

## A reevaluation of the stability relations of andalusite: Thermochemical data and phase diagram for the aluminum silicates

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### ABSTRACT

Until recently, little effort has been made to evaluate critically the numerous experimental studies on andalusite stability relations. In this contribution, we carefully examine most studies done since 1966. Experimental problems include (1) difficulty in measuring small amounts of reaction, (2) the effect of fibrous sillimanite and intergrown quartz, and (3) the effect of elevated  $\text{Fe}_2\text{O}_3$  in sillimanite. By evaluating the effects of these and other factors on previous experiments, we have determined valid, self-consistent reversals and half-reversals for the kyanite = andalusite and andalusite = sillimanite equilibria. Almost all of the experimental studies have provided reversal information. We have determined the best possible molar volumes of the pure  $\text{Al}_2\text{SiO}_5$  end-members. By combining our molar volumes and the thermochemical data of Hemingway et al. (1991) with the acceptable reversals for the above reactions and for kyanite = sillimanite, we have obtained (1) entropy and enthalpy for kyanite, andalusite, and sillimanite, and (2) a phase diagram that has a triple point at  $504 \pm 20^\circ\text{C}$ ,  $3.75 \pm 0.25$  kbar. The andalusite = sillimanite boundary may be up to  $20^\circ\text{C}$  above that for pure  $\text{Al}_2\text{SiO}_5$  because of the effects of  $\text{Fe}_2\text{O}_3$  on sillimanite and andalusite. We emphasize the importance of careful evaluation of experiments and the secondary role of comparison of experimental results with natural systems. Determination of phase diagrams from the positions of equilibria in natural systems may produce significant errors resulting from the experimental calibration of the natural system.

### INTRODUCTION

During the past two decades, few studies have been undertaken to evaluate the various experimental pressure-temperature ( $P$ - $T$ ) results on aluminum silicates. Problems are most acute for the andalusite-sillimanite stability relations, where there is significant disagreement. Many petrologists appear to have arbitrarily accepted one or more experimental studies and rejected others. Holdaway (1971) evaluated several of the studies that were available at the time. Newton (1987) has provided an analysis of the problem, concluding that no clear choice can be made between the experimental studies of Richardson et al. (1969) and Holdaway (1971). Recently, Kerrick (1990) has undertaken an exhaustive review of the various experimental studies of the  $\text{Al}_2\text{SiO}_5$  polymorphs.

Kerrick's (1990) book helps to clear the air on a number of important aspects of  $\text{Al}_2\text{SiO}_5$  stability relations and in so doing provides important background for the present contribution. However, major questions remain. We do not agree with Kerrick's evaluations of several of the studies. There are additional important points to be made, which further constrain the equilibria in a totally self-consistent fashion. Many previous studies provide at least some information regarding the equilibria, and we believe these constraints should be considered seriously. Thus, a principal reason for this communication is to

reevaluate the various experimental studies, determine all valid reversals and half-reversals, and explain any discrepancies.

A second reason for undertaking this project is to arrive at the best possible thermochemical data for the aluminum silicates that can be used with such data for other silicates in data bases. Two recent efforts in this regard are noteworthy: that of Berman (1988) and that of Hemingway et al. (1991). Both of these studies produced aluminum silicate  $P$ - $T$  diagrams in general agreement with the one proposed here. However, the Berman data do not include the more recent calorimetric data of Hemingway et al. (1991). Both approaches include thermal expansion. The Berman data base includes compressibility as well, but the two studies use slightly different values of molar volumes ( $V$ ) for the polymorphs. We seek to determine thermochemical data that meet the following restrictions: (1) They begin with the specific heat ( $C_p$ ) data of Hemingway et al. (1991) and the best possible values of  $V$ . (2) They agree, as well as possible, with the standard entropy ( $S$ ) and enthalpy ( $H$ ) values of Hemingway et al. (1991). (3) They are consistent with acceptable experimental reversals and half-reversals.

### POTENTIAL PROBLEMS WITH SILLIMANITE

Of the three aluminum silicates, sillimanite poses the most difficulty in experimental work. Problems that have

been suggested with sillimanite starting material and perhaps with sillimanite that grows during some experiments are (1) the possibility of Al-Si disorder, (2) the problem of fibrous sillimanite, and (3) the chemical effect of Fe<sup>3+</sup> (discussed later in this report). For either problem 1 or 2, if the starting sillimanite is not in its most stable form, the result is to move the apparent andalusite = sillimanite phase boundary to higher *T*, i.e., to stabilize andalusite relative to sillimanite in the experiments.

### Al-Si disorder

Sillimanite is unique among the aluminum silicates in that it contains both Al and Si in tetrahedral sites (Ribbe, 1980), thus leading to the possibility of Al-Si disorder. Holdaway (1971) appealed to limited Al-Si disorder to explain the fact that his experimental andalusite = sillimanite *P-T* slope was steeper than that calculated from entropy and the volume data available at the time. More recent entropy data (Robie and Hemingway, 1984; Hemingway et al., 1991) show that Al-Si disorder is not necessary to explain Holdaway's slope. More importantly, most crystal structure studies on natural sillimanite fail to detect any Al-Si disorder (Cameron and Ashworth, 1972; Kerrick, 1990). However, Bish and Burnham (1992) have recently shown that a fibrous sillimanite from a granulite from Brittany, France, has about 18% Al-Si disorder, suggesting that under some conditions, perhaps those of rapid growth or high *T*, sillimanite may have some disorder. On the basis of Kerrick's (1990) analysis, we conclude that coarse-grained sillimanite has no significant disorder below about 800 °C; however, at least some fibrous sillimanite has Al-Si disorder.

### Fibrous sillimanite

Kerrick (1990) carefully analyzed the existing data on the nature of fibrous sillimanite. He concluded that fibrous sillimanite and sillimanite are the same mineral. Most fibrous sillimanite has no measurable Al-Si disorder. In most cases, the only significant difference between the two materials is one of grain size. They have identical unit-cell and molar volumes. Hemingway et al. (1991) showed that thermochemical data (*C<sub>p</sub>*, *S*, *H*, and thermal expansion) for fibrous sillimanite are similar to those of sillimanite. The extremely fine grain size of some portions of fibrous sillimanite samples, <0.5 μm in diameter, may destabilize it, perhaps because of surface energy effects (Kerrick, 1990, p. 216) and decrease its *P-T* stability relative to andalusite. By analogy with studies of coarse fragments of cryptocrystalline quartz, Hemingway et al. (1991) suggested that fibrous sillimanite crystallites may have diminished surface energy effects when they occur as intergrown aggregates. They also suggested that differences in preparation of fibrous sillimanite samples may have caused observed differences in the behavior of fibrous sillimanite in various experiments.

A second factor that may well affect fibrous sillimanite behavior in experimental studies is the fact that fibrous sillimanite commonly contains intergrown minerals,

which cannot be completely removed by physical methods. If the fibrous sillimanite contains intergrown quartz, and corundum is added to the experimental starting material, a spontaneous reaction,



occurs. At conditions near the andalusite = sillimanite equilibrium, if seeds of both minerals exist in the system, both minerals may grow, thus possibly giving a false indication of stability. The spontaneous reaction producing both minerals can be expected to proceed faster than the near-equilibrium andalusite = sillimanite reaction producing the stable mineral. Depending on the method of detecting reaction, impurities in fibrous sillimanite may be a serious drawback.

These two factors, fine grain size and possible presence of quartz, must be taken into account when interpreting experimental studies in which part or all of the sillimanite was fibrous.

### THE PROBLEM OF WEIGHING ERROR

One of the experimental methods that has yielded some of the most tightly constrained reversals for andalusite equilibria is the crystal growth method used by Holdaway (1971), Bowman (1975), and Heninger (1984). In these studies, the determination of reaction reversal depends critically on measurement of weight changes of an andalusite crystal reacted in a matrix of ground and elutriated sillimanite or kyanite. In the studies cited above, a Mettler M-5 microbalance was used. For a differential weighing, Holdaway (1971, p. 105) estimated maximum weighing precision of ±4 μg, Bowman (1975, p. 32, 36, 41) between ±2 and ±13 μg, and Heninger (1984, p. 7) about 10 μg (although this must be a minimum value because Heninger apparently did not experiment with weighing the same crystal on different days). Holdaway (1971) standardized the top and bottom of the optical scale throughout the weighing process (see below), Bowman (1975) standardized the optical scale at the beginning of a series of weighings, and Heninger apparently did not standardize the optical scale. Heninger's work was done at the Pennsylvania State University in the laboratory of D. M. Kerrick. In his book, Kerrick (1990, p. 58), criticizing the precision estimates of Holdaway (1971), stated "Our experience with this microbalance, and our conversations with technical personnel of the Mettler Instrument Corp., suggests that even under the best environmental conditions, single crystal weight changes less than about 15 μg are very difficult to determine with confidence." On p. 61 he stated "Holdaway's (1971 and personal communication) meticulous care in balance calibration and replicate weighings *may* [emphasis ours] have resulted in single crystal weight changes *significantly* [emphasis Kerrick's] better than the ±15 μg uncertainty value favored by this author." In our opinion, one cannot ascribe an error to an instrument or technique used by another researcher without evaluating the procedure used. Clearly we need a thorough description and a complete

TABLE 1. Weighing procedure for andalusite crystals (mg)

Time	60 mg wt. bottom of scale	Andalusite crystal wt.	70 mg. wt. top of scale
<b>July 17, 1991; 23.1 °C*</b>			
14:45	60.006		
14:46		66.321	
14:47			70.011
14:48		66.320	
14:49	60.004		
14:50		66.315	
14:51			70.010
14:52		66.316	
14:53	60.005		
<b>February 3, 1992; 22.9 °C**</b>			
16:30	60.016		
16:31		66.342	
16:32			70.039
16:33		66.343	
16:34	60.016		
16:35		66.342	
16:36			70.037
16:37		66.341	
16:38	60.014		

\* Adjusted wts. in order: 66.3118, 66.3116, 66.3072, 66.3078; ave. wt. = 66.3096 mg (Table 2).

