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EXPERMENTAL DETERMINATION OF KYANITE-SILLIMANITE EQUILIBRIUM RELATIONS AT HIGH TEMPERATURES AND PRESSURES*

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ABSTRACT. The equilibrium curve between kyanite and sillimanite has been found to lie at 18,200 bars at 1000°C and 21,000 bars at 1300°C; the kyanite field lies on the high-pressure side of this curve. Kyanite and sillimanite could not be synthesized consistently below 1000°C, and it proved necessary to extrapolate the equilibrium curve to the lower temperatures encountered in regional metamorphism. Thermochemical data suggest that a curvilinear extrapolation is required, although curvature is not demanded by the experimental points. It is concluded that the assemblage quartz plus corundum, which was formed in most of the runs, is metastable under all conditions investigated.

The results demonstrate conclusively that kyanite can be formed in the absence of shearing stress. They also suggest that horizontal gradients of temperature, pressure, or both are required to account for the distribution of kyanite and sillimanite observed in regionally metamorphosed rocks.

INTRODUCTION

Knowledge of the physical conditions existing during their formation is essential to the understanding of metamorphic and igneous rocks. Once the fields of stability of their constituent minerals are known, the possible pressures and temperatures of formation of these rocks can be inferred. The simplest diagrams of mineral stability are those depicting polymorphism in a one-component system, and two very important polymorphs in metamorphic rocks are the aluminosilicates, kyanite and sillimanite. Analyses of these minerals show that the composition of each is remarkably close to Al_2SiO_5.

The results of 55 quenching runs, made in the enlarged version of Bridgman's 30,000-bar apparatus described by Robertson, Birch, and MacDonald (1957), are reported here. Most of the data apply to that portion of the kyanite-sillimanite boundary between pressures of 18,000 and 23,000 bars and at temperatures between 1000 and 1300°C.

APPARATUS AND PROCEDURE

The apparatus is described by Robertson et al. (1957), and only recent modifications will be considered in detail here. The pressure vessel is a tapered cylinder, forced into a conical hole in supporting rings by a hydraulic ram. The pressure is generated inside the cylinder by a piston advanced by an opposing hydraulic ram. The pressure medium is nitrogen.

Charges are held in gold or platinum capsules and are heated by a furnace inside the pressure vessel. The furnace is supported in a steel or copper tube, and it plugs into insulated electrical connections at the bottom of the pressure vessel. For temperatures up to 1000°C, the furnace is wound of kanthal wire on a porcelain tube, one-quarter inch inside diameter. For higher temperatures, the winding is of platinum-10 percent rhodium wire, and the core is an alundum tube, one-eighth inch inside diameter. The use of a smaller furnace at higher temperatures prevents overheating of the inner wall of the

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pressure vessel, and also reduces the power required to reach high temperatures. The winding is about 3 inches long and is insulated by a closely fitting sleeve of massive pyrophyllite, marketed by the American Lava Corp. under the name "Lava".

Considerable difficulty is encountered with thermal gradients in these small furnaces. One of the main sources of trouble is convection of nitrogen through the furnace, which is mounted in a vertical position. Gradients due to the flow of nitrogen are markedly reduced by making the metal furnace sleeve gas-tight at the top, and by filling all open spaces within the furnace and between the furnace and the Lava sleeve with refractory material.

Near the ends of the furnace winding, gradients of the order of 1000°C/inch are inevitable, and the region of essentially uniform temperature in the center of the furnace is extremely short. The windings are more closely spaced near the ends of the furnace than opposite the charges, but steep gradients near the central part of the furnace have persisted. The gradient is reduced to about ten degrees in the length of the charge by placing the capsules in a heavy block of metal. The number of capsules is reduced when the metal block is used, but the more uniform temperature compensates for this sacrifice.

Five insulated leads, accommodating the various electrical circuits, are let into the pressure vessel through the plug at its bottom. The stem of the bottom plug is necessarily rather large, and its seal has not been wholly satisfactory. Leaks at this point terminated many of the runs. An unsupported area packing with five insulated leads has been tried recently; it has eliminated difficulties at pressures up to 20,000 bars.

