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LETTER

Precise determinations of the equilibria kyanite ⇌ sillimanite and kyanite ⇌ andalusite and a revised triple point for Al_2SiO_5 polymorphs

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ABSTRACT

We investigated the equilibria kyanite ⇌ sillimanite and kyanite ⇌ andalusite using the piston-cylinder apparatus to refine the phase relationships among Al_2SiO_5 polymorphs. Experiments at the U.S. Geological Survey constrain the kyanite ⇌ sillimanite equilibrium to 14.3–14.6, 11.4–11.7, 9.5–10.0, and 6.0–6.5 kbar at 1000, 900, 800, and 600 °C, respectively. At UCLA, experiments limit the equilibrium to 14.4–14.6, >12.9, 11.8–12.2, and 7.0–8.0 kbar at 1000, 950, 900, and 700 °C, respectively. The equilibrium kyanite ⇌ andalusite was reversed between 7.4 and 8.0 kbar, 800 °C at UCLA. Our precise reversals require curvature of the kyanite ⇌ sillimanite boundary from 800 to 1000 °C (i.e., dP/dT increases with increasing P and T). The curvature may result from increasing Al-Si disorder in sillimanite with increasing T. Our experiments constrain the invariant point at 4.2 ± 0.3 kbar and 530 ± 20 °C.

INTRODUCTION

Experimental studies of the phase equilibria among Al_2SiO_5 minerals are replete with uncertainties resulting from the inability to demonstrate equilibrium among relatively coarse-grained naturally occurring andalusite, kyanite, and sillimanite, the inadequate calibration of pressure in experimental apparatus, and the misinterpretation of the results of experiments. For example, a historical review indicates that at 700 °C the equilibrium kyanite ⇌ sillimanite has been reported between 6.5 and 16.0 kbar. Such results have been in part responsible for the erratic placement of the Al_2SiO_5 triple point between 2 and 12 kbar (see Zen, 1969). Studies placing the kyanite ⇌ sillimanite equilibrium at relatively high pressures seemed inconsistent with petrologic studies of metamorphic rocks that indicated widespread occurrences of kyanite in rocks from the middle crust. This apparent contradiction led to the proposal of tectonic overpressures (Clark, 1961) to explain the common occurrences of high-pressure kyanite in relatively low-pressure rocks.

Considerable emphasis has been given to the importance of the equilibrium andalusite ⇌ sillimanite in establishing the location of the Al_2SiO_5 triple point (Richardson et al., 1969; Holdaway, 1971). However, the triple point can also be constrained with precise data on the equilibria kyanite ⇌ sillimanite and kyanite ⇌ andalusite in concert with data on molar volumes and entropies (see Newton, 1966b). We have adopted this approach.

EXPERIMENTAL METHODS

Starting materials

Experiments were conducted using coarse-grained natural gem-quality andalusite, kyanite, and sillimanite. In experiments conducted at the U.S. Geological Survey, materials used were kyanite from Faido, Switzerland containing 0.15 wt% Fe_2O_3 and sillimanite from Molodezhnaya Station, Antarctica (a large honey-yellow crystal, 1.5 × 1 × 1 cm, kindly provided by E. S. Grew) containing 0.95 wt% Fe_2O_3. At UCLA, experiments were conducted using two kyanite samples from Bahia, Brazil, one containing 0.20 wt% Fe_2O_3, the other 0.65 wt% Fe_2O_3; the sillimanite used is from Sri Lanka and contains 0.20 wt% Fe_2O_3. Andalusite from Minas Gerais, Brazil, containing 0.25 wt% Fe_2O_3, was used in experiments at UCLA on the equilibrium andalusite ⇌ kyanite.

The large gem-quality crystals were examined optically and with X-ray diffraction and the electron probe. The sillimanite from Molodezhnaya Station contained a few

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inclusions of spinel and biotite. These were easily removed by hand picking from the crushed sample. Microscopic examination of crushed samples indicated the absence of other phases except in the sample of kyanite from Switzerland. It contained a few nearly submicroscopic inclusions of a micaceous material, probably white mica, that occurred along cleavage surfaces. X-ray and electron probe analyses did not reveal the presence of phases other than Al_2SiO_5 and indicated that the andalusite, kyanite, and sillimanite were nearly stoichiometric Al_2SiO_5, with the exception of the Fe contents reported above. Other elements such as Ca, Cr, K, Mg, Mn, Ti, and V were at or below the limits of detection. The electron probe was operated at 15 kV of acceleration potential, a sample current of 15 nA, and counting periods of 20 s.