\*\* Adjusted wts.: 66.3114, 66.3124, 66.3127, 66.3124; ave. wt. = 66.3122 mg (Table 2).

analysis of error for the technique used by Holdaway (1971). This has become necessary at this time because the results of Holdaway (1971) have been rejected by Kerrick (1990, his Fig. 3.46) partly on the basis of Kerrick's evaluation of Holdaway's weighing error.

The Mettler M-5 microbalance at SMU stands on a heavy concrete balance table. The procedure used by Holdaway (1971) and by Haas and Holdaway (1973) for weighing andalusite crystals included the following steps: (1) Weighing was never undertaken while thunderstorms or weather fronts were in the area. Lights were turned on in the room, the balance was uncovered, and the crystal and standard weights were placed inside the balance. The door to the room was kept closed, and no one was allowed to enter. (The room is continuously air conditioned and temperature varies by no more than 1–2 °C over several weeks.) (2) After 30+ min, the operator sat in front of the balance for about 5 min to do a few practice weighings. (3) Actual weighing was begun by weighing a standard weight equivalent to the weight at the bottom of the optical scale; then the crystal was weighed; then a standard weight 10 mg higher was weighed at the top of the optical scale (Table 1). Weighings were taken every minute, with about 30 s required for changing the crystal or standard weight and 30 s allowed for the balance to equilibrate. Throughout the weighing process, no zero adjustments were made, nor were digital settings changed. The sequence of weighings is given in Table 1; the crystal was weighed four times, the bottom of the scale three times, and the top two times. (4) For each of the four crystal weights, the measured value was normalized to the nominal weight of the two adjacent standard weights using linear interpolation. The four adjusted weights were

TABLE 2. Summary of repeat weighings of an andalusite crystal on ten days

Date	Time	T (°C)	Ave. wt. (mg)
July 17, 1991	14:45	23.1	66.3096
July 24, 1991	14:55	23.3	66.3088
July 29, 1991	15:05	22.6	66.3116
July 30, 1991	13:24	22.5	66.3093
Feb. 3, 1992	16:30	22.9	66.3122
Feb. 4, 1992	11:35	22.6	66.3117
Feb. 5, 1992	10:50	22.5	66.3125
Feb. 7, 1992	9:10	22.4	66.3141
Feb. 11, 1992	15:35	22.7	66.3125
Feb. 14, 1992	14:45	22.5	66.3118

Note: Average absolute value difference for all 45 combinations:  $0.0019 \pm 0.0028$  mg ( $2\sigma$ ). Average summer weight:  $66.3098 \pm 0.0012$ , winter weight  $66.3125 \pm 0.0009$  mg ( $1\sigma$ ). Complete weighing procedure for July 17 and February 3 weighings given in Table 1.

then averaged. Repeat weighings of the same crystal on different days demonstrated that the difference between average adjusted weights was never more than 4  $\mu$ g.

Holdaway (1971) and Haas and Holdaway (1973) discovered that the principal source of error in an M-5 microbalance was day-to-day differences in the optical scale, possibly the result of thermal expansion. By standardizing both the bottom and the top of the scale, they were able to eliminate all such deviations except possible slight nonlinear effects within the optical scale.

We recently rechecked the long-term reproducibility of this procedure by weighing the same crystal ten times on different days (Table 2). The crystal was chosen for maximum error, near the middle of the optical scale. Each of the ten results given in Table 2 is the average of four adjusted weighings (Table 1). In order to estimate the relative error of a set of before and after weighings, each of the ten weighings was compared with every other one, thus giving a total of 45 weight differences. The average absolute-value weight difference was  $1.9 \pm 2.8$   $\mu$ g ( $2\sigma$ ). Thus for 95% of the weight differences, the precision was  $\pm 5$   $\mu$ g or less (the average difference plus  $2\sigma$ ), in good agreement with the  $\pm 4$   $\mu$ g quoted by Holdaway (1971) for a weight difference. Four of the weighings from Table 2 were done during the summer while the room was air conditioned, and six were during the winter while the room was heated. The average winter weight was 2.7  $\mu$ g above the average summer weight (Table 2), perhaps because of higher humidity during the warm, moist winter than during the previous summer. The precision of 5  $\mu$ g is expected to be an upper limit because extreme conditions were chosen, both in terms of crystal weight and time.

We emphasize that such small values for weighing errors can only be achieved with the kind of care described here. The only physical differences between the situation in 1971 and that in 1991–1992 are (1) the balance is now in a less favorable, smaller room adjacent to its room in 1971, (2) the balance is 20 years older, and (3) Holdaway's eyes are 20 years older (a magnifying glass was needed to read the optical scale). Based on the foregoing

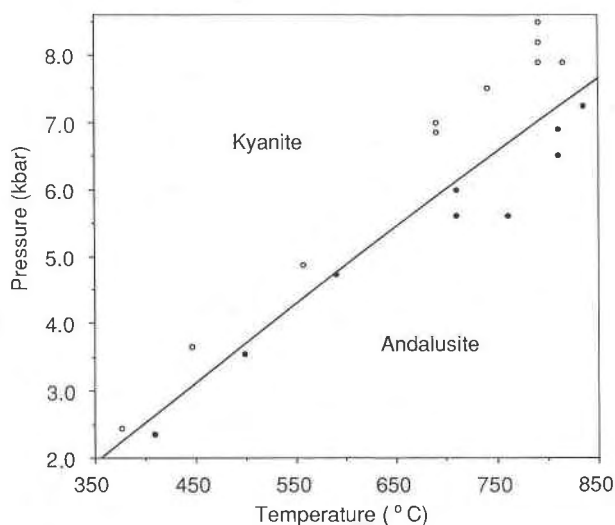


Fig. 1. Pressure-temperature diagram representing kyanite = andalusite reversals from Table 4. Each point represents the point from an experimental error limit as far as permissible from the equilibrium curve, as explained in text. Open circles represent interpreted  $P$ - $T$  conditions of kyanite stability, and solid circles represent interpreted conditions of andalusite stability. The solid line shows conditions of equilibrium for the reaction calculated, using the thermochemical data of Tables 9 and 10 (italicized values),  $C_p$  expression of Hemingway et al. (1991), and thermal expansion and compressibility formulas of Berman (1988).

discussion, we conclude that precision of weight differences for the Holdaway (1971) experiments was  $\pm 5 \mu\text{g}$ , precision for the Bowman (1975) experiments was  $\pm 15 \mu\text{g}$ , and precision for the Heninger (1984) experiments was  $\pm 20 \mu\text{g}$  (Kerrick, 1990, p. 71).

#### EVALUATION OF PREVIOUS STUDIES

In this report we focus on most experimental studies involving andalusite from the year 1966 on. Several investigators (e.g., Richardson et al., 1969; Newton, 1969; Holdaway, 1971; and Kerrick, 1990) have shown that there is nothing more to be gained from further analysis of studies prior to 1966, or that of Althaus (1967). For some post-1965 studies, we will conclude that only sillimanite-stable half-reversals can be accepted, either because of the reactive nature of the sillimanite starting material, or because weight gains of andalusite crystals using the crystal growth method were too small to be meaningful, given the weighing precision. However, in our opinion, it is important to show these half-brackets, keeping in mind that the actual equilibrium conditions lie at substantially lower  $T$ . In tables reporting reversals and in Figures 1 and 2, we report reversals at the limit of experimental error; for example, a kyanite-stable experimental condition is reported at the lowest possible  $T$  and the highest possible  $P$  within the range of quoted (or estimated) experimental error. In this way each reported value should fall within the appropriate stability field. This procedure eliminates all disagreement between stud-

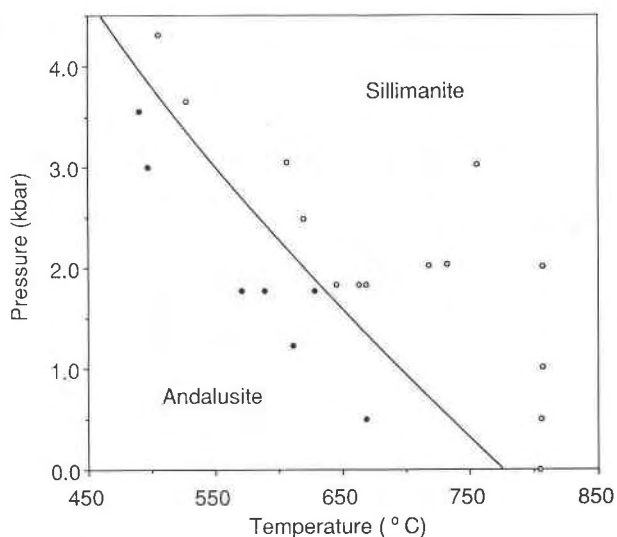


Fig. 2. Pressure-temperature diagram representing andalusite = sillimanite reversals and half-reversals from Table 7. Each point represents the point from an experimental error limit as far as permissible from the equilibrium curve as explained in text. Solid circles represent interpreted  $P$ - $T$  conditions of andalusite stability, and open circles represent interpreted conditions of sillimanite stability. The solid line shows conditions of equilibrium for the reaction calculated using the thermochemical data of Tables 9 and 10 (italicized values), the  $C_p$  expression of Hemingway et al. (1991), and thermal expansion and compressibility formulas of Berman (1988).

ies that is purely the result of experimental error. Finally, we note that discussion of each author's  $\text{Al}_2\text{SiO}_5$  phase diagram is unwarranted, because in every case the diagram is based in part on (1) other authors' work, which may involve incorrect apparent reversals, (2) thermodynamic data that are now known to be incorrect (Robie and Hemingway, 1984; Hemingway et al., 1991), or (3) incorrect interpretations regarding the nature and effect of sillimanite on the experiments. Instead, we evaluate the authors' apparent reversals and draw the best phase diagram consistent with all the acceptable reversals and the most recent thermodynamic data.