Temperature is measured with platinum-platinum 10 percent rhodium thermocouples placed at each end of the capsules containing the charges. The cold junction of the thermocouples is in an ice bath outside the pressure vessel. Each thermocouple lead consists entirely of thermocouple wire except for a distance of three-sixteenth inches, which is in a hardened steel cone forming the pressure-tight seal. The mean thermal gradient in the bottom plug is measured by thermocouples at each end. It has never exceeded 15°C/inch, and hence the error introduced by the cones can hardly exceed 3°C. This small correction and the correction for the effect of pressure on the emf of the thermocouples have been neglected in the results.

Pressure is measured with a manganin coil calibrated against the freezing point of mercury at 0°C. The coil has a resistance of about 51 ohms, and its change of resistance is measured on a Carey-Foster bridge with a precision equivalent to about 20 bars. The coil is mounted on the bottom plug, between leads of thermocouple wire. Measurement of the thermal emf in this circuit gives the mean temperature of the coil. In this position its mean temperature has never exceeded 50°C; the correction to the measured pressure is less than 100 bars at this temperature (Robertson et al., 1957).

In making a run, the pressure is first raised to about 2,000 bars below the desired value, and the furnace is then heated to the desired temperature. The temperature is raised relatively slowly (about 100°C per minute) to reduce thermal shock in the apparatus and to guard against the development of local hot spots in the furnace winding. After the furnace has reached temperature, the pressure is adjusted if necessary.

The charges are quenched by turning off the power to the furnace. The temperature drops below 300°C in 30 seconds and reaches about 100°C in one minute. The pressure is then released.

In the early stages of this work, the duration of runs was limited to about three hours by persistent small leaks and burning out of furnaces. Many of these difficulties have gradually been eliminated, and considerably longer runs are now feasible.

Starting materials tried in the synthesis of kyanite and sillimanite were kyanite from Gorham, Me., sillimanite from near Mt. Monadnook, N. H., andalusite from Laws, Calif., kaolinite from Murfreesboro, Ark., and synthetic gibbsite from the Norton Co. Capsules containing the charges were left unsealed, so that any water present could escape freely. In most of the successful runs the starting material was andalusite, kaolinite, or a mixture of kaolinite and gibbsite. Analyses of the andalusite and kaolinite are given in table 1.

TABLE 1

Chemical Analyses of Andalusite and Kaolinite

J. Ito, Analyst

	(1)	(2)
SiO_2	34.92	44.56
TiO_2	0.63	0.49
Al_2O_3	59.61	39.40
Total Fe as Fe_2O_3	0.66	0.47
MnO	0.00	0.00
MgO	0.00	0.10
CaO	0.28	0.73
Na_2O	0.10	0.09
K_2O	0.13	0.10
H_2O	3.71	14.47
	100.04	100.41
	Traces of Ga, Cu, Au.	Traces of Ga, Cu, Zr.
Mole fractions		
SiO_2	582	743
Al_2O_3	584	386

(1) Andalusite, White Mts., near Laws, Calif. Harvard Museum #95769.
(2) Kaolinite, Murfreesboro, Ark. Harvard Museum #102649.

In some of the runs, kaolinite and gibbsite were mixed to give a 1:1 ratio of Al_2O_3 and SiO_2, but it was thought that dehydration of the gibbsite favored nucleation of corrundum and was partially responsible for the appearance of metastable quartz plus corundum. In later runs, kaolinite alone was used as a starting material; it reacts to form an aluminosilicate plus quartz, but since both kyanite and sillimanite are stable with quartz, this has no effect on the equilibrium curve.

