# Reversal of the metastable kyanite + corundum + quartz and andalusite + corundum + quartz equilibria and the enthalpy of formation of kyanite and andalusite

**Daniel E. Harlov,\* Robert C. Newton**

Department of the Geophysical Sciences, University of Chicago, 5734 S. Ellis Ave., Chicago, Illinois 60637, U.S.A.

## Abstract

The metastable equilibrium kyanite + corundum + quartz has been reversed with a $H_2O$ flux at 800 °C and 7.75 ± 0.25 kbar in the piston-cylinder apparatus with a NaCl pressure medium, and at 700 °C and 5.17 ± 0.32 kbar in an internally heated pressure vessel. The metastable equilibrium andalusite + corundum + quartz was reversed at 700 °C and 7.75 ± 0.25 kbar in the piston-cylinder apparatus. The reversals yield enthalpy of formation values from the oxides of −8.563 ± 0.189 kJ/mol for kyanite and −4.499 ± 0.125 kJ/mol for andalusite at 298 K. For reasons not fully understood, these values are systematically about 3 kJ more negative than values measured by high-temperature oxide-melt solution calorimetry. The kyanite + andalusite equilibrium determined by the present work satisfies all available experimental reversals. Remaining ambiguities concerning sillimanite prevent construction of a definitive $Al_2SiO_5$ triple point diagram.

Addition of Fe to the kyanite + corundum + quartz assemblage, buffered with magnetite-hematite $f_{O_2}$, did not detectably shift the equilibrium. We conclude that coexisting corundum and quartz found in some high-grade rocks are metastable relative to sillimanite.

## Introduction

Stability relations among the three polymorphs of $Al_2SiO_5$ have long been of interest to experimental petrologists (e.g., Althaus, 1967; Richardson et al., 1968, 1969; Holdaway, 1971; Bohlen et al., 1991). Much effort has been expended in mapping out these relations using reversed reactions between kyanite and sillimanite (Newton, 1966a; Richardson et al., 1968, 1969; Bohlen et al., 1991), kyanite and andalusite (Newton, 1966b; Richardson et al., 1969; Holdaway, 1971; Bohlen et al., 1991), and sillimanite and andalusite (Richardson et al., 1969; Holdaway, 1971; Kerrick and Heninger, 1984). In addition, the heat capacity as a function of temperature for each of the aluminum silicates has been accurately determined by Robie and Hemingway (1984), building on earlier work by Pankratz and Kelley (1964).

In contrast, the stability relationships among the aluminum silicates and their component oxides, $Al_2O_3$ and $SiO_2$, are less well known. A number of early workers observed the formation of corundum and quartz in experiments involving kyanite, sillimanite, and other aluminous phases. Clark et al. (1957) conducted experiments (at 750–1340 °C; 7–24 kbar) for 1–7 h in gas pressure apparatus with starting mixes of either andalusite and kaolinite or kaolinite and gibbsite placed in unsealed Au or Pt capsules. The final assemblages consisted of kyanite or sillimanite or both plus, in many cases, coexisting co-

rundum + quartz, which were considered by the authors to be metastable by-products. Aramaki and Roy (1963), using a hydrothermal apparatus with $SiO_2$-$Al_2O_3$ gels sealed in Au capsules, produced corundum + quartz at temperatures ranging from 500 to 800 °C and pressures above 3 kbar, but they were unable to produce a coexisting aluminum silicate. Richardson et al. (1968), in an experimental study of the kyanite + sillimanite equilibrium, observed corundum (but no quartz) in a number of hydrothermal experiments (11–16 kbar, 850–1000 °C) whose starting assemblage consisted of kyanite and sillimanite. In experiments involving stability relations among clinochlore, muscovite, and quartz, Bird and Fawcett (1973) observed that for experiments in the range of 7–10 kbar and 530–725 °C, for a starting assemblage of corundum, quartz, and a few small kyanite seeds, plus other aluminous phases, the final assemblage contained kyanite and quartz but no corundum, with the kyanite demonstrating definitive growth. In similar experiments, which contained quartz and corundum but no kyanite in the starting mix, corundum persisted in the final assemblage. One can conclude from these studies that the aluminum silicates are marginally stable relative to their component oxides. This appears to be especially true of sillimanite, since many of the syntheses of corundum + quartz were performed in the generally accepted field of stability of that polymorph. The several reported natural parageneses of corundum + quartz in granulites from sillimanite-bearing terranes (e.g., Motoyoshi et al., 1990) may perhaps be explained by very slight metastability, although it is possible that a minor component such as

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\* Present address: Department of Earth and Atmospheric Sciences, Purdue University, West Lafayette, Indiana 47907, U.S.A.