Although this report concentrates primarily on the results of experiments with andalusite as a phase, we will need kyanite = sillimanite reversals in order to obtain the best possible values of  $H$  and  $S$  for each phase. Accordingly, we will obtain reversals from the two most recent publications on this reaction, relying heavily on their results.

#### Kyanite = andalusite

For this reaction, the main problems are (1) calibration of experimental equipment, and (2) detection of reaction under unfavorable  $T$  conditions. Table 3 shows the five studies that have been undertaken. The wide range of times required for establishment of reaction direction, 1–66 d, results mainly from the wide range of  $T$  involved. The Newton (1966b), Richardson et al. (1969), and Boh-

TABLE 3. Summary of kyanite = andalusite experimental studies after 1965

Study	Experimental method	Apparatus	Composition (%Fe <sub>2</sub> O <sub>3</sub> )		Duration (d)	Comments
			Kya	And		
Newton (1966b)	X-ray + qtz	piston-cylinder	<0.10	<0.20	1-4	good calibration
Richardson et al. (1969)	X-ray + qtz	gas-medium	0.10	0.40	2-10	prolonged grinding
Brown and Fyfe (1971)	solubility in H <sub>2</sub> O, + cor	hydrothermal	0.38?	low?	14	two techniques
Holdaway (1971)	Xtal growth, ± cor seeding, + cor or qtz	hydrothermal	0.38	0.40	30, 51 30-66	kyanite elutriated minerals elutriated
Bohlen et al. (1991)	X-ray, + qtz	piston-cylinder	0.65	0.25	5-10	very good calibration

len et al. (1991) studies were at  $T$  between 700 and 825 °C, whereas the Brown and Fyfe (1971) and Holdaway (1971) studies were between 350 and 585 °C.

**Newton (1966b).** Newton's experimental work on the kyanite = andalusite reaction (Table 3) has stood the test of time. He used lightly ground natural materials with low Fe<sub>2</sub>O<sub>3</sub> content, calibrated his experimental apparatus against known equilibria, and determined reaction direction by comparing product-reactant X-ray peak ratios with ratios for starting materials. Results were supported by optical examination, which showed well-developed overgrowths on the stable mineral. Synthetic Fe<sub>2</sub>O<sub>3</sub>-absent minerals gave the same results. We agree with Kerrick's (1990) evaluation of this study. Experimental brackets, assuming experimental errors of ±10 °C and ±0.5 kbar, are presented in Table 4 and Figure 1.

**Richardson et al. (1969).** Using an internally heated gas pressure apparatus (Table 3), these authors investigated the kyanite = andalusite equilibrium over the interval from 700 to 825 °C and detected reaction by ratios of X-ray peaks. Pressure error in the gas apparatus is considerably smaller than in the piston-cylinder apparatus, but temperature error may be larger because of thermal gradients. Starting materials were machine ground for 3 h. Newton (1969) has shown that kyanite degrades from intense grinding faster than sillimanite, and such grinding of kyanite starting material leads to nucleation of sillimanite 2-3 kbar into the kyanite field during the experiments. This effect may substantially increase the apparent pressure of the kyanite = sillimanite equilibrium, depending in part on the experimental technique used. A similar effect may also occur for kyanite = andalusite, although there is no evidence for its existence in the experimental results of Richardson et al. (1969). The lightly ground starting materials of Newton (1966b) produced very similar results to the intensely ground starting materials of Richardson et al. (1969), as seen in Table 4. We accept the reversals of Richardson et al. (1969), keeping in mind that the intense grinding may have slightly increased the pressure of equilibrium (Table 4, Fig. 1). Kerrick (1990) reached a similar conclusion, suggesting that the absence of periodic regrinding during the experiments may have allowed the kyanite = andalusite experiments to approach equilibrium.

**Brown and Fyfe (1971).** In this study (Table 3), two methods were used to determine solubility of kyanite or

andalusite crystals with a powder of corundum in a measured amount of H<sub>2</sub>O: (1) measurement of SiO<sub>2</sub> concentration by molybdate complex spectrophotometry on the quench solution, which was rinsed in dilute HF to dissolve quench gel, and (2) measurement of weight loss of crystals of andalusite and kyanite. At any given  $P$ - $T$  condition, the least soluble mineral is the stable one, and the conditions of equal solubility are the equilibrium conditions. Both methods show consistent patterns of andalusite and kyanite solubility as a function of  $T$  at a given  $P$ . However, there are problems: (1) Definitive solubility differences require  $T$  overstepping of 75-100 °C from the apparent equilibrium condition at which measured solubilities are equal. (2) The crystal weight-loss method gives solubilities about 1.4 times the chemical method at apparent equilibrium of 1 kbar, 400 °C, and about 4.3 times the chemical method at apparent equilibrium near 3 kbar, 550 °C. (3) Even with the large overstepping required, three out of four  $P$ - $T$  conditions of apparent kyanite stability (2 kbar, 400 °C, 3 kbar, 450 °C, chemical method; 2 kbar, 400 °C, weight loss method), fall in the andalusite field of most other studies (Newton, 1966b; Richardson et al., 1969; Holdaway, 1971). Kerrick (1990) has suggested that these experiments failed to approach equilibrium from both sides and thus do not constitute true reversals. He also questioned whether the solutions in apparent equilibrium with kyanite contained the same silica complexes as those in apparent equilibrium with andalusite. Considering that the solution reaction was only approached from one side, this is possible. The lack of agreement in solubility between the two methods indicates that equilibrium was not established for at least one method: either a phase preferentially quenched on crystals of kyanite, andalusite preferentially dissolved during quenching, or one or more of the phases did not fully equilibrate with the solution. In our opinion, these experiments cannot be interpreted as reversals.

**Holdaway (1971), crystal growth method.** In this study, large (29-74 mg, Table 5), ground andalusite crystals were immersed in a powder of kyanite or equal amounts of kyanite and corundum (Table 3). A series of experiments was conducted at a constant  $P$  over a range of  $T$ . With the crystal growth method one expects to see a steady progression from weight loss to weight gain with increasing  $T$  and a minimum amount of scatter in the data. Because of the exponential effect of reaction kinetics, a

TABLE 4. Kyanite = andalusite reversals\*

Study	<i>P</i> (kbar)	<i>T</i> (°C)	Duration (d)	Stable phase
Newton (1966b)**	7.00	690	2.5	kya
	5.60	710	2.5	and
	7.50	740	2.0	kya
	5.60	760	2.0	and
	7.90	790	1.0	kya
Richardson et al. (1969)	6.50	810	1.3	and
	6.85	690	9.8	kya
	6.00	710	9.0	and
	8.20	790	2.6	kya
	7.90	815	3.9	kya
Holdaway (1971) A†	7.25	835	3.1	and
	2.44	377	29	kya
	2.36	409	29	and
Holdaway (1971) B†	3.65	447	66	kya
	3.55	499	61	and
	4.87	557	30	kya
Bohlen et al. (1991)	4.73	590	30	and
	8.50	790	10	kya
	6.90	810	5	and

\* Each reversal is positioned as far as permissible from the equilibrium curve within the experimental *P-T* error box.

\*\* Estimated *P* error  $\pm 0.5$  kbar, *T* error  $\pm 10$  °C.

† A = crystal growth method; B = seeding method.

curve fitting the data points in a weight change vs. *T* plot should increase in slope as *T* increases above the zero point *T* and then level off, and perhaps even reverse slope and approach zero weight loss, as *T* decreases below the zero point. (For the andalusite = sillimanite reaction weight loss and weight gain should be reversed because andalusite is a reactant.) Scatter in the observed data is due to (1) *T* error, (2) *P* error, (3) weighing error, (4) chipping or nucleation of some other phase on the crystal, and (5) variation of andalusite crystal surface area from one experiment to another. At *T* within a few degrees of the equilibrium *T*, the first four factors may change the sign of weight change for an experiment, whereas the fifth factor can only change the relative amount of weight change, not its sign. One should also be sure that the andalusite crystal did not lose weight during the first several hours of the experiment, as the saturated H<sub>2</sub>O solution formed.