Samples were prepared for the experiments by crushing for a short period (<20 min) to −120 mesh. The minimum grain size was larger than about 100 μm. At the U.S. Geological Survey, the samples were washed briefly in 1 N HCl and rinsed twice in distilled deionized H_2O in an ultrasonic cleaner before drying in a vacuum oven at 90 °C.

Experimental procedures

For most experiments, equal amounts of kyanite and sillimanite or kyanite and andalusite were mixed together, along with 1–2 wt% Brazilian quartz to ensure that the vapor phase was saturated in SiO_2 during the experiments. The quartz was ground to −200 mesh, washed in HNO_3, and rinsed twice in deionized distilled H_2O before drying. For each experiment, 15 mg of sample was loaded into Pt or $Ag_{80}Pd_{20}$ capsules, 1.6 mm in diameter, that were sealed by arc welding. For experiments above 900 °C, the starting materials were loaded dry and the capsules sealed without any special precautions to eliminate moisture. For experiments conducted at 900 °C and below, 5–13 wt% H_2O was added to the starting materials to promote the rate of reaction. At the U.S. Geological Survey, NH_4OH was used as a flux, both as a pure reagent and in combination with H_2O. NH_4OH was chosen as a flux because both Al and Si are soluble in alkaline solutions, and it was thought that NH_4OH would not react with Al_2SiO_5 to form new phases or be incorporated into the structures of Al_2SiO_5.

All of the experiments were conducted in a piston-cylinder apparatus with furnace assemblies of 2.54 cm diameter fabricated from NaCl (S.R.B.) or KBr (A.M.). The assemblies used at UCLA were described by Boettcher et al. (1981), and those used at the U.S. Geological Survey were described by Bohlen (1984). Both types of furnace assembly are soft, ductile, and low strength. Experiments in the laboratory at the U.S. Geological Survey indicate that even calcite is not deformed structurally during pressurization in our alkali halide furnace assemblies. Consequently, complications arising from the structural deformation of the starting materials are exceedingly unlikely (see Paul, 1988). Temperature was measured with Pt-$Pt_{90}Rh_{10}$ thermocouples. Pressures have been calibrated against the melting points of CsCl, LiCl, and NaCl (see Bohlen, 1984). We used the piston-in technique by bringing pressure to 10–20% below that of the final value, increasing the temperature to that desired for the experiment, and then increasing pressure to the final value. The precision of P and T is ±0.1 kbar and ±2 °C. Accuracy of P and T is estimated to be better than ±0.5 kbar and ±10 °C.

Experimental products

We analyzed the products of all experiments optically and by X-ray diffraction. Reaction directions were determined both from optical examination of the products and by noting a substantial change in the integrated intensities of the diffraction peaks of the Al_2SiO_5 phases. Changes in the intensities of diffraction peaks were almost always consistent with the optical features that indicate growth of one Al_2SiO_5 polymorph and dissolution of the other, specifically grain-size dispersion and grain morphology. The stable Al_2SiO_5 phase always showed a large range in grain sizes, from crystallites several micrometers in maximum dimension to crystals larger than any in the starting mixture. The crystals were usually euhedral or at least showed sharp crystal edges. In contrast the unstable polymorph showed a limited range of grain sizes, as only relatively large grains remained. These large grains showed irregular anhedral shapes with scalloped and embayed edges.

Using the Phillips CM-12 transmission electron microscope at the University of Michigan, we determined the electron diffraction pattern of the small crystallites, inferred from the criteria noted above to be the stable polymorph, to establish with certainty the identity and cell parameters of the newly grown crystals. The electron diffraction patterns of the crystallites were indistinguishable from those of the starting materials, and although only a few products were investigated, the phases identified were those inferred to be stable.

The products of experiments conducted with NH_4OH at 800 and 900 °C did not show any noticeable differences in terms of the amount of reaction or the sizes and shapes of crystals as compared with those in which H_2O or H_2O-NH_4OH mixtures were used as fluxes. However, at 600 °C reaction rates were enhanced with the use of NH_4OH.