**TABLE 1.** Enthalpy of formation determinations for the Al$_2$SiO$_5$ phases

| Kyanite | Andalusite | Sillimanite | References |
|---------|------------|-------------|------------|
| **Solution calorimetry** | | | |
| −5.92 ± 0.84 | −2.07 ± 1.26 | +1.46 ± 0.59 | Anderson and Kleppa (1969) |
| | | | Charlu et al. (1975) |
| | | | Anderson et al. (1977) |
| −5.24 ± 0.59 | −0.40 ± 0.75 | +1.34 ± 1.26 | Kiseleva et al. (1983) |
| −5.72 ± 0.63 | −2.53 ± 0.89 | +0.81 ± 0.73 | Topor et al. (1989) |
| **Experimental phase equilibrium** | | | |
| −7.82 | −3.57 | +0.31 | Berman (1988) |
| −8.80 ± 1.24 | −4.74 ± 1.24 | −0.14 ± 1.24 | Holland and Powell (1990) |
| −8.56 ± 0.19 | −4.50 ± 0.12 | | present study |

*Note:* Values are referenced from the oxides at 298 K, kJ/mol.

Fe$_2$O$_3$ might make the quartz + corundum assemblage slightly more stable than sillimanite.

The free energies of formation of Al$_2$SiO$_5$ phases relative to the oxides and to the elements are not well known. The entropies, and, hence, the entropies of formation, are well determined by precise heat-capacity and heat-content data for the polymorphs and their oxides (Pankratz and Kelley, 1964; Robie and Hemingway, 1984; Hemingway, 1987). The only significant uncertainty in the entropy data consists of possible Al-Si disorder in sillimanite at high temperatures, as envisioned by Greenwood (1972). There is some evidence for such disorder from high-temperature solution calorimetry of heat-treated natural sillimanite (Navrotsky et al., 1973). Robie and Hemingway's (1984) calculations of the Al$_2$SiO$_5$ relations from their heat-capacity data do not require a sillimanite entropy increment of disordering to explain the experimental data on the kyanite + sillimanite equilibrium to 900 °C. A reversed bracket at 1000 °C by Bohlen et al. (1991) is at somewhat higher pressures than that expected from Robie and Hemingway's (1984) calculations, which may require some sillimanite disorder.

A larger uncertainty in the free energy of formation of the Al$_2$SiO$_5$ phases is the enthalpy of formation. Although a few studies exist based on high-temperature solution calorimetry of natural samples (Anderson and Kleppa, 1969; Anderson et al., 1977; Kiseleva et al., 1983), these are not of sufficient precision to define the enthalpies of formation of the Al$_2$SiO$_5$ phases for accurate phase-diagram calculations. The major thermodynamic data sets for minerals (Berman, 1988; Holland and Powell, 1990) tabulate enthalpy of formation derived from experimental phase-equilibrium data. Table 1 lists the enthalpy of formation data of the Al$_2$SiO$_5$ polymorphs from high-temperature solution calorimetry and from experimental phase-equilibrium derivations. In spite of the large uncertainties in the calorimetric values, there is a significant systematic discrepancy of 2–4 kJ between calorimetry and phase-equilibrium derivations, with the calorimetry yielding less negative values of $\Delta H_f^\circ$.

In this study we perform the most direct possible phase-equilibrium determination of the enthalpy of formation of kyanite and andalusite, by reversing the metastable reactions of formation from the oxides. It has long been known that reactions in seeded mixes in the Al$_2$O$_3$-SiO$_2$ and other mineral systems may be reversed metastably in the absence of seeds of more stable phases. The reversals secured in this study at 700 and 800 °C are metastable relative to sillimanite, which is a slowly nucleating phase. They provide accurate determinations of the free energy of formation of kyanite and andalusite. Volume considerations indicate that analogous reversal of the metastable formation reaction of sillimanite is not feasible. The high-quality volume and heat-capacity data available for the Al$_2$SiO$_5$ minerals and their component oxides allow a superior determination of the enthalpy of formation of kyanite and andalusite, which may then be checked against the results of solution calorimetry and of direct experimental reversals of the kyanite + andalusite equilibrium.

