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EXPERIMENTAL DETERMINATION OF KYANITE-ANDALUSITE AND ANDALUSITE-SILLIMANITE EQUILIBRIA; THE ALUMINUM SILICATE TRIPLE POINT

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ABSTRACT. The kyanite-andalusite and andalusite-sillimanite transitions have been experimentally bracketed by observation of reversals of the polymorphic transitions in mixtures of the appropriate pair of polymorphs. Experiments were made in hydrostatic-medium pressure apparatus. Only reactions that showed about 20 percent conversion or more were accepted as diagnostic.

The triple point occurs within a polygon of experimental uncertainty around the coordinates 5.5 kb, 622°C. The equations that best express the univariant equilibrium boundaries, in terms of kilobars pressure and degrees Celsius temperature, are:

kyanite-andalusite	$P = 0.0107T - 1.173$
andalusite-sillimanite	$P = -0.0243T + 20.59$.

From our previous work may be added:

kyanite-sillimanite	$P = 0.0243T - 9.63$

INTRODUCTION

In a previous paper (Richardson, Bell, and Gilbert, 1968) we reported determination of the univariant kyanite-sillimanite (K-S) equilibrium between 700° and 1500°C. Determination of one of the other univariant transitions, kyanite-andalusite (K-A) or andalusite-sillimanite (A-S), fixes the pressure and temperature at which the three Al_2SiO_5 polymorphs kyanite, sillimanite, and andalusite can coexist at invariant equilibrium. In this paper experiments on both these transitions are reported.

EXPERIMENTAL PROCEDURE

Kyanite-andalusite experiments.—Reversals of K-A metastable equilibrium within the sillimanite stability field, without growth of sillimanite, have been obtained. Starting material for these experiments consisted of equal (weight) amounts of natural kyanite from Burnsville, North Carolina, and andalusite from Standish, Maine, with about 3 to 5 wt percent quartz. Chemical analyses of the aluminum silicates are given in table 1. Cell parameters of the natural reactants and of the products are given in table 2.

The starting material was ground in an automatic agate mortar for 3 hrs to an average grain size of 10 to 20 μ. Portions were sealed, with weighed amounts of water, into platinum capsules and run in gas-medium pressure apparatus (Yoder, 1950; Richardson, Bell, and Gilbert, 1968). Reported pressures and temperatures are believed to be accurate to $\pm$ 0.1 kb and $\pm$ 5°C, respectively; precision is indicated in the table of run data (table 3). These experiments can be compared with those of

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Newton (1966), who employed a solid-media apparatus in the same pressure range.

Reaction direction was detected by comparison of the peak-height ratio kyanite ($02\bar{1}$)/andalusite (220) in X-ray diffractograms of starting material and products. The method used to prepare the specimen mounts is described by Richardson, Bell, and Gilbert (1968).

TABLE 1

Chemical analyses of natural aluminum silicates used as starting materials

	Kyanite, Burnsville, North Carolina*	Sillimanite, Brandywine Springs, Delaware**	Sillimanite, Brandywine Springs, Delaware***	Andalusite, Standish, Maine****
Al_2O_3	63.20	63.9 ± 1.3	63.36	63.15
SiO_2	36.90	36.0 ± 0.7	35.84	36.84
TiO_2	None	—	trace	<0.01
FeO	None	—	trace	None
Fe_2O_3	0.10	0.03 ± 0.015	0.13	0.11
MgO	None	—	<0.1	<0.01
CaO	0.05	—	<0.1	0.02
MnO	None	—	<0.02	<0.01
Na_2O	None	—	0.20	None
K_2O	None	—	0.02	None

* Original analysis reported in Todd (1950). Richardson, Bell, and Gilbert (1968) reported a re-analysis for Fe and Ca with a M.A.C. electron microprobe as 0.06 (Fe_2O_3) and 0.01 (CaO). This material is from the same lot used by Pankratz and Kelley (1964) for high temperature heat capacity measurements.

** Analysis carried out with a M.A.C. electron microprobe and reported in Richardson, Bell, and Gilbert (1968).

*** Analysis reported in Aramaki and Roy for sillimanite from same locality (1963, table 2).

**** Original analysis reported in Todd (1950). Re-analysis for total Fe as Fe_2O_3 with a M.A.C. electron microprobe yielded the value 0.4 ± 0.1 wt percent. This material also from the same lot used by Pankratz and Kelley (1964).