RESULTS

Kyanite ⇌ sillimanite

The results of the experiments on the equilibrium kyanite ⇌ sillimanite are listed in Table 1 and Figure 1. Richardson et al. (1968) reversed the equilibrium in an internally heated gas-pressure vessel. Their experiments constrain the phase boundary to lie between 8.0 kbar, 695 °C and 7.2 kbar, 700 °C; at 9.0 kbar, 750 and 775 °C; at 800 °C, 9.0 and 10.0 kbar; and at 825 °C, <10.0 kbar. Our results are consistent with these. However, the results of experiments conducted by Richardson et al. (1968)

TABLE 1. Experimental conditions and results

Experiment no.	Temperature (°C)	Pressure (kbar)	Duration (d)	Stable phase
Kyanite ⇌ sillimanite				
Experiments conducted at the U.S. Geological Survey				
1006	1000	14.6	6	kyanite
1034	1000	14.3	3	sillimanite
1022*	900	11.7	6	kyanite
1016*	900	11.4	6	sillimanite
1040*	800	9.8	10	kyanite
1007*	800	9.5	14	sillimanite
1020**	600	6.5	12	kyanite
1041**	600	6.0	12	sillimanite
Experiments conducted at UCLA				
3676	1000	14.6	12	kyanite
3675	1000	14.4	11	sillimanite
3691	950	12.9	6	sillimanite
3674	900	11.8	7	kyanite
3678	900	11.5	5	sillimanite
3694†	900	12.2	28	kyanite
3693‡	900	11.8	25	sillimanite
3681	700	8.3	28	kyanite
3670	700	7.5	31	sillimanite
Kyanite ⇌ andalusite				
Experiments conducted at UCLA				
3690	950	9.5	3	no change
3688	800	8.0	10	kyanite
3686	800	7.8	7	no change
3685	800	7.4	5	andalusite

* The reaction direction was the same as determined from the contents of two capsules placed in the same furnace assembly, one containing H_2O as a flux, the other containing NH_4OH or H_2O-NH_4OH mixtures as a flux.

** Experiments conducted using NH_4OH as a flux.

† Experiments conducted using a kyanite with wt% Fe_2O_3 = 0.20.

‡ Initial ratio of kyanite/sillimanite = 5.4/1.

in the piston-cylinder device are inconsistent with ours and generally locate the equilibrium boundary at higher pressures and with a somewhat larger d*P*/d*T* slope than that shown in Figure 1. Such discrepancies are very likely the result of problems with the calibration of pressure in the piston-cylinder device when using talc furnace assemblies with a diameter of 1.27. Our data agree with the reversals of Newton (1966a), 7.7–8.5 at 750 °C and 10.9–12.1 kbar at 900 °C (the latter as reported in Day and Kumin, 1980), obtained using 2.54-cm diameter talc furnace assemblies with a diameter of 2.54 calibrated against the melting of LiCl.

Inspection of Figure 1 indicates that a straight line cannot be fitted through all of our reversals. Our data require that the kyanite ⇌ sillimanite boundary has positive curvature with the d*P*/d*T* slope increasing with increasing *P* and *T*. However, the boundary has a constant d*P*/d*T* slope over the range of conditions of our experiments if it is calculated using the thermodynamic data of Hemingway et al. (in preparation) in conjunction with the molar volume data of Winter and Ghose (1979). The discrepancy between calculation and experiment can be resolved if sillimanite is partially disordered at temperatures below 1000 °C. The results of our experiments are consistent with about 10–15% disorder of Al and Si in sillimanite, but unfortunately our reversals are not sufficiently precise to allow an estimate of the temperature at which Al-Si disorder becomes significant. Our data allow for a boundary with a constant d*P*/d*T* at temperatures below about 900 °C. See Kerrick (1990) for a complete discussion of disorder in sillimanite.

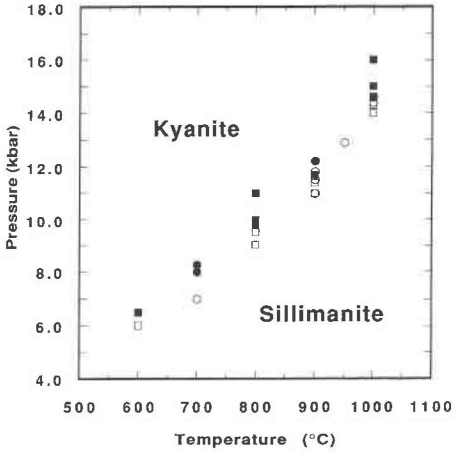

Fig. 1. *P-T* projection showing the results of experiments on the equilibrium kyanite ⇌ sillimanite. Square and circular symbols indicate experiments conducted at the U.S. Geological Survey and UCLA, respectively. Solid symbols indicate that kyanite grew at the expense of sillimanite; open symbols indicate that sillimanite grew at the expense of kyanite.

Kyanite ⇌ andalusite

The results on kyanite ⇌ andalusite are in Table 1 and in Figure 2 along with previous determinations by Newton (1966b), Richardson et al. (1969), and Holdaway (1971). The data reported here are consistent with previous reversals, although the extreme low pressure limit of our reversal is the same as the extreme high pressure limit of Newton's reversal at 800 °C.