## EXPERIMENTAL PROCEDURE AND CHARACTERIZATION OF EXPERIMENT PRODUCTS

### Apparatus

Experiments above 6 kbar were performed in both a ¾-in. (1.94-cm) and a 1-in. (2.54-cm) piston-cylinder apparatus using a NaCl-graphite furnace assembly as described in Bohlen (1984). Charges, consisting either of equimolar amounts of kyanite, corundum, and quartz or of andalusite, corundum, and quartz, in 10-mg batches + 2 mg of H$_2$O, were loaded into Pt capsules, which were sealed by arc welding. In the 1-in. piston-cylinder experiments, two Pt capsules were placed side by side in the salt assembly. Care was taken that the capsules touched neither each other nor the graphite sleeve. The ceramic-sheathed chromel-alumel thermocouple was placed atop the capsules. The tip of the thermocouple was protected by a thin layer of Al$_2$O$_3$ cement. The accuracy of the thermocouple was determined to be within ±2 °C of the measured temperature, with no correction for pressure. Total error in temperature, which takes into account thermal gradients within the NaCl setup, is ±5 °C. In bringing an experiment up to pressure, the piston-out technique was used by elevating the pressure to a point approximately 20% below the desired pressure, then increasing

**TABLE 2.** Kyanite + corundum + quartz experiments in piston-cylinder apparatus

| Expt. | $T$ (°C) | $P$ (kbar) | $t$ | Ky used | Diameter (in.) | Results | Comments |
|-------|----------|------------|-----|---------|----------------|---------|----------|
| 90-KS-6 | 800 | 10 | 14 h | 4959 | ¾ | *Ky* (Cor Qtz) | |
| 90-KS-7 | 800 | 8 | 36 h | 4959 | ¾ | *Ky* Cor Qtz | |
| 90-KS-8 | 800 | 6 | 36 h | 4959 | ¾ | (Ky) *Cor Qtz* | |
| 90-KS-9 | 800 | 7 | 48 h | 4959 | ¾ | Ky *Cor Qtz* | |
| 90-KS-13 | 800 | 7.5 | 3.5 d | 4959 | ¾ | Ky *Cor Qtz* | |
| 90-KS-15 | 850 | 8.5 | 2.5 d | 4959 | ¾ | Ky *Cor Qtz* | |
| 90-KS-16 | 850 | 8 | 24 h | 4959 | ¾ | (Ky) *Cor Qtz* | |
| 90-KS-20 | 800 | 8 | 48 h | Bahia | 1 | *Ky* Cor Qtz | +90-KS-21 |
| 90-KS-21 | 800 | 8 | 48 h | 4959 | 1 | *Ky* Cor Qtz | +90-KS-20 |
| 90-KS-22 | 800 | 7.5 | 48 h | Bahia | 1 | Ky *Cor Qtz* | +90-KS-23 |
| 90-KS-23 | 800 | 7.5 | 48 h | 4959 | 1 | Ky *Cor Qtz* | +90-KS-22 |
| 90-KS-28 | 800 | 8.5 | 48 h | 4959 | 1 | *Ky* Cor Qtz | +90-KS-29 |
| 90-KS-29 | 800 | 8.5 | 48 h | Bahia | 1 | *Ky* Cor Qtz | +90-KS-28 |
| 90-KS-30 | 800 | 7 | 48 h | 4959 | 1 | (Ky) *Cor Qtz* | +90-KS-31 |
| 90-KS-31 | 800 | 7 | 48 h | Bahia | 1 | (Ky) *Cor Qtz* | +90-KS-30 |
| 90-KS-37 | 800 | 10 | 23 h | 4959 | ¾ | *Ky* Cor Qtz | +Hm |
| 90-KS-38 | 800 | 10 | 48 h | 4959 | ¾ | *Ky* (Cor Qtz) | +Hm |
| 90-KS-39 | 800 | 9 | 16 h | 4959 | ¾ | *Ky* (Cor Qtz) | +Hm |
| 90-KS-40 | 800 | 7 | 5 d | 4959 | ¾ | (Ky) *Cor Qtz* | +Hm |
| 90-KS-42 | 850 | 11.5 | 48 h | 4959 | ¾ | *Ky* (Cor Qtz) | |
| 90-KS-46 | 800 | 7.5 | 75 h | 4959 | ¾ | Ky *Cor Qtz* | |
| 90-KS-47 | 800 | 7.5 | 46 h | 4959 | ¾ | (Ky) *Cor Qtz* | |
| 90-KS-48 | 800 | 8 | 44 h | 4959 | ¾ | *Ky* (Cor Qtz) | |