Andalusite-sillimanite experiments.—Starting materials for andalusite-sillimanite experiments were equal amounts of natural andalusite from Standish, Maine, and sillimanite from Brandywine Springs, Delaware (see tables 1 and 2 for chemistry and cell parameters). Procedures were similar to those employed in the K-A experiments, except that all runs were made in externally heated "cold-seal" pressure vessels, with water as the pressure medium. R41 or stellite vessels, 12 in. long, 1¼ in. diam, were placed horizontally in a split furnace. Pressure was measured on Heise Bourdon tube gauges. Temperature was measured by a chromel-alumel thermocouple placed in a 1/16 in. well drilled parallel to the bore of the vessel to a depth opposite the sample capsules. Power to the furnace was controlled by a platinum resistance element linked to a solid-state controller, designed by C. Hadidiacos. The reported pressures are believed to be accurate to ± 10 bars; the temperatures, to ± 5°C; precision is indicated in the table of run data (table 4).

TABLE 2

Cell parameters of natural reactants and products*

	a,Å	b,Å	c,Å	α,°	β,°	γ,°	V,Å³
1	7.124(0.001)	7.843(0.002)	5.566(0.005)	89.92(0.05)	101.32(0.03)	105.97(0.03)	292.7(0.3)
2	7.120(0.0003)	7.848(0.0004)	5.571(0.001)	90.00(0.01)	101.24(0.006)	105.91(0.005)	293.1(0.1)
3	7.7955(0.001)	7.8968(0.001)	5.5585(0.001)				342.18
4	7.794(0.001)	7.901(0.003)	5.555(0.002)				342.1(0.1)
5	7.795(0.001)	7.901(0.002)	5.551(0.001)				341.9(0.1)
6	7.797(0.001)	7.899(0.002)	5.561(0.002)				342.5(0.1)
7	7.479(0.002)	7.670(0.001)	5.770(0.001)				331.0(0.1)
8	7.483(0.005)	7.668(0.002)	5.771(0.001)				331.2(0.2)
9	7.484(0.005)	7.669(0.003)	5.771(0.001)				331.2(0.2)

* Burnham's least squares refinement program (1962) was used, and resulting uncertainties in the refinement are shown in parentheses. Si was employed as an internal standard.

1. Kyanite, Burnsville, North Carolina. From Richardson, Bell, and Gilbert (1968, table 3).

2. Kyanite, KA9. From Richardson, Bell, and Gilbert (1968, table 3).

3. Andalusite, Standish, Maine. From Skinner, Clark, and Appleman (1961, table 5).

4. Andalusite, Standish, Maine. Thirteen reflections used.

5. Andalusite, KA15. Twelve reflections used.

6. Andalusite, AS6. Seven reflections used.

7. Sillimanite, Brandywine Springs, Delaware. From Richardson, Bell, and Gilbert (1968, table 2). Comparable parameters are given by Aramaki and Roy (1963) in their table 3 for sillimanite from same locality.

8. Sillmanite, AS5. Ten reflections used.

9. Sillimanite, AS9. Ten reflections used.

TABLE 3

Kyanite-andalusite runs

Capsule no.	Wt percentage of water	P, kb	T, °C	t, hr	$\frac{K(02\bar{1})}{A(220)}$	Result	Comments*
KA-5	4.0	8.95 ± 0.05	950 ± 7	6½	.....	.....	cor + qz only
KA-6	tr				0.69	.....	some sill, trace cor
KA-7	tr	7.45 ± 0.05	800 $^{+30}_{-5}$	43½	0.75	.....	T overshot by 30° for 2½ hr
KA-8	4.8				0.72	.....	
KA-9	19.3	8.10 ± 0.05	800 ± 10	63	∞	K	
KA-10	4.5				1.39	K	
KA-11	tr				0.72	.....	
KA-12	tr	7.25 ± 0.1	800 ± 7	38	0.78	.....	
KA-13	5.9				0.69	.....	
KA-14	19.6				0.80	.....	
KA-15	28.1	7.10 ± 0.05	825 ± 7	95½	0	A	
KA-16	4.0				0.13	A	
KA-17	tr				0.58	A	
KA-18	tr	7.6 ± 0.1	825 ± 10	46	0.77	.....	
KA-19	4.5				0.68	A?	Compare KA-20
KA-20	22.1				1.04	.....	
KA-21	23.8	7.85 ± 0.05	825 ± 7	48	1.00	.....	
KA-22	5.3				0.84	.....	
KA-23	tr				0.76	.....	
KA-24	25.3	7.35 ± 0.05	825 ± 5	74½	0.34	A	
KA-25	5.3				0.43	A	
KA-26	tr				0.70	.....	
KA-27	tr	7.8 ± 0.1	825 ± 5	94	0.74	.....	
KA-28	22.2				1.13	K	
KA-29	2.6				0.78	.....	
KA-30	20.0	6.5 ± 0.1	700 ± 7	124	1.01	.....	
KA-31	6.6				0.79	.....	
KA-32	tr				0.84	.....	
KA-33	21.3	6.1 ± 0.1	700 ± 10	215			
KA-34	2.5				0.65	A	
KA-35	tr						
KA-36	25.1	6.75 ± 0.05	700 ± 5	234	1.59	K	
KA-37	tr	9.95 ± 0.05	1100 ± 7	45	.....	.....	sill + qz, trace glass, no cor
KA-40	dry				0.56	.....	some sill, no glass or cor