The results of Holdaway (1971, his Fig. 2) show the predicted relationships. The only significant deviation from the pattern is the unusually large weight loss for 323, which relates partly to the large size of the andalusite crystal (74 mg, Table 5). Experiments with and without corundum show the same pattern, but those with 50% corundum powder had smaller weight changes than those without corundum or quartz and required longer times. At higher *T*, Heninger (1984) found that experiments on andalusite = sillimanite containing no additional mineral tended to nucleate corundum on the andalusite crystals from incongruent dissolution of sillimanite. The agreement between the two approaches used by Holdaway (1971) suggests that this was not a problem at lower *T* with the andalusite = kyanite reaction. Nucleation of corundum probably was a problem at higher *P* and *T*, where

TABLE 5. Andalusite crystal weight changes from experiments of Holdaway (1971)\*

Expt.	<i>T</i> (°C)	Duration (d)	Wt. (mg)**	ΔWt. (μg)	Stable phase
<b>Kyanite = andalusite, 2.4 kbar</b>					
349	373	29	29	-6	kya
323	382	29	74	-16	kya
348	393	29	38	0	?
347	404	29	38	+10	and
365	413	29	53	+20	and
<b>Andalusite = sillimanite (Connecticut), corundum added, 3.6 kbar</b>					
519	481	30	40	+25	and
517	496	30	42	+50	and
507	510	30	39	+59	?
542	511	59	38	-12	?
511	522	30	42	-89	sil
509	538	30	52	-109	sil
503	569	15	44	-120	sil
502	585	15	53	-205	sil
500	631	16	45	-287	sil
494	671	15	37	-364	sil
<b>Andalusite = sillimanite (Connecticut), corundum added, 1.8 kbar</b>					
518	594	30	44	+18	and
543	611	59	41	+1	?
516	612	30	39	+16	?
540	625	29	52	+4	?
506	626	30	37	-36	?
510	640	30	44	-33	sil
508	655	30	40	-92	sil
501	657	15	39	-32	sil
504	672	15	42	-71	sil
499	701	15	39	-75	sil
493	740	15	40	-187	sil

\* Tabulated from original experiment sheets, not adjusted for experimental error, as was done for Tables 4 and 7. Note that for andalusite = sillimanite, weight changes for 30- and 60-d experiments were divided by 2 and 4, respectively, for plotting in Holdaway (1971). Also, there are a few minor plotting errors in *T* in Holdaway (1971).

\*\* Crystal weight rounded off to the nearest milligram.

the crystal growth method did not produce consistent results on kyanite = andalusite (Holdaway, 1971).

Perhaps a more important problem for both the kyanite = andalusite and the andalusite = sillimanite experiments is that of initial weight loss of the andalusite crystal during the first few hours as the equilibrium fluid formed. Heninger (1984) found that 2-d experiments on the andalusite = sillimanite reaction produced no andalusite weight change, suggesting that the assumption of no significant andalusite weight loss during the early stages is valid. MacInnis et al. (1990) found that andalusite crystals in pure H<sub>2</sub>O and in H<sub>2</sub>O with powder of quartz or corundum lost significant amounts of weight. The following points suggest that initial crystal weight loss was not a problem when another aluminum silicate was present in powdered form: (1) For the kyanite = andalusite reaction, 51-d experiments showed the same zero point *T* as 30-d experiments. Had there been significant initial weight loss, the longer times would have indicated a lower zero point *T* closer to the true equilibrium *T* (Holdaway, 1971, his Fig. 2). (2) For the andalusite = sillimanite reaction, longer times indicated slightly lower zero point *T* (greater andalusite crystal weight losses per 15 d), the reverse of what would have occurred had there been a significant initial weight loss of andalusite crystals (Hol-



TABLE 6. Summary of andalusite = sillimanite experimental studies after 1965

Study	Method	Apparatus	Composition (%Fe <sub>2</sub> O <sub>3</sub> )		Duration (d)	Comments
			and	sill		
Weill (1966)	solubility in cryolite	1 atm	0.38	0.98	10–15	corundum-saturated
Richardson et al. (1969)	X-ray + qtz	hydrothermal	0.40	0.13	71–117	periodic regrinding
Holdaway (1971)	Xtal growth + cor	hydrothermal	0.38	1.15	15–60	minerals elutriated
	seeding + qtz or cor	hydrothermal	0.38	1.15 or 0.98	59–62	minerals elutriated
Bowman (1975)	Xtal growth + qtz or cor	hydrothermal	0.38	0.98	50–90	SEM study as well
	solubility in cryolite	1 atm	0.38	0.98	20	sillimanite-saturated
Heninger (1984)	Xtal growth + cor	hydrothermal	0.25	0.15	14–28	fibrous sillimanite elutriated

daway, 1971, his Fig. 4; Table 5 of this report). A probable explanation for this shift in zero point is given in the section on Fe<sub>2</sub>O<sub>3</sub> in sillimanite.

For both the kyanite = andalusite and the andalusite = sillimanite reactions, we have used the following criteria for establishing that a weight-change experiment is a half-reversal: (1) The weight change in question must be more than the precision ( $\pm 5 \mu\text{g}$  for Holdaway, 1971, see above). (2) As  $T$  increases or decreases away from equilibrium  $T$ , there must be no weight differences for other experiments less than the precision. On the basis of the data of Table 5, the 2.4 kbar  $T$ -adjusted reversal is between 377 and 409 °C (Table 4, Fig. 1). The only experiment that comes close to the 5- $\mu\text{g}$  error is 349 (Table 5), which shows the kinetic effects of low  $T$ . This set of data has been rejected by Kerrick (1990) on the grounds that he believes Holdaway's (1971) errors are larger than  $\pm 5 \mu\text{g}$ . Justification of Holdaway's (1971) error estimates in the preceding section and the very limited scatter of the data support our determination.

**Holdaway (1971), seeded experiments.** Seeded experiments with 74% of one aluminum silicate, 1% of the other, and 25% quartz or corundum (Table 3) were used to bracket the equilibrium at 3.6 kbar (60–66 d) and 4.8 kbar (30 d). Experiments with andalusite seeds were more sensitive to detection of reaction than those with kyanite seeds. Corrosion or overgrowths were observed with the petrographic microscope. The results (Holdaway, 1971, Table 3) indicate reversals between 447 and 499 °C at 3.6 kbar and between 557 and 590 °C at 4.8 kbar (Table 4, Fig. 1). These results are fully consistent with the crystal growth reversals and with the higher  $T$  reversals of Newton (1966b) and Richardson et al. (1969).

**Bohlen et al. (1991).** Using a well-calibrated piston-cylinder apparatus at UCLA, Montana (Bohlen et al. 1991) determined a single reversal at 800 °C (Table 3). These experiments were conducted with 2% quartz and no flux. Reaction direction was determined by X-ray diffraction and optical study. In addition, crystallites of the stable phase were identified by transmission electron microscopy. The reversal, between 6.9 and 8.5 kbar, is given in Table 4.

#### Andalusite = sillimanite

The five studies involving the reaction andalusite = sillimanite are summarized in Table 6. This equilibrium

has a substantially smaller  $\Delta S$  than the kyanite = andalusite and kyanite = sillimanite equilibria (Hemingway et al., 1991), and therefore a given  $\Delta T$  overstepping of the andalusite = sillimanite equilibrium corresponds to a smaller  $\Delta G$  than the same  $\Delta T$  overstepping of the kyanite = andalusite equilibrium. This in turn makes experimental study of the andalusite = sillimanite reaction more difficult. At the same time, good reversals for this reaction have great value because they provide better constraints on the values of  $\Delta S$  and  $\Delta H$  for this pair of minerals than calorimetric results alone. The most significant difficulties in dealing with this reaction are those related to the small  $\Delta G$ : (1) the effect of fine grain size or quartz impurities in fibrous sillimanite, (2) the effect of Fe<sub>2</sub>O<sub>3</sub> content of the polymorphs, and (3) the necessity to detect small amounts of the andalusite = sillimanite reaction and eliminate the effects of other possible reactions. Many of the problems encountered in studies of this reaction relate to the nature of the sillimanite starting material and to the fact that at low  $P$  and  $T$  not only is an unstable form of sillimanite less likely to convert to its stable form than at higher  $P$  and  $T$  on the kyanite = sillimanite reaction, but also its presence is more likely to have a significant effect due to the small  $\Delta S$  and  $\Delta G$  of the andalusite = sillimanite reaction. For these reasons, plus the fact that reaction rates increase with increasing  $P$  and  $T$ , most of these problems do not exist with the kyanite = sillimanite reaction (Kerrick, 1990; Bohlen et al., 1991).

A general shortcoming of all sillimanite used to date for experimental studies is that the samples either contain fibrous sillimanite or they have elevated Fe<sub>2</sub>O<sub>3</sub> content. This may be because natural sillimanite often contains fibrous sillimanite near its condition of initial formation (e.g., Holdaway et al., 1982). Sillimanite that formed at higher  $T$  can be expected to have higher solubility for Fe<sup>3+</sup>, and the rocks containing it, in some cases, formed under more oxidizing conditions. Thus, in the discussions that follow, it is necessary to account for the effect of fibrous sillimanite and the effect of Fe<sub>2</sub>O<sub>3</sub> in sillimanite. A discussion of the effect of elevated Fe<sub>2</sub>O<sub>3</sub> in the sillimanite samples used in three of the studies is given in the section on Fe<sub>2</sub>O<sub>3</sub> in sillimanite.