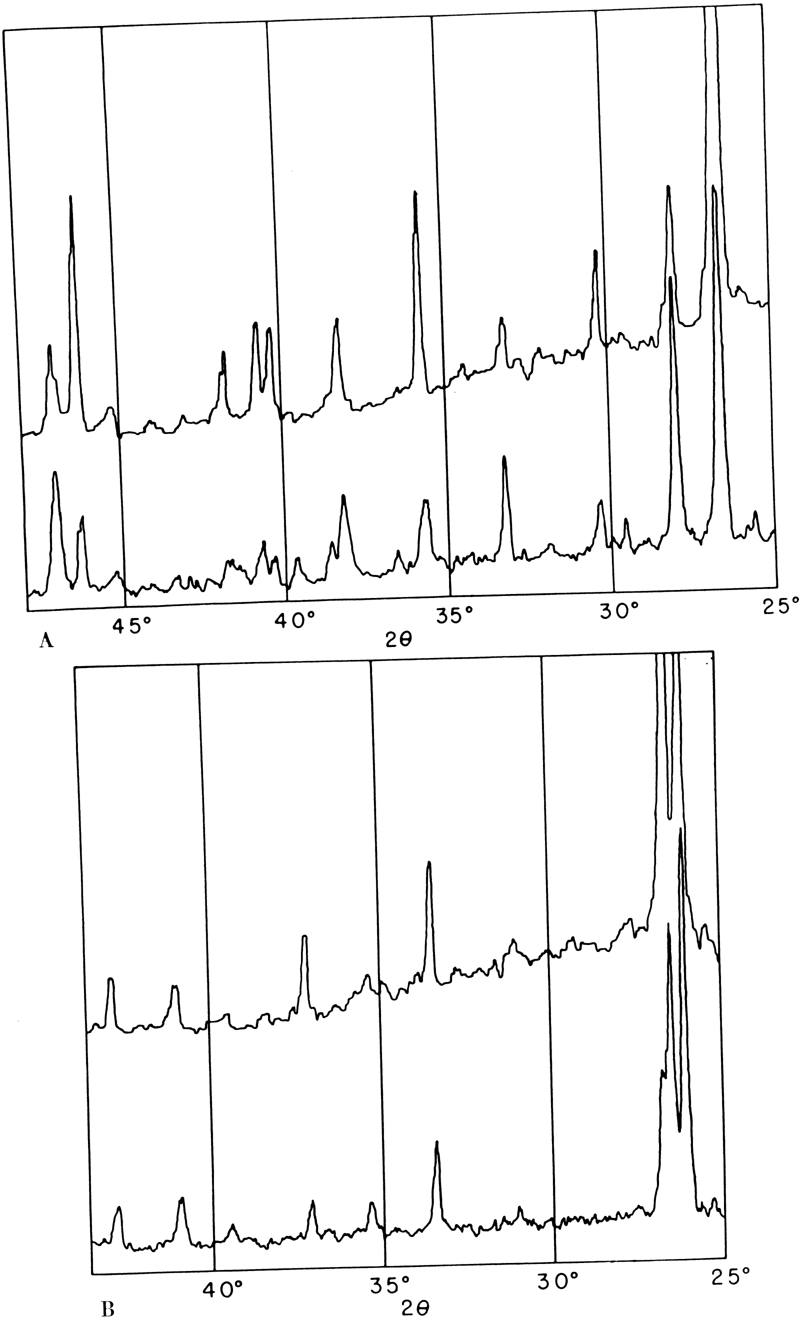

Fig. 1. X-ray diffraction patterns of natural and synthetic kyanite and sillimanite (Cu-K_a radiation). A: upper curve—natural kyanite; lower curve—synthetic kyanite. B: upper curve—natural sillimanite; lower curve—synthetic sillimanite.

TABLE 2

Experiments Results

(Kao = kaolinite, G = gibbsite, A = andalusite, Ky = kyanite, S = sillimanite, Q = quartz, C = corundum. *Metastable phase.)

Run No.	Pressure (bars)	Temperature (°C.)	Duration (hrs.)	Reactants	Products
38	19,100 ± 100	975 ± 25	1½	Kao + G	Ky
40	18,600 ± 500	1000 ± 100	1	Kao + G	Ky
41	21,200 ± 100	910 ± 90	1¼	Kao + G	Ky + Q* + C*
44	18,900 ± 300	1000 ± 25	1½	A	Ky + Q* + C*
48	21,400 ± 200	1035 ± 20	1¾	Kao + G	Ky
				A	Ky
49	12,100 ± 100	1045 ± 30	1½	A	S + Q* + C*
				Kao + G	S + Q* + C*
51	24,400 ± 300	1320 ± 20	1	A	Ky
53	12,500 ± 100	1050 ± 25	1¼	Kao + G	S + Q* + C*
66	23,400 ± 100	1080 ± 50	1¼	Al_2SiO_5 gel	Ky + Q* + C*
78	16,000 ± 100	1100 ± 20	1	Kao + G	S + Q* + C*
				A	S + Q* + C*
79	7,500 ± 100	750 ± 100	1½	Kao + G	S + Q* + C*
85	12,200 ± 200	845 ± 20	3¼	Kao + G	S + Q* + C*
88	22,600 ± 400	>1280	¼	Kao + G	Ky
				A	S
90	17,000 ± 100	975 ± 30	2¾	Kao + G	S + Q* + C*
		1055 ± 30		Kao + G	Ky* + Q* + C*
91	17,000 ± 100	1020 ± 20	3¼	Kao + G	S + Q* + C*
93	18,600 ± 200	1015 ± 10	3	Kao + G	Ky + Q* + C*
95	22,900 ± 400	1325 ± 50	1	Kao	Ky + Q
101	21,800 ± 100	1250 ± 200	½	Kao	Ky + Q
				A	S
106	21,000 ± 100	1245 ± 30	1	A	Ky
		1305 ± 30		Kao	Ky + S + Q
112	19,600 ± 100	1260 ± 25	1½	Kao	S + Q
				A	S + Q* + C*
115	18,100 ± 100	1110 ± 30	½	Kao	S + Q + C*
117	19,000 ± 100	1105 ± 15	3	Kao	S + Q
120	23,900 ± 200	1220 ± 50	2¾	S	Ky
127	17,700 ± 100	995 ± 10	6½	Kao	S + Q + C*
128	18,600 ± 100	1340 ± 30	7¾	Ky	S + Ky*