* Abbreviations: cor = corundum; qz = quartz; sill = sillimanite.

The majority of experiments attempted on this sluggish reaction required interruption for grinding. In fact, every run that finally showed a definite direction of reaction was interrupted at least twice. During each interruption the samples were quenched, taken from their capsules, ground for from 15 to 30 min by hand or about 5 min in a small agate ball-mill, X-rayed, and sealed into new capsules. The grinding was never sufficient to produce noticeable broadening of the X-ray reflections.

Reaction direction was detected by comparison of the peak-height ratio andalusite (220)/sillimanite (120) in X-ray diffractograms of starting material and products.

RESULTS

Starting materials.—Mean values of the peak-height ratios obtained from replicate mounts of the starting materials are given as histograms in figure 1. As with the K-S starting material reported earlier (Richardson, Bell, and Gilbert, 1968), a greater range of values is obtained from different X-ray mounts of the same sample than is obtained from replicate scans of individual mounts. This is assumed to be due to failure to reproduce in each mount the same conditions of grain orientation even though the same method was used to prepare all mounts (sifting onto Vaseline-coated slides). There is no obvious time correlation.

Kyanite-andalusite runs.—Table 3 shows the results of runs in the gas-pressure apparatus with kyanite-andalusite starting material and various amounts of water. Great changes in K/A occurred in some of the capsules that contained 20 to 30 percent water: in two capsules, complete conversion of one polymorph to the other was achieved (KA-9, KA-15). Although capsules containing 4 to 5 percent water showed only moderate changes from the K/A values of the starting material, changes were consistent (except possibly for KA-19) with those observed in the runs containing greater amounts of water. Comparison of these results indicates that the amount of water present has an effect on the amount of conversion of one polymorph to the other.

Andalusite-sillimanite runs.—Even at the highest temperatures employed (850°-950°C) the andalusite-sillimanite reaction proved much more sluggish than either the K-S or K-A transition. In contrast to the experiments involving kyanite-bearing equilibria, in none of our andalusite-sillimanite runs did we observe complete conversion of one polymorph to the other. Since values of A/S for the starting material ranged from 0.53 to 0.70 (see fig. 1), we have accepted as diagnostic only those runs that showed A/S outside the range 0.40 to 0.90: a range selected *a priori* from examination of the starting material. This would correspond to conversion of 20 percent of one polymorph to the other where the starting material A/S = 0.60. The experimental results are listed in table 4.

DISCUSSION

The position of the triple point.—The P-T coordinates of the significant runs made with the K-A and A-S starting materials are plotted in figure 2. These data, together with the limits of uncertainty of K-S equilibria taken from Richardson, Bell, and Gilbert (1968), define an area of uncertainty (shaded) in which the invariant triple point must occur. This area of uncertainty is the *largest* permissible, taking maximum and minimum slopes for the univariant reactions.

Our preferred equation expressing the K-A reaction takes into account the amounts of reaction observed on each side of our brackets of this equilibrium:

$$P(kb) = 0.0107T(°C) - 1.173.$$

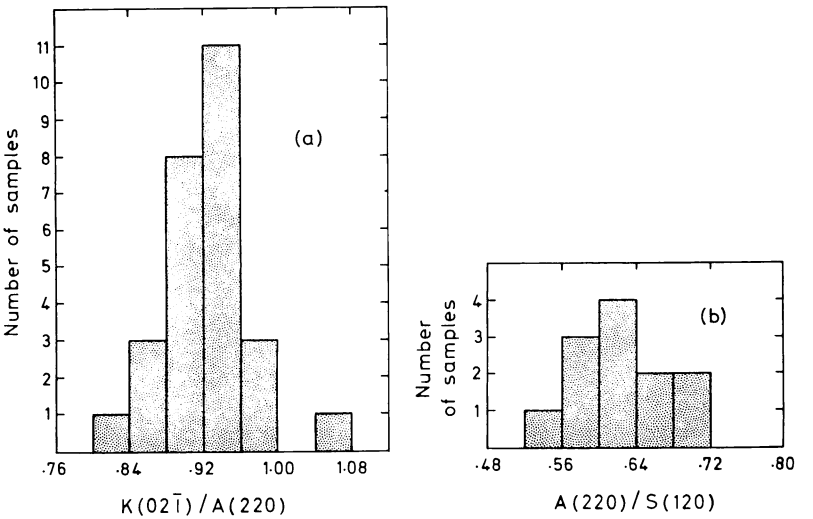


Fig. 1. X-ray diffraction peak-height ratios of the starting materials. (A) Kyanite (02$\bar{1}$)/andalusite (220); (B) andalusite (220)/sillimanite (120).

This equation, combined with the equation of K-S equilibrium (Richardson, Bell, and Gilbert, 1968),

$$P(kb) = 0.0243T(°C) - 9.63,$$

gives the coordinates of the triple point: 5.5 kb and 622°C. The region of uncertainty around the triple point is reduced somewhat if both Newton's (1966) and our data are used to determine the maximum and minimum slopes of the K-A transition.

Of the three univariant transitions, A-S is the least well defined by our experiments; therefore, an equation for this transition was calculated, using the experimentally determined slopes of the K-S and K-A transitions and the molar volume data of Skinner, Clark, and Appleman (1961) at the triple point. We observe that $\Delta\bar{S}_{A\text{-}S} = \Delta\bar{S}_{K\text{-}S} - \Delta\bar{S}_{K\text{-}A}$, where $\Delta\bar{S}_{i\text{-}j}$ denotes the molar entropy difference between two phases i and j. The Clapeyron equation,

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

applies to each of the three univariant equilibria radiating from the triple point. Solving for $\Delta\bar{S}_{K\text{-}S}$ and $\Delta\bar{S}_{K\text{-}A}$ and substituting for $\Delta\bar{S}_{A\text{-}S}$, we have

$$\left(\frac{dP}{dT}\right)_{AS} = \frac{\left(\frac{dP}{dT}\right)_{KS} \times \Delta\bar{V}_{K\text{-}S} - \left(\frac{dP}{dT}\right)_{KA} \times \Delta\bar{V}_{K\text{-}A}}{\Delta\bar{V}_{A\text{-}S}},$$

which yields:

$$\left(\frac{dP}{dT}\right)_{AS} = -0.0243 \text{ kb/°C}$$

at the triple point.

TABLE 4

Andalusite-sillimanite runs*

Run no.	P, kb	T, °C	t, hr	$-\frac{A(220)}{S(120)}$	Result	Comments
AS-1	0.5	900	282½	0.54	.....	
AS-2	0.5	850 ± 10	624	0.87	A?	
	0.50 ± 0.02	849 ± 2	480	0.54	.....	
	0.51 ± 0.02	850 ± 1	602	.....	.....	Capsule ruptured, only cor left
AS-3	0.5 ± 0.02	972 ± 5	116¼	0.62	.....	Run terminated by vessel failure
AS-4	$3.00^{+0.05}_{-0.02}$	706 ± 1	953	0.67	.....	
	3.01 ± 0.02	708 ± 1	982	0.54	.....	
	3.01 ± 0.02	708 ± 1	879	0.77	.....	Total t = 2814 hr
AS-5	$3.01^{+0.03}_{-0.02}$	750^{+0}_{-3}	953	0.53	.....	
	$3.01^{+0.02}_{-0.01}$	751^{+0}_{-1}	982	0.32	S	Total t = 1935 hr
AS-6	$3.01^{+0.03}_{-0.02}$	650^{+1}_{-2}	953	0.70	.....	
	$3.01^{+0.02}_{-0.01}$	650^{+2}_{-1}	982	0.70	.....	
	3.01 ± 0.02	651^{+3}_{-2}	879	1.07	A	Total t = 2814 hr
AS-7	$3.01^{+0.03}_{-0.02}$	597^{+7}_{-4}	953	0.75	.....	
	$3.01^{+0.01}_{-0.00}$	601 ± 3	982	0.74	.....	
	$3.01^{+0.02}_{-0.01}$	598^{+2}_{-3}	879	1.00	A	Total t = 2814 hr
AS-8	2.00 ± 0.02	748 ± 2	624	0.85	A?	
	1.98 ± 0.01	748 ± 2	1080	0.99	A	Total t = 1704 hr
AS-9	2.02 ± 0.02	802 ± 2	1005	0.47	.....	
	$2.00^{+0.01}_{-0.02}$	802 ± 1	962	0.36	S	Total t = 1967 hr
AS-10	3.99 ± 0.03	651 ± 2	984	0.71	.....	
	4.00 ± 0.02	642 ± 1	961	0.90	A	Total t = 1945 hr
AS-11	4.02 ± 0.02	700 ± 1	984	0.51	.....	
	$4.01^{+0.02}_{-0.01}$	700^{+5}_{-4}	961	0.61	.....	Total t = 1945 hr
					.....	Third stage terminated by vessel failure—run lost.