**Weill (1966), and Bowman (1975), cryolite melt experiments.** In our opinion, the study of Weill (1966) supported by further cryolite melt work of Bowman (1975) (Table 6), continues to be one of the seminal studies of

aluminum silicate stability relations. They have not only developed a very useful method for the study of aluminum silicate stability, but they have provided a most important 1-atm half-reversal for andalusite = sillimanite. We discuss these studies together because they both used cryolite melt, they both worked at the same conditions, and A. F. Bowman worked with D. F. Weill in his laboratory at the University of Oregon.

Working in the ternary system  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_3\text{AlF}_6$ , Weill (1966) conducted a series of experiments on the join  $\text{Al}_2\text{SiO}_5\text{-Na}_3\text{AlF}_6$ . All such compositions are saturated with corundum and melt. As  $\text{Al}_2\text{SiO}_5$  content is increased, the melts saturate in an aluminum silicate phase as well. Weill carried out experiments along the join using andalusite in one series and sillimanite in the other. In experiments at 800 °C, he found that at 70.4%  $\text{Al}_2\text{SiO}_5$  andalusite starting material completely dissolved, whereas minor sillimanite starting material remained in the parallel experiment. In order for andalusite to persist, the melt had to reach 70.7%  $\text{Al}_2\text{SiO}_5$ . For sillimanite to dissolve, the melt had to be 70.2%  $\text{Al}_2\text{SiO}_5$ . The composition was accurately controlled by the amount of aluminum silicate added, and it was easy to detect small amounts of andalusite or sillimanite in the glass. Several experiments were repeated at different lengths of time to assure that equilibrium had been achieved. The sharp cut-off between experiments containing aluminum silicate and those not containing aluminum silicate is further evidence that equilibrium was attained. Thus andalusite is more soluble than sillimanite at 800 °C, but their solubilities are very nearly the same.

Bowman (1975) also experimented with cryolite melts at 800 °C (Table 6). These are probably the phantom experiments referred to by Holdaway (1971, p. 117) and by Kerrick (1990, p. 77). His experiments were in a different part of the system  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_3\text{AlF}_6$  than those of Weill (1966): in the two-phase field bounded by melt and an aluminum silicate phase. In Bowman's experiments the melt was first saturated with sillimanite at 800 °C, and then, in a repeat experiment, a weighed andalusite crystal was added. After a small correction for loss during dissolution of the glass, the crystal lost 42  $\mu\text{g}$  at 800 °C, again showing that andalusite is more soluble than sillimanite at this  $T$ . Had andalusite been less soluble (more stable) than the sillimanite already present in the melt, andalusite would have increased in amount or perhaps showed no change (if it had nucleated and grown elsewhere in the charge). The combination of these two sets of experiments performed in different parts of the system  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_3\text{AlF}_6$  and performed using different techniques shows conclusively that sillimanite is slightly more stable than andalusite at 800 °C (Table 7, Fig. 2). At 1010 °C both Weill (1966) and Bowman (1975) reported that andalusite is substantially more soluble (less stable) than sillimanite.

Kerrick (1990) has criticized Weill's (1966) results primarily on the basis of the probable inaccuracy of the Temkin model used by Weill to estimate equilibrium  $T$

TABLE 7. Andalusite = sillimanite reversals and half-reversals\*

Study	$P$ (kbar)	$T$ (°C)	Duration (d)	Stable phase
Weill (1966)	1 atm	805	15	sil
Richardson et al. (1969)	3.03	756	80	sil
	2.01	807	82	sil
Holdaway (1971) A**	3.55	491	30	and
	3.65	527	30	sil
	1.77	589	30	and
	1.83	645	30	sil
	1.77	628	35	and (?)
	1.83	669	25	sil
Holdaway (1971) B**	1.77	571	59	and
	1.83	663	59	sil
	3.00	497	60	and
	4.31	506	60	sil
	1.23	611	60	and
	2.49	620	60	sil
Bowman (1975) A**	2.02	718	50	sil
	0.50	669	66	and
	0.50	806	90	sil
Bowman (1975) C**	1 atm	805	20	sil
Heninger (1984)	3.05	607	14	sil
	2.03	732	14	sil
	1.02	807	14	sil

\* Each reversal is positioned as far as permissible from the equilibrium curve within the experimental  $P$ - $T$  error box. See text for discussion of significance of half-reversals.

\*\* A = crystal growth method; B = seeding method; C = solubility in cryolite.

for andalusite = sillimanite. In our opinion, the experimental results of Weill (1966) can only be used as a half-reversal and as an argument that the andalusite = sillimanite equilibrium is probably not far below 800 °C because the solubilities at 800 °C are nearly equal. Regardless of the model used, if one polymorph is more soluble than another in any medium, it is less stable. Kerrick (1990) questioned whether equilibrium was achieved, because the solubility was only approached from one direction. He also suggested that speciation may have been different in melts saturated in andalusite than in melts saturated in sillimanite. In our opinion, such criticism is not warranted in light of the great fluxing effect of cryolite melts and the fact that Weill varied times of critical experiments by as much as two orders of magnitude (10–1000 h) without any measurable effect on the results (Weill, 1966, p. 228). Kerrick (1990) has criticized the Bowman (1975) results because he was unable to show conclusively that sillimanite grew. This demonstration is not necessary because solution of andalusite increased the  $\text{Al}_2\text{SiO}_5$  content of the sillimanite-bearing melt, establishing that andalusite is more soluble than sillimanite at 800 °C. Kerrick (1990) has shown that the data at 800 and 1010 °C indicate different equilibrium temperatures with the Temkin model. This is a condemnation of the model, not a condemnation of the experimental result indicating that sillimanite is more stable than andalusite at 800 °C. Finally, we note that Weill (1966) and Bowman (1975) have clearly shown that the andalusite = sillimanite equilibrium is much closer to 800 °C than to 1010 °C. Kerrick's (1990, his Fig. 3.46) preferred equilibrium  $T$  for andalusite = sillimanite at 1 atm is 910 °C.



**Richardson et al. (1969).** The experiments of Richardson and his coworkers (Table 6) on andalusite = sillimanite involved low-Fe sillimanite and long times. However, the sillimanite had substantial fibrous sillimanite content (Richardson et al., 1968), the starting materials were machine ground for 3 h, and the experiments were interrupted and the materials reground at least twice during each critical experiment (Richardson et al., 1969). Holdaway (1971) and Kerrick (1990) have shown experimentally that high fibrous sillimanite content in the sillimanite greatly expands the andalusite field, with commensurate reduction of the sillimanite field. Newton (1969) has shown that intense grinding can also produce large shifts in equilibrium boundaries. Kerrick (1990) has provided arguments and evidence to indicate that intense grinding of starting materials may further destabilize fibrous sillimanite relative to coexisting andalusite. We agree with Kerrick's (1990) analysis to the effect that the andalusite = sillimanite boundary of Richardson et al. (1969) is at  $T$  values substantially above the equilibrium boundary for coarsely crystalline minerals. However, two of their experiments produced an increase of sillimanite relative to andalusite. These may be regarded as half-reversals (Table 7); however, it is very important to note that, whereas we can be certain these two experiments were in the sillimanite field, we cannot be sure that they were near the andalusite = sillimanite phase boundary.

**Holdaway (1971), crystal growth method.** Using a sillimanite sample from Connecticut (Table 6) free of fibrous sillimanite with 1.15%  $\text{Fe}_2\text{O}_3$  [corresponding to atomic  $\text{Fe}^{3+}/(\text{Al} + \text{Fe}^{3+})$  of 1.17%], Holdaway performed crystal growth experiments at 3.6 and 1.8 kbar. The individual weight changes are given in Table 5 of this report, and the data are presented diagrammatically by Holdaway (1971, his Fig. 4). The diagrams reveal relatively little scatter, most of which can be explained by crystal size and shape,  $T$  error,  $P$  error, and weighing error. Using the criteria discussed in the section on kyanite = andalusite crystal growth experiments, reversals are between 491 and 527 °C at 3.6 kbar and between 589 and 645 °C at 1.8 kbar. The diagrams show that, on average, the weight change per 15 d is slightly more negative for longer experiments than for shorter ones; i.e., longer times indicate slightly lower reversal  $T$  than shorter times. Experiments 542 and 507 illustrate this behavior, and for this reason were rejected as a possible reversal pair. This observation may be related to the  $\text{Fe}_2\text{O}_3$  content of the sillimanite and will be discussed in more detail in a later section on the effect of  $\text{Fe}_2\text{O}_3$ .