IDENTIFICATION OF PHASES

Preliminary identification of phases produced was made on a Norelco high-angle x-ray diffractometer, using Cu-K_α radiation. The diffraction patterns of the synthetic products were compared with those of natural kyanite and sillimanite (fig. 1). The x-ray patterns of sillimanite and mullite differ in 2θ between 50° and 60° (Kennedy, 1955 and personal communication), and the patterns of the synthetic sillimanite match that of natural sillimanite in this interval. The synthetic sillimanite has $n_\alpha = 1.655 \pm 0.005$ and $n_\gamma = 1.675 \pm 0.005$. These indices are slightly lower than those of natural sillimanite ($n_\alpha = 1.657 - 1.661$, $n_\gamma = 1.677 - 1.684$), but they are considerably higher than those of mullite ($n_\alpha = 1.642$, $n_\gamma = 1.654$). Most natural sillimanite contains a small amount of iron, and this may account for the higher indices.

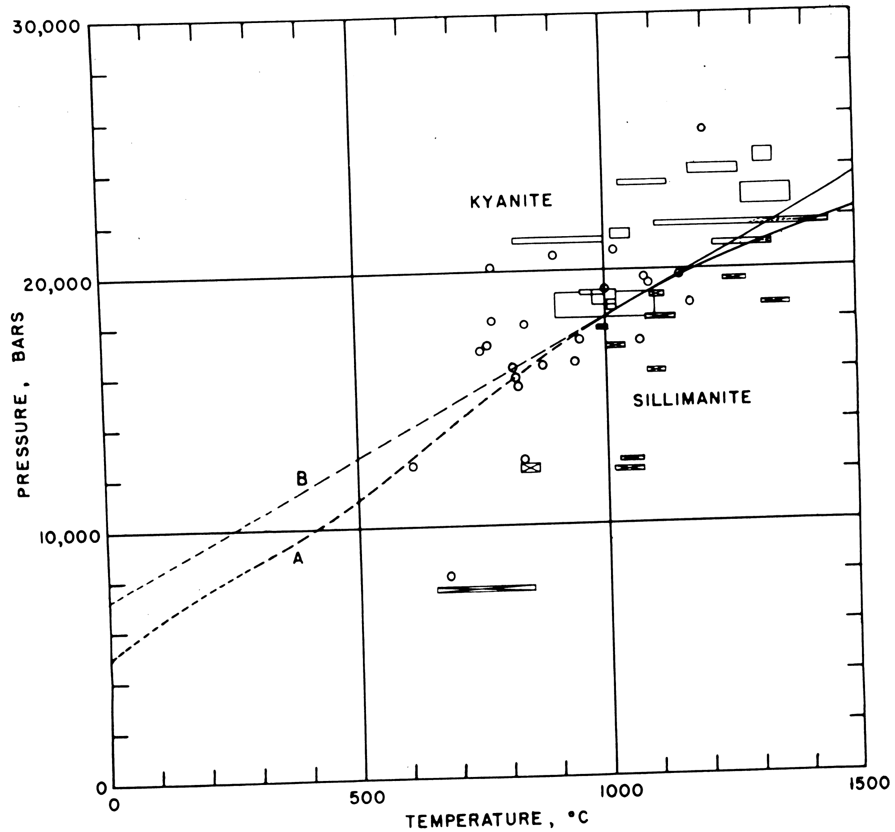

Fig. 2. Results of quenching experiments. Curve A is the "best" equilibrium curve. Curve B is a straight line extrapolation. Open boxes represent runs in which kyanite was produced, boxes with crosses represent runs in which sillimanite was produced, and circles represent runs which produced only quartz + corundum.