A REVISED TRIPLE POINT

Much has been written about the importance of the equilibrium andalusite ⇌ sillimanite in constraining the location of the invariant point for Al_2SiO_5 polymorphs. However, the invariant point can also be constrained by the intersection of the equilibra kyanite ⇌ sillimanite and kyanite ⇌ andalusite (Newton, 1966b).

As noted above, we cannot assess the degree of curvature of the equilibrium kyanite ⇌ sillimanite in the temperature range of 600–800 °C. Because Al-Si disorder can be expected to decrease with decreasing temperature, the d*P*/d*T* slope of the reaction should approach a constant value below some unknown temperature; based on the data given here, that temperature could be as high as 900 °C. If we assume that the d*P*/d*T* slope is constant between 500 and 800 °C, we can limit the location of the invariant point by combining the calculated d*P*/d*T* slopes of the equilibria kyanite ⇌ sillimanite and kyanite ⇌ andalusite that are consistent with the experimental data (Fig. 2). For our calculations we have used the entropy data of Hemingway et al. (in preparation) and the molar volume data of Winter and Ghose (1979). Using this method, the invariant point is located at 4.2 kbar and

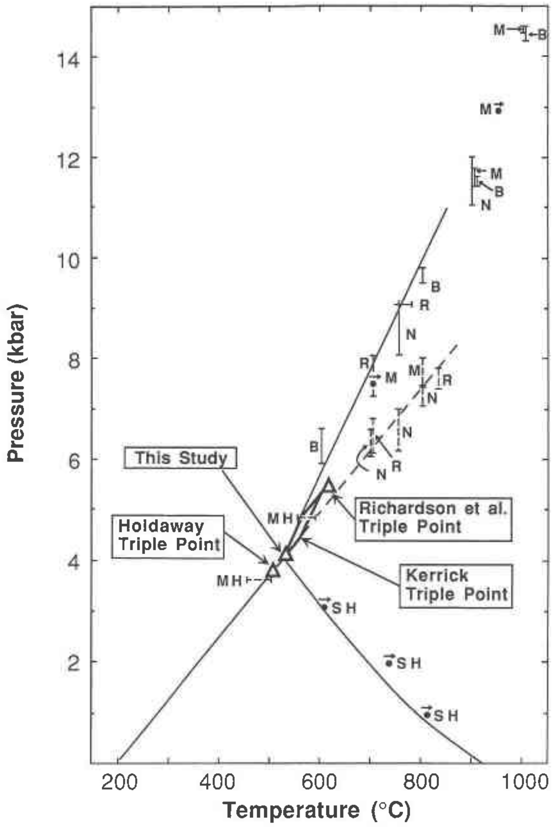

Fig. 2. *P-T* projection (modified from Kerrick, 1990, Fig. 3.46) showing results for kyanite = sillimanite (solid brackets) and kyanite = andalusite (dashed brackets). The dashed line is the metastable extension of the kyanite = andalusite boundary. Dots with arrows indicate conditions at which kyanite or andalusite reacted to sillimanite. B = Bohlen and M = Montana (reported in this study), MH = Holdaway (1971), N = Newton (1966b), R = Richardson et al. (1969), andalusite = sillimanite, SH = Heninger (1984) for andalusite → sillimanite. The data constrain the triple point to the narrow range of 4.2 ± 0.3 kbar and 530 ± 20 °C.

530 °C. Consideration of the imprecision in the measurement of *P* and *T* stated here and in the other experimental results shown in Figure 2 leads to uncertainty in the location of the invariant point of ±0.3 kbar and ±20 °C.

Our inferred location of the triple point is consistent with numerous petrologic studies, as discussed by Kerrick (1990), and in the detailed study of the Ballachulish aureole in Scotland (Pattison, 1990). It is something of a surprise to see that our inferred triple point is not much different from that deduced by Newton (1966b). Given the great deal of effort expended in trying to understand these equilibria and the numerous triple points published, the near coincidence of experiment, thermodynamic calculations, and field studies is heartening. However, the invariant point at 4.2 ± 0.3 kbar and 530 ± 20 °C pertains only to coarse-grained sillimanite. As emphasized by Salje (1986) and by Kerrick (1987), among others, there are likely to be many triple points that result from the energetic differences between coarse sillimanite and fibrolite. Therefore the interpretation of natural assemblages containing andalusite and sillimanite must be made with caution, even though the triple point for coarse sillimanite is now well constrained.

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