study of a thick sedimentary pile where the geothermal gradient is much lower. Given these types of data we can begin asking the big question: why?

6.2. *Equilibrium between the polymorphs of Al_2SiO_5*

When clay rich sediments are heated to moderate temperatures, three forms of Al_2SiO_5 commonly appear. These are the minerals kyanite, sillimanite and andalusite. Geologists could tell us that kyanite seems characteristic of deep environments and sillimanite of hot environments. Can we find the exact conditions of these reactions? At first sight the problem looks simple because these are supposed to be compounds of identical chemical composition.

Entropy and volume data are available for the three substances. Thus we know that

$$S_{\text{Sillimanite}} > S_{\text{Andalusite}} > S_{\text{Kyanite}}$$
$$V_A > V_S > U_K.$$

The slope of a phase boundary between two polymorphs is given by the relation

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

and hence with these facts alone we can say that the phase diagram must look like Fig. 6. It remains to find where the lines lie in space.

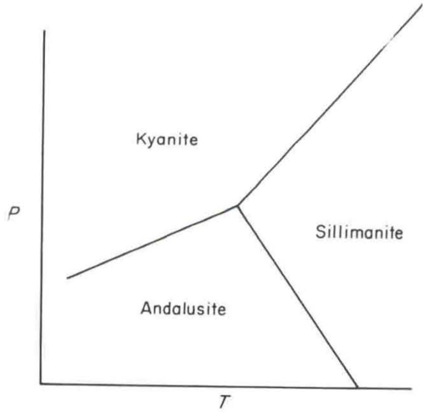

Fig. 6. Form of phase diagram for the three polymorphs of Al_2SiO_5 necessitated by entropy and volume data.

When we examine the values of entropy changes and relate these to chemical affinities through the relation

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$$

where ΔG is the change in free energy, we again see that we are dealing with trivial chemical affinities. In fact, for the andalusite–sillimanite reaction, ΔS is almost zero over a large range of temperatures.

Today, we know a little about this phase diagram, and the cost of obtaining the data probably exceeds a million dollars. Many methods of study have been tried and many were obviously useless even before they were tried. Geology tells us that these are very slow reactions for often a single rock contains two or even three forms together one or two of which must be unstable.

At very high temperatures, mixtures of A and K and S and K will react at measurable rates and hence a good fix on the boundaries is possible. Reactions

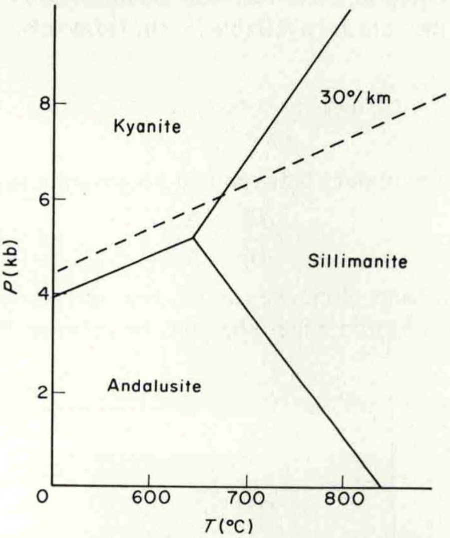

Fig. 7. Experimental phase diagram for Al_2SiO_5 polymorphs. While the boundary between kyanite and sillimanite is rather well determined, that between andalusite and sillimanite is not well known.

between A and S have not yet been shown convincingly. Another profitable approach has been used. If kinetics of growth and nucleation are slow, we can make use of the much faster rates of solution to find equilibrium. If we dissolve two polymorphs in the same solvent under identical P–T conditions, and if an equilibrium solubility can be measured, then we know that if

$$\text{Solubility of A} > \text{Solubility of B}$$

then free energy of A > free energy of B.

We can find points of equilibrium ($G_A = G_B$) by this technique.

Weill[5] used this technique and chose the very excellent solvent, fused cryolite, Na_3AlF_6.

If we use the available data, the phase diagram must be about as in Fig. 7.