The synthetic crystals of sillimanite have the shape of stubby prisms, elongate parallel to the *c*-axis. Crystal outlines of the synthetic kyanite are less well-developed; it has the same mean index of refraction as natural kyanite (1.72). Crystals of both kyanite and sillimanite contain abundant inclusions of quartz and corundum.

RESULTS

The results of the quenching runs are given in table 2, and the positions of the runs are shown in figure 2. The uncertainties in pressure indicate the maximum fluctuation in pressure during the run. No uncertainty less than 100 bars is reported; although the precision of the pressure measurements is higher than this, uncertainties in the correction for the temperature of the coil and imperfect compensation for the effect of temperature on the resistance of the leads make this a more realistic estimate of the minimum uncertainty.

The uncertainties in temperature are determined by readings of the thermocouples at the ends of the capsules. The temperature recorded by each thermocouple was averaged over the duration of the run, and the mean of the two readings was taken as the temperature of the run. The uncertainty is half the difference between the readings of the thermocouples. This is a generous estimate of the uncertainty in the temperature of the charge, for the metal capsule in which the charge is held tends to even out its temperature.

The uncertainties define a rectangle on the P-T plane, but the conditions of the run do not lie at a single point within it because of the thermal gradient and fluctuations in temperature during the run. It is incorrect to assume that the conditions of the run could be at either the high or low-temperature sides of the rectangles.

The most troublesome aspect of this investigation was the formation of quartz plus corundum. Runs in which these phases were the only products are shown as circles in figure 2; they formed from both andalusite and kaolinite. The assemblage persisted at high temperatures and was present in most of the runs in which kyanite or sillimanite was also formed. It was decidedly less abundant at the higher temperatures, however. Quartz and corundum were characteristically included in larger grains of kyanite or sillimanite; the converse relationship was not observed.

In the portion of the P-T plane where we were able to synthesize kyanite or sillimanite consistently, the assemblage quartz plus corundum seems clearly to be metastable. It is well-known that when kaolinite is dehydrated at low pressure, this assemblage appears as an intermediate stage in the reaction which eventually produces the stable assemblage, mullite plus quartz (Eitel, 1954, p. 1104, 1106). Since quartz and corundum occur as inclusions in aluminosilicate grains and become less abundant at high temperatures, where equilibrium should be most closely approached, it is inferred that the aluminosilicates grow at their expense. This is presumptive evidence that at high pressure the reaction proceeds in the same stepwise manner as the decomposition of kaolinite at low pressure. Both andalusite and kaolinite gave similar results.

It is perhaps less clear that quartz plus corundum is a metastable assemblage below 1000°C, but this is inferred from the stepwise nature of the reaction. Our failure to form kyanite or sillimanite consistently below 1000°C is interpreted as due to the slow rate at which early-formed quartz and corundum react at these temperatures. There is no way in which our runs can be separated into well-defined fields of aluminosilicates and quartz plus corundum; on the other hand the fields of kyanite and sillimanite can be cleanly separated. The stability of quartz plus corundum can only be established by demonstrating that they can be formed reversibly from kyanite and sillimanite. Lacking such evidence, and faced with ample evidence of the reluctance with which quartz and corundum combine, we regard them as metastable in all of our runs.

This conclusion is consistent with the thermochemical data on these minerals (table 3). From these data we estimate that if the heat of formation of sillimanite from the oxides is algebraically less than −500 to −1000 cal/mol, quartz plus corundum is a metastable assemblage under all of the conditions we have investigated. The uncertainty in this estimate is probably a few kilocalories per mole. Calorimetric determinations of the heat of formation of sillimanite give values of about –50 kilocalories per mole (Kubaschewski and Evans, 1956).