All the andalusite = sillimanite crystal growth experiments of Holdaway (1971) have been rejected by Kerrick (1990, his Fig. 3.46). The reasons are (1) in Kerrick's opinion, it is not possible with a Mettler M-5 microbalance to detect the sign of the weight change if its value is less than 15  $\mu\text{g}$ , and many of the weight changes measured by Holdaway (1971) were thought to be less than 15  $\mu\text{g}$ ; (2) by analogy with the experimental results of Heninger (1984) (discussed below), the crystal growth method is

not sensitive enough to provide reversals as tight as those claimed by Holdaway (1971); and (3) the  $\text{Fe}_2\text{O}_3$  content of the sillimanite, not in equilibrium with the coexisting andalusite, makes the results unpredictable. Concerning the weight changes, the smallest weight changes outside of the zero point range of uncertainty are 18 and 25  $\mu\text{g}$ , and all the rest are over 30  $\mu\text{g}$  (Table 5). In addition, we have shown above that Holdaway's (1971) weight changes were precise to  $\pm 5 \mu\text{g}$ . Concerning a comparison with Heninger's (1984) experiments, the two situations were very different: (1) The elutriated fibrous sillimanite in Heninger's experiments may have contained quartz, perhaps in variable amounts, which would have reacted with the added corundum and possibly produced variable amounts of andalusite growth, adding to the scatter in the plot of  $T$  vs. weight change and the zero point  $T$ . The fibrous sillimanite also contained muscovite (D. M. Kerrick, written communication); (2) The weighing error for Heninger's experiments ( $\pm 20 \mu\text{g}$ ) was four times that for Holdaway's (1971) and therefore must have produced a larger scatter; (3) In the critical range of conditions near equilibrium, Holdaway's experiments were for 30 d, and Heninger's were for 14 d; (4) Heninger's andalusite crystals were spheres weighing 7–15 mg, whereas Holdaway's andalusite crystals were cylindrical, with rounded ends (Holdaway, 1971), weighing 37–53 mg (Table 5). On the basis of average weights of 11 and 45 mg and an average aspect ratio of 3:1 for the Holdaway andalusite crystals, the larger, more elongate crystals used by Holdaway (1971) have about three times the surface area of the spheres used by Heninger (1984). If we assume that time and andalusite surface area (e.g., Wood and Walther, 1983) are linearly related to the amount of reaction and thus crystal weight change, Holdaway's experiments should have produced about six times as much reaction as Heninger's. For 30-d experiments, the average slope of Holdaway's 1.8-kbar weight-loss curve is 2.66  $\mu\text{g}/^\circ\text{C}$ , and the analogous figure for 14-d experiments for Heninger's 2-kbar weight-loss curve is 0.32  $\mu\text{g}/^\circ\text{C}$ , corresponding to a factor of 8; (5) Some of the limited scatter in Holdaway's data probably was caused by the decreasing effect of  $\text{Fe}_2\text{O}_3$  content of sillimanite with time. This effect should not be as significant in Heninger's (1984) experiments. The effect of elevated  $\text{Fe}_2\text{O}_3$  in sillimanite can be evaluated qualitatively and is discussed in detail below.

Another series of crystal growth experiments at 1.8 kbar deserves mention (Holdaway, 1971, p. 109, his Fig. 3B). An andalusite crystal was immersed in a matrix of corundum and sillimanite (0.13%  $\text{Fe}_2\text{O}_3$ ) from Jefferson Co., Colorado, with about 10% fibrous sillimanite. The crystal was weighed at 5-d intervals and returned to the experimental conditions with the same powder. Experiments at 604 and 633 °C showed significant andalusite weight gains for seven consecutive 5-d periods, whereas andalusite at 664 °C gained weight for one 5-d period and then lost significant weight for the next four periods. These results are interpreted to indicate that the finest grain-size fraction of the fibrous sillimanite and any quartz reacted away

during the first one or two 5-d periods, leaving the remaining time for equilibrium reaction, giving a reversal between 628 and 669 °C (Table 7). There is a minor discrepancy between this andalusite-stable experiment at 633 °C and those described above with a more Fe-rich sillimanite and no fibrous sillimanite, which suggest a zero point near 617 °C (reversal between 589 and 645 °C), but the two sets of data are consistent within the stated reversal ranges. The remaining fibrous sillimanite content of the Colorado sillimanite may have displaced the equilibrium 15–25 °C higher than that for pure coarsely crystalline sillimanite. Because of this possibility, we question the half-reversal at 628 °C (Table 7). However, this half-reversal does fall on the andalusite-stable side of the final accepted andalusite = sillimanite curve (Fig. 2). This reversal pair, with low-Fe<sub>2</sub>O<sub>3</sub> sillimanite, was apparently not considered by Kerrick (1990, his Fig. 3.46).

**Holdaway (1971), seeded experiments.** A number of seeded experiments (Table 6) were also performed by Holdaway. With this method, it is not possible to bracket the equilibrium very closely. All the seeded experiments were consistent with the crystal growth experiments and with each other. The 1.8-kbar reversal (Table 7) involved Connecticut sillimanite free of fibrous sillimanite and the remaining reversals involved capsules with Connecticut sillimanite and capsules with Benson Mines sillimanite (0.98% Fe<sub>2</sub>O<sub>3</sub>) free of sillimanite fibers. These reversals were not accepted by Kerrick (1990, his Fig. 3.46), possibly because of the Fe<sub>2</sub>O<sub>3</sub> content of the sillimanite. However, half of the capsules at each *P* and *T* contained only 1% of sillimanite, indicating low-Fe<sub>2</sub>O<sub>3</sub> bulk compositions, and results for all were consistent with each other.

**Bowman (1975), crystal growth method.** The andalusite = sillimanite experiments of Bowman (Table 6) using weighed crystals of andalusite and Benson Mines sillimanite were similar to those of Holdaway (1971) except for a few important differences: (1) Bowman did experiments at only four temperatures for each pressure; (2) experiments were done with corundum and with quartz, and it was not possible to determine whether experiments with corundum or with quartz were more meaningful; and (3) andalusite crystals and sillimanite matrix were examined with the SEM to determine possible growth or dissolution. The great scatter of weight changes for a single *T* in Bowman's experiments suggests the possibility that some crystals may have become chipped during the experiments, or that other minerals or quench product nucleated on the andalusite sample. Thus, it is necessary to reject experiments at temperatures where one crystal lost a lot of weight and another crystal was essentially unchanged in weight. If we apply the criteria discussed above to all the results collectively, and take into consideration the results of the SEM study, we have a sillimanite-stable half-reversal at 2 kbar, 718 °C, and a reversal at 0.5 kbar, between 689 and 806 °C (Table 7). These results were rejected by Kerrick (1990, his Fig. 3.46) presumably because of the high Fe in the sillimanite. Bow-

man's (1975) cryolite solubility measurements are discussed above with those of Weill (1966).

**Heninger (1984).** This study involved single-crystal experiments (Table 6) with andalusite spheres (7–15 mg) in a matrix of corundum and fibrolitic sillimanite (0.15% Fe<sub>2</sub>O<sub>3</sub>). The sillimanite was sieved to accept grains between 325- and 400-mesh and then ultrasonically washed in H<sub>2</sub>O, acetone, and 5% HF, 1% H<sub>2</sub>SO<sub>4</sub>. The sillimanite used for the experiments consisted of aggregate grains of fibrolitic material from which most of the finest free crystals had been elutriated. Most experiments were 14 d in duration. The weighing precision is estimated at ±20 μg (Kerrick, 1990, p. 71). Applying our criteria for reversals, we obtain the half-reversals given in Table 7. It was not possible to show andalusite-stable half-reversals because the weight gains ranged from 2 to 30 μg in the apparent andalusite field. As stated in the section on the Holdaway (1971) crystal growth experiments, longer duration and larger crystals would probably have increased the amount of reaction by a factor of 6–8. More careful weighing procedures and purer, sillimanite free of fibrous sillimanite would have reduced the scatter in the data. These experiments were considerably less sensitive than those of Holdaway (1971).

In interpreting Heninger's (1984) results, Kerrick (1990) obtained the same sillimanite-stable half-reversals that we do (600 °C at 3 kbar, 725 °C at 2 kbar, and 800 °C at 1 kbar). However, Kerrick based his andalusite = sillimanite curve only on these half-reversals, discarding the significant contributions of Weill (1966), Richardson et al. (1969), Holdaway (1971), and Bowman (1975). In addition, he drew the curve within 5 °C of Heninger's (1984) half-reversals at 1 and 3 kbar (Kerrick, 1990, his Fig. 3.46). Because of the low sensitivity of the Heninger procedure, the apparent zero points in Heninger's (1984) work are substantially lower than the half-reversals cited by Kerrick (1990): 450 °C at 3 kbar, 610 °C at 2 kbar, and about 780 °C at 1 kbar. With allowances for error, these are in approximate agreement with the zero points of Holdaway (1971); even the Heninger experiments suggest that the andalusite = sillimanite curve lies at much lower temperatures than those shown by Kerrick (1990, his Fig. 3.46). A second important point is that whereas Heninger (1984) was able to circumvent the possible problem of high Fe in sillimanite, he may not have totally eliminated the fibrous sillimanite problem, especially the possibility of quartz or muscovite impurity in the fibrous sillimanite (see above). At present, it is not possible to estimate the magnitude of this effect. Thus, the quoted reversals (Table 7) may lie at *T* substantially above equilibrium values.