* All capsules contained 15 to 40 wt percent water.

The A-S equilibrium curve may, therefore, be written as:

$$P(kb) = -0.0243T(°C) + 20.59$$

for pressures near the triple point. In fact, this line satisfies our direct reversals of the equilibria down to 2 kb. The high-temperature heat capacity measurements of Pankratz and Kelley (1964) as well as the variation of molar volume with temperature (Skinner, Clark, and Appleman, 1961) suggest that the equilibrium boundary may curve toward higher temperatures at low pressure.

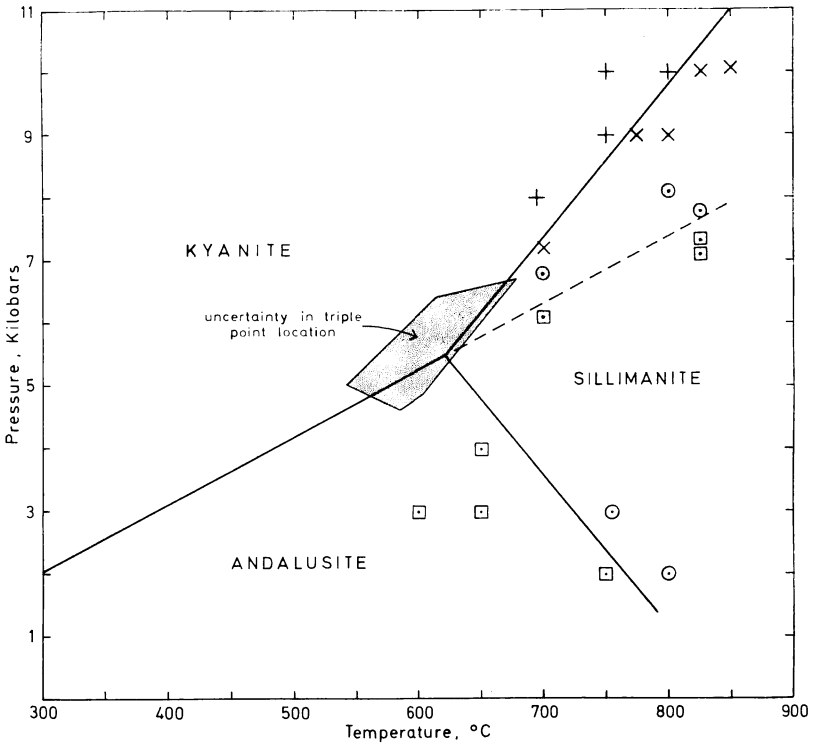


Fig. 2. The P-T coordinates of runs in which reaction could be detected. Stippled symbols: circles, kyanite grew from andalusite; squares, andalusite grew from kyanite. Open symbols: squares, andalusite grew from sillimanite; circles, sillimanite grew from andalusite. The plus signs and crosses are the P-T coordinates of gas-pressure apparatus runs on the kyanite-sillimanite transition, from Richardson, Bell, and Gilbert (1968). The uncertainty in the location of the triple point is based on extreme interpretations of the data shown; our preferred placing of the triple point and the transition curves is discussed in the text.

Comparison with previous work.—The K-A transition was reversed by Newton (1966) in solid-medium (piston-cylinder) pressure apparatus that had been calibrated against melting curves of the alkali halides, determined in gas-medium pressure apparatus (Clark, 1959). Our brackets, shown in figure 3, are in excellent agreement with Newton's, and his were taken into account when the equation of the reaction, given above, was formulated.