TABLE 3

Thermochemical Data Used in Calculations

The room-temperature data were taken from the compilation of
Prof. Gordon J. F. MacDonald

	Kyanite	Sillimanite	Andalusite	Quartz	Corundum
Entropy, cal/mol°C. 300 °K	20.02 ± 0.1[8]	22.97 ± 0.1[8]	22.28 ± 0.1[8]	10.0 ± 0.1[3]	12.16 ± 0.02[4]
1600 °K	90.85 ± 0.6[2,8]	92.17 ± 0.6[2,8]	94.27 ± 0.6[2,8]	35.9 ± 0.2[2,3]	57.53 ± 0.1[2,4]
Volume, cm^3/mol. 300 °K	43.3 ± 1.0[5]	49.0 ± 1.0[7]	51.6 ± 1.0[1]	22.6 ± 0.03[9]	25.5 ± 0.2[6]
Enthalpy, kcal/mol. $H_{1600\,°K}-H_{300\,°K}$	57.7 ± 0.6[2]	56.3 ± 0.6[2]	56.8 ± 0.6[2]	21.1 ± 0.1[2]	37.0 ± 0.1[2]

References.

[1] Hey and Taylor, 1931; MacDonald and Merriam, 1938.

[2] Kelley, 1949.

[3] Kelley, 1950.

[4] Kerr, Johnston, and Hallett, 1950.

[5] Naray-Szabo, Taylor, and Jackson, 1929.

[6] Palache, Berman, and Frondel, 1944.

[7] Taylor, 1928; Taylor, 1929.

[8] Todd, 1950.

[9] Wyckoff, 1926; Gibbs, 1926.

The minerals in this system are among the best refractories known, and they are extraordinarily reluctant to take part in chemical reaction. Metastable persistence of kyanite and sillimanite outside their respective fields of stability made the demonstration of the reversibility of the reaction extremely difficult. Natural kyanite held for four days at 1000°C and one atmosphere showed no sign of reaction; this run is 18,000 bars below the equilibrium curve. The reaction was reversed at higher temperature. Synthetic sillimanite produced in run 88 was completely converted to kyanite at 1220°C and 23,900 bars. Natural kyanite, after grinding for 60 hours, was converted to a mixture of kyanite and sillimanite at 18,600 bars and 1340°C. The reaction was thus reversed at points about 3000 bars from the equilibrium curve. This is the maximum uncertainty in its position.

Metastable formation of kyanite or sillimanite in the field of the other is known to have occurred only in run 90 (table 2). Subsequent runs showed that the kyanite formed in this run was metastable, and it is not shown in figure 2.

The preliminary results published by Griggs and Kennedy (1956) show an equilibrium curve between kyanite and sillimanite which lies at slightly over 20,000 bars at 1000°C; our curve lies at 18,000 bars at the same temperature.

EXTRAPOLATION OF THE EQUILIBRIUM CURVE TO LOWER TEMPERATURES

The equilibrium curve between kyanite and sillimanite is located between 1000°C and 1300°C by this work. These temperatures are too high *for im-*

mediate geological application, and it is desirable to extrapolate the curve to lower temperatures. High-temperature heat capacity data (Kelley, 1949) show that ΔS, the entropy change of the reaction, depends on temperature at one atmosphere; hence a curvilinear extrapolation is required. Differences in thermal expansion and compressibility of kyanite and sillimanite, $\Delta\alpha$ and $\Delta\beta$ respectively, will be neglected. This introduces only a small error insofar as these quantities affect ΔV, the volume change of the reaction. $\Delta\alpha$ is likely to be less than 10^{-5} deg^{-1}, and $\Delta\beta$ can hardly exceed 10^{-6} bars^{-1}. The correction to ΔV is thus unlikely to exceed 3 percent at the highest temperatures and pressures. But the entropy change of the reaction is dependent on $\Delta\alpha$ through the relation $(\partial \Delta S/\partial P)_T = -\Delta(V\alpha) = -\overline{V}\Delta\alpha$, where $\overline{V}$ is a mean volume. $\overline{V}$ is about 45 cm^3/mol, and with $\Delta\alpha$ assumed to be 10^{-5} deg^{-1}, we find that ΔS changes by about 9 dj (decijoules)/mol°C in 20,000 bars. This is about 8 percent of the entropy change at room temperature or 15 percent of the change at 1100°C.

The equilibrium curve is given by the equation

$$P(T) = P(T_0) + (\Delta S/\Delta V)_0\,(T - T_0) + \frac{1}{\Delta V}\int_{T_0}^{T} \Delta S(T)\,dT \tag{1}$$

where $\Delta S(T)$ is chosen to vanish at $T = T_0$. $(\Delta S/\Delta V)_0$ and $P(T_0)$ are fixed by the equilibrium pressures at two temperatures. These were chosen to be 1300 and 1600°K. The integral in (1) was evaluated from the high-temperature entropy data given by Kelley (1949).