#### **Kyanite = sillimanite**

In order to retrieve thermochemical data for the aluminum silicates, it is necessary to examine the kyanite = sillimanite reversals as well as those involving andalusite. Most of the studies since 1966 agree rather well, and there is no controversy regarding the validity of experimental results. Table 8 and Figure 3 present the reversals in the

TABLE 8. Kyanite = sillimanite reversals\*

Study	<i>P</i> (kbar)	<i>T</i> (°C)	Duration (d)	Stable phase
Newton (1966a)**	9.0	740	2	kya
	7.2	760	2	sil
Richardson et al. (1968)†	8.2	685	2	kya
	7.0	710	9	sil
	9.2	740	4	kya
	8.8	785	5	sil
	10.2	790	2	kya
	9.8	835	2	sil
Newton (1969)**	9.5	740	2	kya
	7.5	760	2	sil
	7.0	590	12	kya
Bohlen et al. (1991)	5.5	610	12	sil
	8.8	690	28	kya
	7.0	710	31	sil
	10.3	790	10	kya
	9.0	810	14	sil
	12.2	890	6	kya
	11.3	910	25	sil
	12.4	960	6	sil
	15.1	990	6	kya
	13.9	1010	11	sil

\* Each reversal is positioned as far as permissible from the equilibrium curve within the experimental *P-T* error box.

\*\* Estimated *P* error ±0.5 kbar; *T* error ±10 °C.

† Estimated *P* error ±0.2 kbar; *T* error ±10 °C.

same format as for the andalusite reactions. The most complete study is that of Bohlen et al. (1991), showing agreement between the laboratories at UCLA and USGS, and a *T* range from 600 to 1000 °C. The previous results of Newton (1966a, 1969) and Richardson et al. (1968) are consistent with those of Bohlen et al. (1991) and provide additional constraints.

#### THE PROBLEM OF HIGH Fe<sub>2</sub>O<sub>3</sub> IN SILLIMANITE

Ideally, aluminum silicate experiments should be carried out with sillimanite free of fibrous sillimanite and Fe-free andalusite and sillimanite and applied to nature with a Fe<sup>3+</sup> correction (e.g., Grambling and Williams, 1985; Holdaway and Goode, 1990). However, this is generally not feasible if natural minerals are used. In addition, as discussed above, in order to eliminate the problem of fibrous sillimanite, several workers have used Benson Mines (0.98% Fe<sub>2</sub>O<sub>3</sub>) or Connecticut (1.15% Fe<sub>2</sub>O<sub>3</sub>) sillimanite both free of fibrous sillimanite. Partly on the basis of elevated Fe<sup>3+</sup> in sillimanite, Kerrick has rejected the experimental results of Weill (1966), Holdaway (1971), and Bowman (1975). Kerrick (1990, p. 61), in discussing the Holdaway (1971) experiments, stated "A parallel reaction driven by disequilibrium Fe<sup>3+</sup> solid solution clouds Holdaway's interpretations which implicitly assume polymorphic reactions involving end-member compositions." Similar statements might be made regarding the results of Weill (1966) and Bowman (1975). Here we qualitatively analyze the effect of elevated Fe<sub>2</sub>O<sub>3</sub> in reactant sillimanite, which is out of equilibrium with the coexisting andalusite.

For the sake of simplicity, we assume that equilibrium

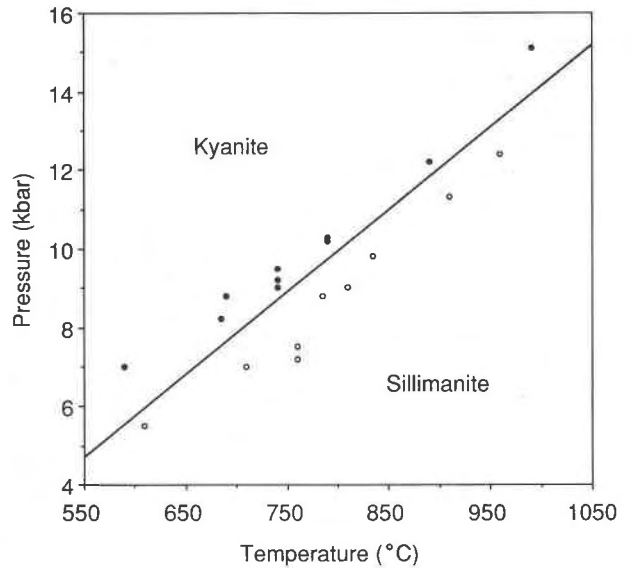


Fig. 3. Pressure-temperature diagram representing kyanite = sillimanite reversals and half-reversals from Table 8. Each point represents the point from an experimental error limit as far as permissible from the equilibrium curve, as explained in text. Solid circles represent interpreted *P-T* conditions of kyanite stability, and open circles represent interpreted conditions of sillimanite stability. The solid line shows conditions of equilibrium for the reaction calculated using the thermochemical data of Tables 9 and 10 (italicized values), the *C<sub>p</sub>* expression of Hemingway et al. (1991), and thermal expansion and compressibility formulas of Berman (1988).

andalusite contains twice as much Fe<sub>2</sub>O<sub>3</sub> as coexisting sillimanite (Holdaway and Goode, 1990, p. 1050). The effect of Fe<sub>2</sub>O<sub>3</sub> on the andalusite = sillimanite reaction is to increase the *T* of reaction in proportion to the amount of Fe<sub>2</sub>O<sub>3</sub> in the minerals undergoing reaction (Grambling and Williams, 1985; Holdaway and Goode, 1990). Considering first the crystal growth experiments, when the initial synthetic corundum (0% Fe<sub>2</sub>O<sub>3</sub>) and sillimanite (~1% Fe<sub>2</sub>O<sub>3</sub>) powder and andalusite crystal (~0.4% Fe<sub>2</sub>O<sub>3</sub>) are confined with H<sub>2</sub>O at *P* and *T*, the following reactions occur: (1) The H<sub>2</sub>O becomes saturated with Si, Al, and Fe<sup>3+</sup> species dissolved primarily from the granulated corundum and sillimanite (Heninger, 1984, p. 16). This process occurs rapidly, in our experience in less than a day. (2) The H<sub>2</sub>O, andalusite, sillimanite, and corundum approach equilibrium with each other in terms of Fe<sup>3+</sup>/Al ratio by exchange of Fe<sup>3+</sup> and Al. H<sub>2</sub>O and corundum will increase in Fe<sup>3+</sup>, sillimanite will decrease in Fe<sup>3+</sup>, and andalusite will increase in Fe<sup>3+</sup>. Only the surface layers of each crystal equilibrate, the inner portions being less affected as a result of slow solid diffusion rates. (3) The net-transfer reaction andalusite → sillimanite or vice versa occurs.

We consider two extreme models: Model A is the case in which the sillimanite and andalusite in the surface layers equilibrate rapidly with H<sub>2</sub>O and corundum and at-

tain compositions such as andalusite  $\sim 0.8\%$   $\text{Fe}_2\text{O}_3$  and sillimanite  $\sim 0.4\%$   $\text{Fe}_2\text{O}_3$ , before reaction proceeds to any great extent; Model B is the case in which no equilibration occurs, and the starting sillimanite ( $\sim 1\%$   $\text{Fe}_2\text{O}_3$ ) immediately begins reacting to equilibrium andalusite ( $\sim 2\%$   $\text{Fe}_2\text{O}_3$ ), or starting andalusite ( $\sim 0.4\%$   $\text{Fe}_2\text{O}_3$ ) begins reacting to equilibrium sillimanite ( $\sim 0.2\%$   $\text{Fe}_2\text{O}_3$ ). If Model B prevailed, the crystal weight change pattern shown in Figure 4c would occur, with two overlapping reactions competing at the zero point, and a rapid change with  $T$  from one reaction to the other. If Model A prevailed, the pattern shown in Figure 4b would occur.

In fact, Model B is only valid for a small initial period of time, because as sillimanite with  $\sim 1\%$   $\text{Fe}_2\text{O}_3$  begins to react to andalusite with  $\sim 2\%$   $\text{Fe}_2\text{O}_3$ , the remaining sillimanite must become depleted in  $\text{Fe}_2\text{O}_3$ , and successive layers of andalusite must then also decrease in  $\text{Fe}_2\text{O}_3$ . In addition, if andalusite is reacting, the remaining andalusite must accumulate  $\text{Fe}_2\text{O}_3$  so that the sillimanite product must also increase in  $\text{Fe}_2\text{O}_3$ . The net effect is a steady change with time from the appearance of Model B behavior (Fig. 4c) toward Model A behavior (Fig. 4b).

Study of the 3.6- and 1.8-kbar weight change series (Holdaway, 1971, his Fig. 4) suggests that Model A comes closer to the actual behavior. However, some randomness near the zero point may well result from a degree of Model B behavior at conditions near equilibrium. The important point to be made is that the observed behavior can be explained, and regardless of which model best applies, both the andalusite  $\rightarrow$  sillimanite and the reverse reaction must occur at higher  $T$  with  $\text{Fe}^{3+}$  present than with pure Al.

This situation can be compared with a familiar analogy, the melting of plagioclase. Regardless of whether coexisting melt and solid plagioclase are initially in equilibrium, Ca-bearing melt and Ca-bearing plagioclase must undergo melting and crystallization reactions at  $T$  higher than the melting  $T$  of pure albite. The fact that the andalusite = sillimanite reaction is actually



suggests that the reacting andalusite (or sillimanite) will produce a sillimanite (or andalusite) with equilibrium partitioning of Al and Fe between the two minerals, because surface layers of each mineral tend to equilibrate with the solution. At the temperatures in question, supercritical  $\text{H}_2\text{O}$  equilibrates rapidly with solid phases (Walther and Wood, 1984). This provides further support for Model A, since the  $\text{H}_2\text{O}$  would tend to equilibrate the solid phases at the surface layers.