*Note:* The italicized phases indicate relative increase; parentheses indicate that the phase either totally disappeared or only remained in trace amounts; +Hm = $Fe_2O_3$-saturated experiments. Double-capsule experiments indicated in Comments. (For instance, capsules 90-KS-20 and 90-KS-21 were contained in the same experiment.)

the temperature to the experimental conditions such that thermal expansion of the salt brought the experiment to the final pressure. The uncertainty in the pressure is estimated to be ±200 bars. Experiments lasted from 14 h to 25 d. The pressure, current, and voltage of the graphite furnace were monitored during the experiment. Only those experiments in which the capsule seals held, in which there was no significant shift in either pressure or heater power and in which there was no disruption in the experimental setup are listed in the final tabulations (Tables 2–4).

Experiments on the kyanite + quartz + corundum equilibrium below 6 kbar were performed in an internally heated Ar pressure vessel. Capsules and the starting material were the same as in the piston-cylinder experiments. The capsules (two identical samples in each experiment) were held in a thick Cu holder to reduce temperature gradients. Chromel-alumel thermocouples at

opposite ends of the capsules never read more than 2 °C apart. Pressures were measured to ±15 bars by a manganin cell calibrated against a precision Heise gauge. Pressures were checked several times during the duration of the experiments, which was 12–21 d.

### Starting materials

Starting materials included Fisher certified reagent $Al_2O_3$ annealed at 1300 °C for 48 h; purified natural quartz from Lisbon, Maryland, crushed to <1-mm grain size, leached with dilute HF + $H_2SO_4$, and ignited; two samples of natural kyanite, and one sample of natural andalusite. One of the kyanite samples was from an unknown locality (University of Chicago, Department of the Geophysical Sciences collection no. 4959) and consisted of a polycrystalline aggregate of pale blue crystals. A portion of this aggregate was crushed, and individual blades of kyanite, free of sheet silicate, were selected. Microscopic examination in refractive index oil ($n = 1.540$) showed

**TABLE 3.** X-ray diffractogram peak-height ratios of quenched charges of 700 °C experiments showing changes in amount of kyanite (Ky) relative to corundum (Cor) and quartz (Qtz)

| Expt. | Conditions | Ky (0$\bar{2}$1)/ Cor (012) Caps. 1 | Caps. 2 | Ky (0$\bar{2}$1)/ Qtz (100) Caps. 1 | Caps. 2 |
|-------|-----------|------|------|------|------|
| 91-KS-50 | 4.85 kbar 21 d | 0.78 | 0.75 | 0.72 | 0.84 |
| Starting material (2 portions) | untreated | 1.03 | 0.95 | 1.07 | 1.12 |
| 91-KS-52 | 5.48 kbar 12 d | 1.04 | 1.09 | 1.23 | 1.20 |

**TABLE 4.** Andalusite + corundum + quartz experiments in piston-cylinder apparatus

| Expt. | $T$ (°C) | $P$ (kbar) | $t$ (d) | Diameter (in.) | Results |
|-------|----------|-----------|---------|----------------|---------|
| 91-AC-4 | 700 | 9 | 12 | ¾ | And *Cor Qtz* |
| 91-AC-5 | 700 | 6.1 | 11 | ¾ | *And* Cor Qtz |
| 91-AC-6 | 700 | 8 | 16 | ¾ | And *Cor Qtz* |
| 91-AC-7 | 700 | 7 | 17 | ¾ | *And* Cor Qtz |
| 91-AC-9 | 700 | 7.5 | 9 | ¾ | And Cor Qtz* |
| 91-AC-10 | 700 | 7.5 | 25 | ¾ | *And* Cor Qtz |

*Note:* The italicized phases indicate relative increase.
* Reaction direction could not be determined.

no foreign phases. Both the second sample of kyanite (pale green) and the andalusite were gem-quality specimens from Bahia, Brazil. Microprobe analysis of the kyanite and andalusite samples indicated a $Fe_2O_3$ content of <0.1 oxide wt% as the major impurity.