The non-linearity of the equilibrium curve is contained in the third term on the right of (1), and this term is subject to large uncertainties that do not affect the others. The high-temperature entropy data are estimated to be uncertain by about 20 dj. Random errors tend to cancel in the integration, but the integral is nevertheless subject to an uncertainty of perhaps 30 percent. Further errors are introduced by neglect of $\Delta\alpha$ and $\Delta\beta$. Finally, $\Delta V = 5.7 \pm 1.3$ cm^3/mol (table 3); the uncertainty in this factor is almost 25 percent. Combining these independent errors, we estimate the uncertainty in this term to be about 3,000 bars at 25°C and 1500 bars at 500°C.

Utilizing (1), curve A in figure 2 was extrapolated to room temperature; it was fitted to the experimental data between 1000°C and 1300°C by placing it about halfway between adjacent points in the kyanite and sillimanite fields. Curve B in figure 2 is a linear extrapolation.

TABLE 4

Parameters of the Equilibrium Curves at 25°C

Curve	Intercept (bars)	$\frac{dP}{dT}$ at 25 °C. (bars/°C)	ΔS at 25 °C. (dj/mol/°C)
"A"	5650	19 ± 5	108 ± 24
Steepest	3650	21 ± 5	119 ± 25
Flattest	7550	18 ± 5	100 ± 23
"B"	7600	11	63 ± 14
From Low-Temperature Heat Capacities (Todd, 1950)			123 ± 6

Intercepts are listed in table 4 for these curves and for the flattest and steepest curves which could be drawn, using (1), without conflicting with any of the runs. The extreme curves bracket the uncertainties in the experimental location of the equilibrium curve, but there is an additional uncertainty of 3,000 bars in the intercept as discussed above. All of the curves are metastable below the kyanite-sillimanite-andalusite triple point.

The entropy change of the reaction at 25°C, computed from the slopes with $\Delta V = 5.7$ cm^3/mol. is compared in table 4 with the ΔS found by Todd (1950) from low-temperature heat capacities. The difference between Todd's value and those calculated from the curvilinear extrapolations are less than the estimated uncertainties. Linear extrapolation leads to a serious discrepancy.

FIELDS OF ANDALUSITE AND MULLITE

Other stable assemblages in this system are andalusite and mullite plus quartz, neither of which was synthesized under the conditions described here. Mullite is stable at zero pressure and high temperature (Eitel, 1954, p. 691); mullite plus quartz is converted to sillimanite at a pressure of about 5,000 bars at 600°C (Kennedy, 1955). At higher temperatures this reaction takes place at pressures which are assumed to be moderate but which are unknown. Work on this transition is in progress in this laboratory.

Data on the location and shape of the andalusite field are in conflict. Andalusite, kyanite, and sillimanite have been found together in nature, for example at Goat Mountain, Idaho (Heitanen, 1956). This suggests that a triple point exists at a pressure and temperature realized in the earth. Roy (1954) synthesized andalusite at pressures below 1,000 bars. The molar volume of sillimanite appears to be definitely smaller than that of andalusite (Taylor, 1928, 1929), and hence pressure favors sillimanite. If sillimanite is also the high-temperature phase, the equilibrium curve between andalusite and sillimanite has a negative slope; this is compatible both with the existence of a triple point and with Roy's observations. But heat capacity data (Kelley, 1949; Todd, 1950) suggest that the ΔS of the reaction changes sign at about 100°C and that andalusite is the high-temperature phase above that temperature.

The ΔS of the reaction sillimanite = andalusite is small, and we believe that the above data can best be reconciled by neglecting the measurements of heat capacity. On this assumption, a tentative phase diagram of the composition Al_2SiO_5 has been constructed (fig. 3); the relation of the andalusite field to those of sillimanite and kyanite is qualitatively the same as that proposed by Miyashiro (1949) and Thompson (1955). The diagram is complicated by the intersection of the sillimanite-mullite plus quartz and andalusite-sillimanite equilibrium curves. The slopes of these curves are hypothetical, as are the locations of the triple points.