Althaus (1967) has determined the position of the A-S equilibrium in hydrostatic pressure apparatus. With the exclusion of his experiments in which more than two aluminum silicate polymorphs were present (discussed in Richardson, Bell, and Gilbert, 1968), there are two runs in which Althaus reported the growth of sillimanite in the andalusite field defined by the present study (fig. 3). In one of these runs (Althaus, 1967, table 3) 5 percent sillimanite in the charge was reported to have grown to 6.5 percent; in the other, 5 percent sillimanite was reported

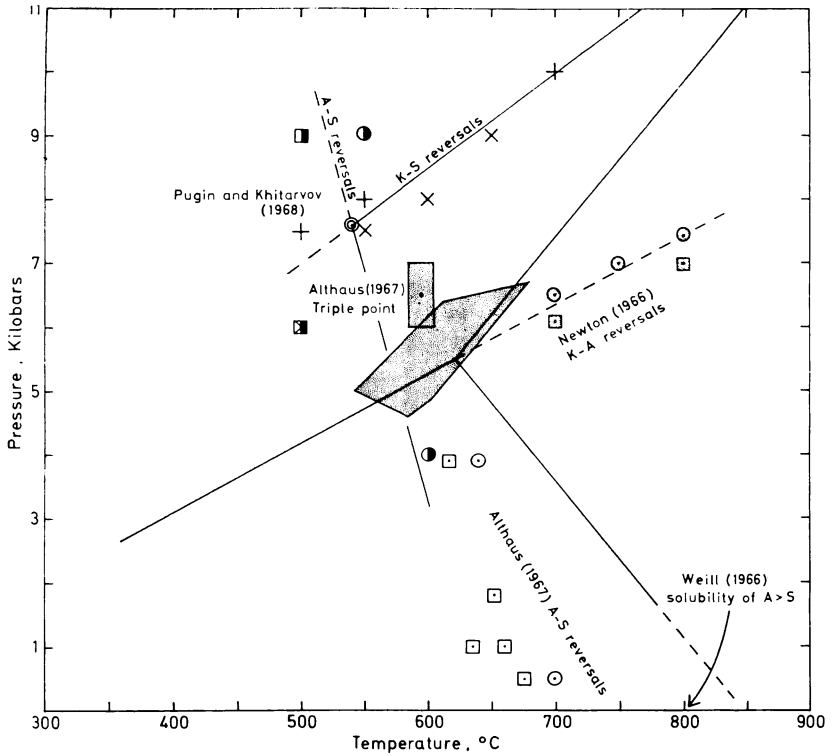


Fig. 3. Comparison of our P-T curves with direct reversals reported in the literature. Symbols: stippled circles and squares, Newton's (1966) reversals of kyanite-andalusite equilibrium; open squares and circles, Althaus's (1967) reversals of andalusite-sillimanite equilibrium in which only quartz, andalusite, and sillimanite were present; half-filled squares and circles, Pugin and Khitarov's (1968) reversals of andalusite-sillimanite equilibrium; plus signs and crosses, Pugin and Khitarov's (1968) reversals of kyanite-sillimanite equilibrium. Also shown is the point at which Weill (1966) found andalusite more soluble (that is, less stable) than sillimanite in a cryolite melt.

to have grown to 5.9 percent. These are very small changes, and a question is thus raised as to the sensitivity of the X-ray technique Althaus used to detect reaction. Nevertheless, Althaus's experiments show a high degree of internal consistency, and it may well be that small differences in starting materials and experimental procedures do affect the position of equilibrium curve. Althaus (personal commun., 1968) has indicated that the andalusite he used contained 0.77 wt percent Fe_2O_3 and 1.27 wt percent MnO; the sillimanite contained 0.45 percent Fe_2O_3 (compare with table 1 in this study).

Pugin and Khitarov (1968) have recently reported reversals of both the K-S and A-S transitions in solid-medium pressure-apparatus: the coordinates of their runs near the curves are shown in figure 3. Pugin and Khitarov give no details of their experimental procedures, but a comparison of their K-S results with the kyanite-sillimanite brackets of

Newton (1966) and Richardson, Bell, and Gilbert (1968) suggests that Pugin and Khitarov are reporting uncorrected nominal pressure. Run durations given for the A-S experiments of Pugin and Khitarov (5-12 hrs) suggest that the changes observed must have been slight and very difficult to detect. Finally, the chemical analyses presented by them for their reactants show they were impure mineralogically.