## Detection of reaction

Charges were characterized using X-ray powder diffraction. Figure 1 shows the diffractograms of the standard kyanite + corundum + quartz mixture before and after two experiments. Growth or decrease of a phase by 15–20% was determined by comparing the heights of kyanite or andalusite peaks with nearby corundum and quartz peaks. At 800 °C and 8 kbar, the kyanite peaks decreased relative to the corundum and quartz peaks, whereas at the same temperature and 7.5 kbar, corundum and quartz decreased relative to kyanite. In general, the increase or decrease in the relative peak heights was sufficient to locate both the andalusite + quartz + corundum equilibrium at 700 °C and the kyanite + quartz + corundum equilibrium at 700 and 800 °C within ±300 bars.

## Effect of trivalent Fe

We performed a number of experiments in which 1 mg of $Fe_2O_3$ was added to the quartz + corundum + kyanite mix, and a high $f_{O_2}$ was created by surrounding the Pt capsule with hematite, plus a small amount of $H_2O$, in a large welded Au capsule. The large Au capsule was in turn surrounded by an equal-weight mixture of NaCl and $Fe_2O_3$. This mixture was separated from the graphite heater by a thin shield of crushable ceramic. These experiments were designed to test the possibility that $Fe_2O_3$ might stabilize corundum and quartz relative to kyanite at pressures near the sillimanite-kyanite boundary.

## RESULTS AND DISCUSSION

Tables 2 and 3 list the results for the kyanite + corundum + quartz experiments. At 800 °C the equilibrium pressure for the metastable breakdown of kyanite to corundum + quartz was reversed at 7.75 ± 0.25 kbar in experiments with a duration of 48 h. At 700 °C, much longer experiments were required to detect a reaction. For these experiments, a carefully homogenized starting mix was used in which the powder XRD peak heights of se-
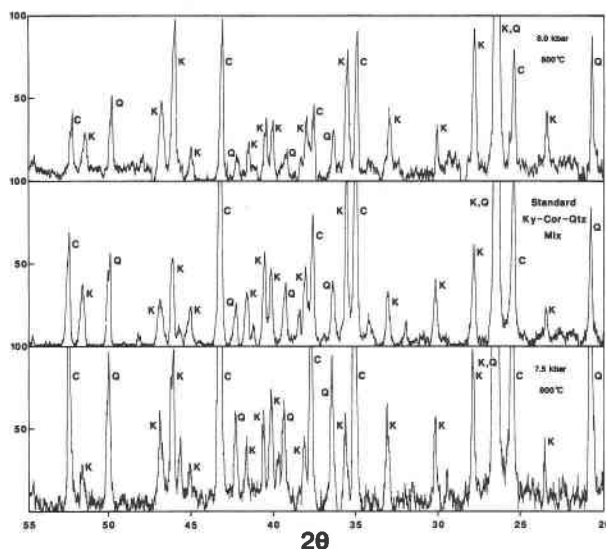


Fig. 1. X-ray powder diffraction scans (CuKα, ½°/min) of quenched charges from experiments at 8.0 and 7.5 kbar and 800 °C along with the standard kyanite + corundum + quartz mix before the experiment (K = kyanite, C = corundum, Q = quartz). X-ray peaks of kyanite have generally increased in strength relative to those of corundum or quartz for the 8.0-kbar experiment, whereas at 7.5 kbar X-ray peaks from corundum and quartz have increased in strength relative to kyanite.

lected maxima of kyanite (0$\bar{2}$1), corundum (012), and quartz (100) were initially very nearly equal (Table 3). The results from pairs of capsules equilibrated for 21 d at 4.85 kbar and for 12 d at 5.48 kbar were consistent. XRD peak-height ratios indicating the reversed direction of the reaction in this pressure range at 700 °C are given in Table 3. The metastable breakdown of andalusite to corundum + quartz at 700 °C was reversed definitively in experiments lasting 11–25 d at 7.75 ± 0.25 kbar. The experiments are listed in Table 4. At 750 and 800 °C and 6–8 kbar, melting occurred in the andalusite + corundum + quartz + $H_2O$ charges, as detected by the presence of glass and the decrease of quartz peaks in the X-ray patterns. This metastable melting prevented higher temperature reversal of the equilibrium.