GEOLOGICAL APPLICATIONS

The chemical potential of water determines whether aluminosilicates can be formed in most rocks at low temperatures. Hydrous phases, rich in alumina, take their place in many cases (Thompson, 1955). Were the chemical potential of water to have its highest possible value, the assemblage andalusite plus

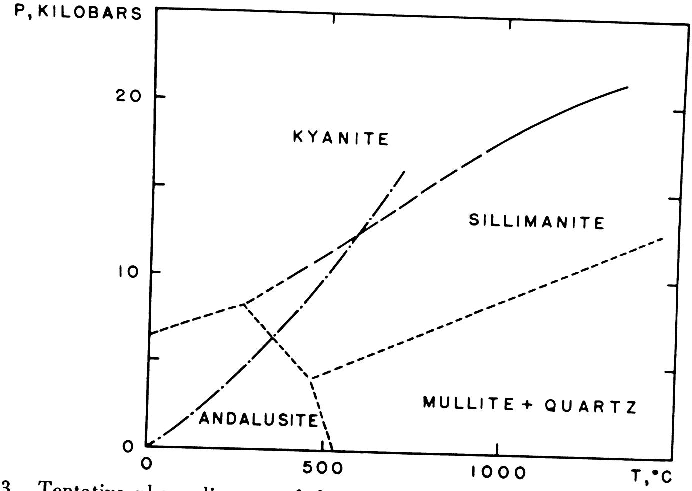

Fig. 3. Tentative phase diagram of the composition Al_2SiO_5. Phase boundaries indicated by short dashes are *not* experimentally determined, and no quantitative significance should be attached to them. The dot-dash curve indicates the *shape* of a typical geothermal gradient curve; its position has significance only at the origin.

quartz could not exist stably at pressures greater than a few hundred bars; pyrophyllite would appear in its place (Kennedy, 1955). We shall henceforth consider only cases in which either the temperature is sufficiently high or the chemical potential of water is sufficiently low so that one of the aluminosilicates may appear in the rock.

The stress mineral concept was introduced to account for the distribution in nature of kyanite, andalusite, and certain other minerals (Harker, 1939). The present work clearly demonstrates that kyanite can be formed in the absence of shear, but it is nevertheless a stress mineral in the sense that high pressures are necessary for its formation as a stable phase. The metastable prolongation of the steepest curve extrapolated by (1) intersects the pressure axis at 3,350 bars, and the stable boundary between the andalusite and kyanite fields must lie at higher pressures. Additional uncertainty in the extrapolated steepest curve is about 3,000 bars, but it is probable that kyanite is not stable under surface conditions.

A geothermal curve is superimposed on the phase diagram of the Al_2O_3-SiO_2 composition in figure 3. The gradient curve represents the pressures and temperatures that might be found in a vertical bore hole. In such a hole andalusite would be encountered in rocks of appropriate composition at shallow depths, and kyanite would appear at the greatest depths. Sillimanite would be found *above* kyanite if it appeared at all. This conclusion follows directly from the positive intercept of the kyanite-andalusite boundary; if the gradient curve is to enter the kyanite field at all, it must do so at elevated temperature and pressure.

Sillimanite-bearing rocks often occupy the central parts of regionally metamorphosed terrains, and kyanite occurs in rocks around the margin of the sillimanite zone. This spatial distribution of the aluminosilicates is observed in New Hampshire and in the southeast Scottish Highlands. It would not be observed if the metamorphism resulted from deep burial in a region in which the geothermal gradient was everywhere the same and was "normal" in the sense that its curvature was as shown in figure 3. Horizontal gradients of temperature, pressure, or both during metamorphism are required to account for this distribution of kyanite and sillimanite. The existence of such horizontal gradients has previously been deduced from field studies (Harker, 1939, p. 185).

Field studies have revealed a "complete absence of cyanite from aureoles of thermal metamorphism" (Harker, 1939, p. 151), although sillimanite and andalusite are often found near the contacts of intrusive rocks. It appears that there is no known example of an igneous rock emplaced at suffiicently high pressure (and sufficiently low chemical potential of water) to make kyanite stable at the temperature prevailing in the wall rock. Once this temperature is better known, an upper limit to the pressure at which igneous rocks are known to solidify can be determined from the kyanite-sillimanite curve.

Syntectonic granites occurring in rocks in which kyanite had previously been formed through regional metamorphism are of special interest. Kyanite is never observed to persist up to the contacts, although sillimanite is characteristically present. This implies that a region of relatively high temperature or relatively low pressure existed near the contacts; the first alternative is a natural consequence of the emplacement of magma. The second alternative, which would be preferred by transformists, may require unlikely stress distributions.

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