Weill (1966), in a novel approach to the aluminum silicate problem, bracketed the equilibrium solubilities of the three polymorphs in a cryolite-bearing melt by observing the presence or absence of Al_2SiO_5 in the assemblage corundum + liquid ± Al_2SiO_5. His results may be used directly to deduce the relative stabilities of the polymorphs under the experimental conditions. For example, at 1 atm and 1010°C, sillimanite is clearly the most stable polymorph (Weill, 1966, fig. 1). At 800°C, however, the brackets of andalusite and sillimanite saturation touch, suggesting that the A-S transition boundary passes through, or slightly below, 800°C (see fig. 2, this paper). This value is about 50°C lower than the 1 atm intersection of our A-S transition curve. It may be that fluorine causes some difficulties by dissolving preferentially in one of the polymorphs. Another reason for the discrepancy may be the presence of different amounts of trace components in our starting materials and Weill's. A possibility also is suggested by the experiments of G. C. Kennedy (personal commun., 1968), in which sillimanite appears to form a solid solution with 3:2 mullite which is controlled by pressure (amount of solution increases with lower pressure). If this is so, then our experiments and Weill's may not be controlled by the same equilibrium boundary.

Geologic application of the phase diagram.—The application of the aluminum silicate phase diagram to natural metamorphic rocks has been discussed at length by previous reviewers (for example, Miyashiro, 1949, 1961; Pitcher, 1965; Chinner, 1966a; and Strens, 1968); we will confine our attention to three points.

First is the problem of metastability. Differences in free energy (ΔG) between the polymorphs at pressures and temperatures near the triple point are small by comparison with ΔG of those reactions, involving dehydration, that commonly generate the Al_2SiO_5 minerals. Thus, the energy potential for selection of the stable polymorph is very low in nature. One way of illustrating this problem is to examine the width of the temperature band that would result along an aluminum silicate univariant curve from a variation in the free-energy change as small as 100 cal/mole. The source of the variation need not be identified for purposes of this discussion. At an equilibrium temperature, T_e, near the triple point, $\Delta G = 0 = \Delta H - T_e\Delta S$.
Thus,

$$\Delta \overline{H} = T_e \Delta S.$$

From the Clapeyron relation,

$$\Delta \overline{S} = \Delta V \frac{dP}{dT}, \text{ and thus } \Delta \overline{H} = T_e \Delta V_{T_e} \frac{dP}{dT}.$$

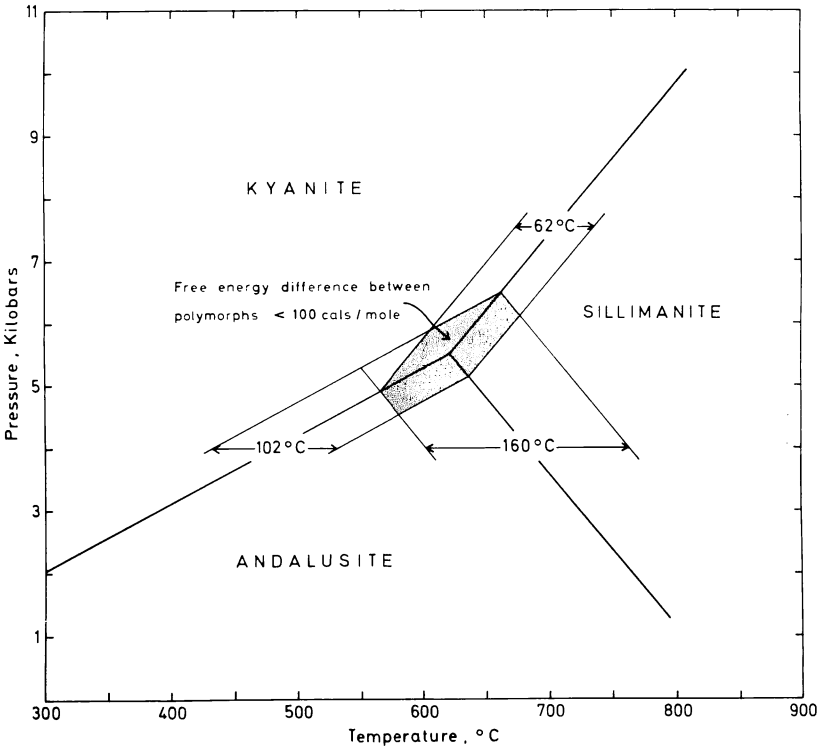


Fig. 4. A diagrammatic illustration of the fact that free-energy differences between the Al_2SiO_5 polymorphs are very small.

Then, for a variation of 100 cal/mole (4184 bar cc/mole) in ΔG,

$$\pm \Delta G = \pm 4184 = T_e \Delta V_{T_e} \frac{dP}{dT} - T\Delta V_T \frac{dP}{dT}$$

where T represents the resultant temperature.
But $\Delta V_{T_e} \approx \Delta V_T$, so that

$$\Delta T \approx \frac{\pm 4184}{\Delta V_{T_e} \dfrac{dP}{dT}}.$$

below, 800°C (see fig. 2 this paper). This value is about 50°C lower than Values for ΔV were taken from Skinner, Clark, and Appleman (1961) and for dP/dT from the equations for the transitions given earlier in the paper. The results are illustrated in figure 4. The free energy difference between kyanite and sillimanite is less than 100 cal/mole at the pressure of the triple point, over about 62°C; between kyanite and andalusite, over about 102°C; and between andalusite and sillimanite, over 160°C!