Measured thermodynamic data of high quality are available for the $Al_2SiO_5$ minerals and their component oxides (Table 5). These data allow calculation of the stan-

TABLE 5. Standard molar entropy ($S°_{298}$), heat capacity coefficients ($a$–$e$), standard molar volume ($V°_{298}$), thermal expansivity ($\alpha V$), and compressibility ($\beta V$), in J, bar, K with sources (thermal properties; volume properties)

| | $S°_{298}$ | $a$ | $b \times 10^5$ | $c \times 10^{-4}$ | $d \times 10^6$ | $e$ | $V°_{298}$ | $\alpha V \times 10^5$ | $\beta V \times 10^6$ | Refs. |
|---|---|---|---|---|---|---|---|---|---|---|
| Kyanite | 82.30 | 303.90 | −1339.0 | −89.520 | 0 | −2904.3 | 4.414 | 11.2 | 1.9 | 1, 2 |
| Andalusite | 91.39 | 290.40 | −1052.0 | −110.90 | 0 | −2627.8 | 5.153 | 12.7 | 2.8 | 1, 2 |
| α-quartz | 41.46 | 81.145 | 1828.3 | −18.099 | 5.4058 | −698.46 | 2.269 | 8.0 | 5.9 | 3, 2 |
| β-quartz | | 57.959 | 933.02 | 183.47 | 0 | 0 | 2.367 | 0 | 2.6 | 3, 2 |
| Corundum | 50.92 | 157.36 | 71.899 | −189.69 | 0 | −988.04 | 2.558 | 6.4 | 0.9 | 4, 2 |

*Note:* $V(T,P) = V°_{298} + (\alpha V)(T − 298) − (\beta V)P$. $C_p = a + bT + c/T^2 + dT^2 + eT^{-\frac{1}{2}}$; $\Delta H°(\alpha\text{-Qz} \to \beta\text{-Qz}) = 625$ @ 844 K (Ref. 3); $dP/dT$ ($\alpha$-Qz → $\beta$-Qz) = 42.0 (Ref. 5).
Refs.: 1 = Robie and Hemingway (1984); 2 = Holland and Powell (1990); 3 = Hemingway (1987); 4 = Robie et al. (1978); 5 = Cohen and Klement (1967).
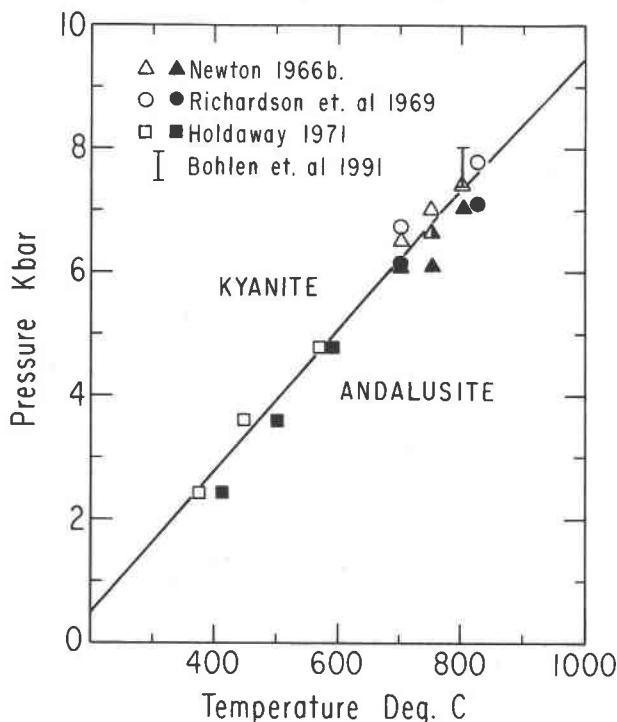
Fig. 2. Kyanite + andalusite equilibrium calculated from the present determinations of the enthalpy of formation of the phases and the measured data of Table 5. The calculated curve satisfies all of the available experimental reversals of the equilibrium. The equilibrium is metastable with respect to sillimanite above 530 °C, according to the definitive work of Bohlen et al. (1991).
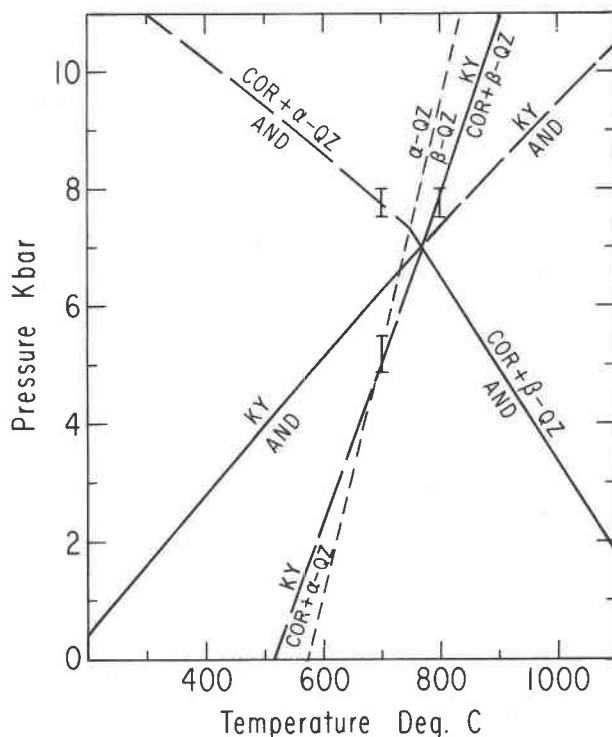


