium boundaries, uplift part of P-T paths ABCDE, AFGHI, and lines of constant transformation rate (isokines). Transformations can only start once the nucleation barrier has been passed and this cannot easily occur in the vicinity of the equilibrium boundary.

segments. Beginning at point A along path ABCDE, Kfs would begin to transform to Sil between BC, but the transformation could not start until the equilibrium boundary had been "overstepped" enough to permit sillimanite nucleation. Even if this path took several million years both Kfs and Sil could remain in this sample. Even though the transformation to And should begin at D, perhaps only partial conversion of Sil to And would occur. In such a rock all three  $\text{Al}_2\text{SiO}_5$  polymorphs might be found but the P-T path passed nowhere near the triple point.

Along the path AFGHI, Kfs may never transform to Sil between FH or to And along HI, because kinetics are unfavourable. A path passing from A directly through the triple point could preserve Kfs and perhaps And (formed from Kfs), but would not be expected to produce Sil. Thus the finding of all three  $\text{Al}_2\text{SiO}_5$  polymorphs in a rock sample must mean, on the basis of these kinetic considerations, that the P-T path passed to much higher temperatures than the equilibrium triple point.

- 3 - The regional metamorphic distribution of mineral polymorphisms alone is of limited use in geothermometry -barometry!

The above discussion emphasizes the caution that should be exercised when using mineral polymorphs for geothermometry-barometry. Other methods discussed elsewhere in this volume should be used in addition whenever possible.

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