Variations of 100 cal in the Gibbs function change of some experimentally determined mica breakdown reactions (using the wt of 1 mole

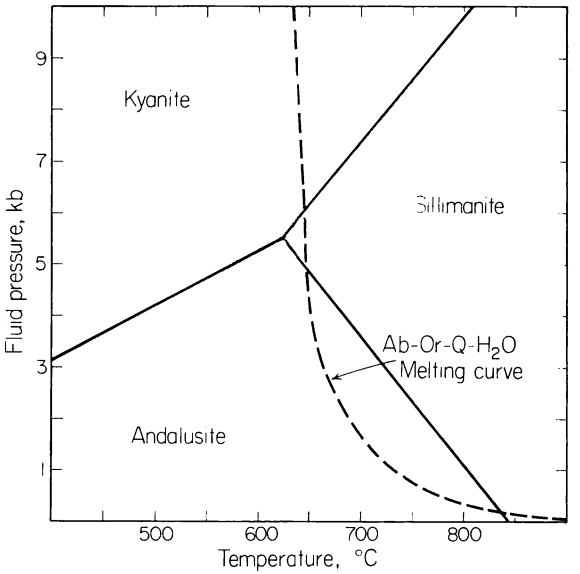


Fig. 5. Stability relations of the Al_2SiO_5 polymorphs in relation to the Ab–Or–Q–H_2O ($NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O) melting curve which models minimum melting in granitic systems. The curve is taken from Luth, Jahns, and Tuttle (1964).

Al_2SiO_5 : 162 g) can be used for comparison. For example, for a potential difference of 100 cal, a band 40°C wide is possible for the reaction muscovite + quartz = sillimanite + K-feldspar + H_2O at 2 kb (data from Evans, 1965). Corresponding figures for annite oxidation on the NNO buffer (data from Eugster and Wones, 1962) and phlogopite breakdown at 2 kb (data from Yoder and Eugster, 1954) are about 16° and 8°C, respectively.

Since both nucleation and growth rate of new phases are strongly dependent on ΔG (see Fyfe, Turner, and Verhoogen, 1958, chap. 3), it is not surprising to find that relations in nature between the Al_2SiO_5 polymorphs near the transition boundaries or the triple point appear somewhat muddled (see Heitanen, 1956; Woodland, 1963; Pitcher and Read, 1960; Chinner, 1966b). Clearly, rocks metamorphosed at pressures and temperatures near the triple point may produce, or fail to digest, the "wrong" polymorph. Nevertheless, the overall consistent pattern of Al_2SiO_5 occurrences (see Miyashiro, 1961) suggests that the equilibrium diagram may be used in a general way to divide kyanite-sillimanite from andalusite-sillimanite sequences, the former usually occurring above and the latter usually below 5.5 kb pressure.

Our second point is that attention should be directed to the time relations between polymorph growth, which may give an indication as to the relative stability of the later mineral, rather than to isolated occurrences. For example, Tilley's (1935) description of the development of

kyanite from andalusite in the vicinity of Carn Chuinneag indicates that kyanite growth must have taken place either in the kyanite field or in that part of the sillimanite field over which kyanite is more stable than andalusite. If we accept a guess that the temperature of the kyanite-producing metamorphism in that case was in excess of 550°C, then the effective pressure must have been greater than 4.7 kb.

Similarly, an episode in which sillimanite has grown from both kyanite and andalusite along a preexisting kyanite-andalusite isograd must have taken place at a temperature above 622°C whether or not part of the K-A isograd is an equilibrium feature of the sillimanite growth episode. Such an "overprinting" has been suggested by Chinner (1966b) for the northeast Grampian Highlands.

Our third point is to note that the minimum melting curve of granite, under conditions where $P_{H_2O} = P_{total}$, intersects the andalusite-sillimanite transition but apparently does not involve the triple point (fig. 5). Thus, the Dartmoor granite, with its abundant partly digested andalusite-bearing xenoliths (Flett and Dewey, 1912, p. 45-46; Brammall and Harwood, 1932, fig. 7) must have been intruded with a high ratio of P_{H_2O} to P_{total}, at a total pressure less than about 5 kb.

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