Fig. 3. Calculated phase-equilibrium relations among kyanite (KY) and andalusite (AND), quartz (QZ), and corundum (COR). Experimental brackets of metastable formation reactions of kyanite and andalusite are shown. Long dashed lines are metastable with respect to andalusite or kyanite. Equilibria depicted by continuous lines are actually metastable with respect to sillimanite, except for the kyanite-andalusite line below 530 °C.

dard enthalpy of formation from the oxides of kyanite and andalusite. The experimental data for the reaction with kyanite at 800 °C yields $\Delta H^\circ_{f,298,ox}$ (kyanite) = $-8.624 \pm 0.117$ kJ/mol, and the bracket at 700 °C yields $-8.501 \pm 0.149$ kJ/mol. The mean value is taken as $-8.563 \pm 0.189$ kJ/mol or $-2594.96$ kJ from the elements. This value falls between the data set values of $-2594.22$ (Berman, 1988) and $-2595.33$ kJ (Holland and Powell, 1990) and is in satisfactory agreement with them.

Our $\Delta H^\circ_f$ (kyanite) value at 973 K of $-10.36 \pm 0.15$ kJ is not in good agreement with the value derived from high-temperature enthalpy of solution measurements in $Pb_2B_2O_5$ melts. The data of Anderson and Kleppa (1969) for kyanite, coupled with the data of Charlu et al. (1975) for quartz and corundum, all measured at 970 K, give $-7.78 \pm 0.83$ kJ. The data of Kiseleva et al. (1983) at 973 K, which yield $-7.11 \pm 0.59$ kJ and those of Topor et al. (1989) at 1000 K, which give $-7.58 \pm 0.63$ kJ, are in similar disagreement with the present phase-equilibrium work.

The standard enthalpy of formation of andalusite at 298 K determined by this study is $-4.50 \pm 0.12$ kJ/mol from the oxides ($-2590.90$ from the elements), where the uncertainty reflects only the width of the phase-equilibrium bracket. Agreement with the values of Berman (1988)

and Holland and Powell (1990), respectively, $-3.57$ and $-4.74$ kJ/mol, is quite good. However, the high-temperature solution calorimetric values of Anderson et al. (1977: $-4.60 \pm 0.77$ kJ/mol at 970 K), Kiseleva et al. (1983: $-2.93 \pm 0.75$ kJ/mol at 973 K), and Topor et al. (1989: $-4.88 \pm 0.95$ kJ/mol at 1000 K) are not in good agreement with our value of $-7.03 \pm 0.12$ kJ/mol at 973 K. We have no explanation for the consistent disagreement of 2–4 kJ/mol between the values derived from solution calorimetry and the phase-equilibrium studies.

The kyanite + andalusite equilibrium can be calculated accurately from the experimental data and the measured data of Table 5. Figure 2 shows that the existing hydrothermal reversals of this equilibrium under well-controlled conditions are all in close agreement with the calculated curve. The agreement further demonstrates the validity of the present experimental $\Delta H^\circ_f$ values for kyanite and andalusite. Figure 3 shows all of the P-T phase relations of the $Al_2O_3$-$SiO_2$ system calculated from the data of Table 5. The equilibria depicted are metastable with respect to sillimanite except for the portion of the kyanite-andalusite curve below 530 °C.

The experiments made with $Fe_2O_3$-rich starting materials showed metastable reversal of the kyanite + quartz

+ corundum equilibrium at the same $P$-$T$ conditions as in the Fe-free system (Table 2). This result indicates that Fe$^{3+}$ does not stabilize the assemblage corundum + quartz relative to kyanite under high-grade metamorphic conditions.

## INTERPRETATION OF NATURAL OCCURRENCES

The presence of corundum + quartz + aluminum silicate as a natural assemblage has been noted by a few authors, chiefly in high-pressure, high-temperature terranes. In two of these terranes, the northwest Adirondacks (sillimanite + corundum + quartz: Powers and Bohlen, 1985), and the Elkhorn district, Montana (andalusite + corundum + quartz: Steefel and Atkinson, 1984), this assemblage does not appear to be texturally in equilibrium. In the Adirondacks, sillimanite + corundum + quartz is found only in the high-temperature area immediately bordering the Diana syenite. Here corundum grains are encased in plagioclase and thus isolated from the sillimanite and quartz. In the Elkhorn district, andalusite occurs as islands surrounded by halos of muscovite within a potassium feldspathized quartz-feldspar porphyry, or as euhedral to subhedral laths or granules within intensely sericitized and silicified feldspar porphyry. In both occurrences the andalusite appears to be of hydrothermal origin. The corundum also appears to be of hydrothermal origin and consists principally of anhedral grains surrounded by a corona of fine muscovite and is found only in certain localities, specifically to the north of a fault zone that divides the district.

In some other high-grade terranes, aluminum silicates appear to be more nearly in textural equilibrium with quartz and corundum. An Fe-Mn deposit on the island of Hinnøy in the Lofoten-Vesterålen islands of northern Norway (Krogh, 1977) contains quartz-banded hematite ore and quartz-banded magnetite ore interbedded with fine-grained quartzo-feldspathic gneisses and impure quartzites. In the quartz-banded magnetite ore, kyanite occurs locally in the form of secondary aggregates surrounding the corundum grains in the presence of quartz. In this occurrence, corundum + quartz appears to be in arrested reaction to form kyanite. Another occurrence of the assemblage corundum + quartz is a spinel-bearing quartzite from the Napier complex in Enderby Land, Antarctica (Motoyoshi et al., 1990). The spinel occurs as clusters of small equant grains. Corundum is always found in direct association with a spinel grain, usually in the form of a partial rim. In a number of cases the corundum is separated from the surrounding quartz matrix by a thin rim of aluminum silicate, which the authors tentatively assume to be sillimanite.

Since the quartz-banded magnetite ore from northern Norway is an oxidized Fe-rich system, Krogh (1977) speculated that the presence of Fe$^{3+}$ could conceivably shift the kyanite + corundum + quartz equilibrium upward into the kyanite stability field. However, the results of our hematite-saturated experiments indicate that the presence of Fe$^{3+}$ in the kyanite + corundum + quartz system does not produce any significant stabilization of quartz + corundum relative to kyanite. Metastable appearance of quartz + corundum in the sillimanite field could be possible under some conditions because of the difficulty of nucleation of stable (Al-Si) ordered sillimanite.

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