The study of Holdaway and Goodge (1990) provides a method to estimate  $\Delta T$  resulting from the  $\text{Fe}^{3+}$  content of the Holdaway (1971) experiments, assuming Model A with surface layers of andalusite containing  $\sim 0.8 \pm 0.3\%$   $\text{Fe}_2\text{O}_3$  ( $0.016 \pm 0.006 \text{ Fe}^{3+}$  ions) in equilibrium with surface layers of sillimanite containing  $\sim 0.4 \pm 0.15\%$   $\text{Fe}_2\text{O}_3$  ( $0.008 \pm 0.003 \text{ Fe}^{3+}$  ions). This estimate takes into account the fact that as corundum and  $\text{H}_2\text{O}$  saturate with

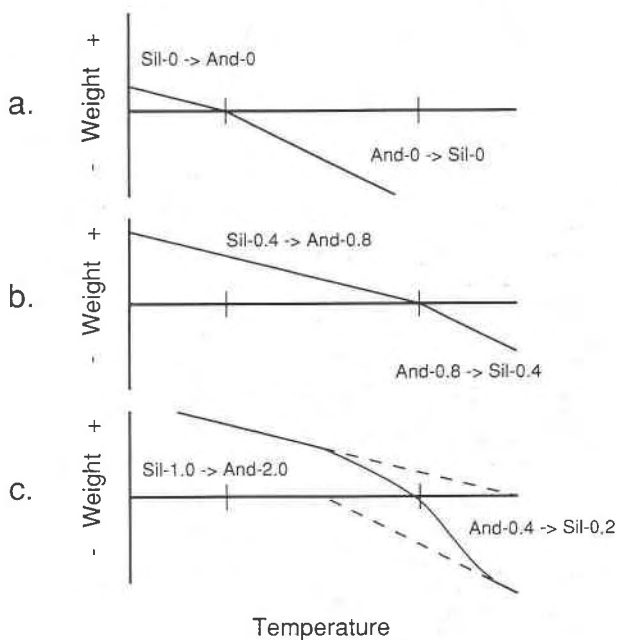


Fig. 4. Alternative models for andalusite weight change curves for the andalusite = sillimanite reaction. (a) Ideal case for andalusite and sillimanite with no  $\text{Fe}_2\text{O}_3$ . (b) Model A (see text) in which surface layers of  $\text{Fe}_2\text{O}_3$ -bearing starting materials equilibrate rapidly. (c) Model B in which surface layers of  $\text{Fe}_2\text{O}_3$ -bearing starting materials equilibrate slowly. The numbers following abbreviations for minerals are mol%  $\text{Fe}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ .

$\text{Fe}_2\text{O}_3$ , they reduce the bulk  $\text{Fe}_2\text{O}_3$  available for aluminum silicates. The resulting value of  $\Delta T$  is  $-15 \pm 5^\circ\text{C}$ , with the main source of estimated error being the uncertainty in composition. Thus, the determinations of Holdaway (1971) may be up to  $20^\circ\text{C}$  higher in  $T$  than the equilibrium in a pure  $\text{Al}_2\text{SiO}_5$  system. Figure 4 suggests that within the error given, any situation between Model A and Model B produces a similar offset.

These considerations provide a possible explanation for the slight shift in zero point with time seen in the results of Holdaway (1971, his Fig. 4). In this figure a slight downward shift in  $T$  is seen when comparing 15- and 30-d experiments. In addition, Table 5 (this report) shows that in two pairs of experiments at the same  $T$  near the zero point, experiments 507 and 542 and experiments 543 and 516, the 59-d time produced a more negative weight change than the 30-d time, consistent with lower zero-point  $T$  for longer times. A likely explanation for this phenomenon is that the bulk reacting  $\text{Fe}^{3+}/\text{Al}$  ratio was decreasing with time. If we compare the geometry of small grains of sillimanite vs. a large crystal of andalusite, successive reacting or equilibrated layers of sillimanite become progressively smaller in volume if their thickness remains the same, whereas such layers on the large, relatively flat andalusite crystal decrease in volume much more slowly. Thus, the amount of sillimanite available as a source of high  $\text{Fe}^{3+}$  decreases more rapidly than the

amount of low-Fe<sup>3+</sup> andalusite available decreases. The net effect is to cause an overall reduction in Fe<sup>3+</sup> available to the reacting system with longer times.

For the solubility experiments of Weill (1966) and Bowman (1975) similar arguments may be made regarding the Fe<sup>3+</sup> content of the sillimanite. A disproportionately large amount of Fe<sub>2</sub>O<sub>3</sub> in the sillimanite has the effect of stabilizing melt relative to sillimanite, since Fe<sub>2</sub>O<sub>3</sub> is more soluble in the melt than in the sillimanite. The effect would presumably decrease with time as the remaining sillimanite decreased in Fe<sub>2</sub>O<sub>3</sub> content. Restoring the sillimanite to pure Al<sub>2</sub>SiO<sub>5</sub> would move the sillimanite phase boundary toward melt, thus further reducing the solubility of sillimanite in melt, and further reducing the andalusite = sillimanite equilibrium *T* below 800 °C (Weill, 1966, his Fig. 1).

In conclusion, the Holdaway (1971), Weill (1966), and Bowman (1975) results with a nonequilibrium aluminum silicate pair can be qualitatively interpreted in light of our knowledge of Fe<sup>3+</sup>-Al partitioning and its effect on the andalusite = sillimanite reaction boundary. The reversals determined with Fe-rich sillimanite are up to 20 °C higher in *T* than the equilibrium for pure Al<sub>2</sub>SiO<sub>5</sub>. This figure would be lowered if a substantial fraction of the Fe<sup>3+</sup> in the system were reduced to Fe<sup>2+</sup> and therefore eliminated as a reactant. Because of larger Δ*S*, this Fe<sup>3+</sup> effect is considerably less for kyanite = andalusite and because of the still larger Δ*S* and more even Fe<sup>3+</sup>/Al partitioning, it is almost nonexistent for kyanite = sillimanite (Holdaway and Goodge, 1990).

#### THERMOCHEMICAL DATA AND THE Al<sub>2</sub>SiO<sub>5</sub> DIAGRAM

The approach we have used to obtain the best possible overall set of thermochemical data, as consistent as possible with experimental reversals and calorimetric measurements, includes two steps: (1) Obtain the best possible *V* and *C<sub>p</sub>* expressions for each of the phases independent of the experimental reversals. (2) Make small adjustments in calorimetrically measured standard *S* and *H* for each of the phases (Hemingway et al., 1991) to provide the best overall fit of the experimental reversals.

Because all calorimetric and molar volume measurements are made on natural samples, some consideration should be given to the possible effect of impurities on the measurements. For most samples, the only significant impurity is Fe<sub>2</sub>O<sub>3</sub>. Where necessary, Hemingway et al. (1991) have made impurity corrections to calorimetrically determined *S*. These corrections primarily relate to effects that are registered at *T* below 298 K. There is no significance to making such corrections to *C<sub>p</sub>* and *H* because (1) the corrections have a trivial effect on the result; (2) the amounts of the corrections are far less than the errors of the measurements; and (3) the combined effects on Δ*G* tend to cancel between the high *T* contributions to *H* and to *S* and among samples, all of which contain a little Fe<sub>2</sub>O<sub>3</sub>. However, as seen in the discussion below,

there is value to correcting aluminum silicate *V* measurements for Fe<sub>2</sub>O<sub>3</sub>.

#### Molar volume

In Table 9 are given composition and *V* measurements for aluminum silicates having less than 0.5 mol% Fe<sub>2</sub>O<sub>3</sub> and no other significant contaminant. The *V<sub>c</sub>* column includes small corrections for Fe<sub>2</sub>SiO<sub>5</sub> component. The corrections used are those of Langer and Fentrup (1973) for synthetic kyanite, Gunter and Bloss (1982) for andalusite, and Grew (1980) for sillimanite. Five values in Table 9 are highly inconsistent with other values for the same mineral and were not used for averages. These five values were probably affected by X-ray diffraction error, imperfect standardization, or the presence of an unanalyzed impurity. In our opinion, the Fe<sub>2</sub>O<sub>3</sub>-corrected values are the best possible molar volumes for the aluminum silicates. The andalusite and sillimanite volumes are precise, each being the average of ten or more very similar determinations on low-Fe minerals, corrected for Fe<sub>2</sub>O<sub>3</sub>. However, based in part on our own experience, it is difficult to measure precise kyanite unit-cell dimensions, especially *c*. Kyanite *V*, the average of only two determinations (Table 9), must be regarded as provisional.

#### Specific heat

The most recent and most accurate determinations of *C<sub>p</sub>* are those of Hemingway et al. (1991). In order to use these data with the Berman (1988) data base and the Brown et al. (1988) GE0-CALC program we converted the *C<sub>p</sub>* data to the Berman and Brown (1985) *C<sub>p</sub>* formula. The mathematical expression for each mineral (Hemingway et al., 1991) was refitted to the expression of Berman and Brown (1985). The results were not very satisfactory, especially for andalusite, which showed significant differences in *S<sub>T</sub>* - *S<sub>298</sub>* between the two expressions. Apparently the Berman and Brown (1985) *C<sub>p</sub>* expression, although theoretically correct at high *T*, does not adequately express the measured *C<sub>p</sub>* of some phases. For this reason, we used the unmodified Hemingway et al. (1991) *C<sub>p</sub>* expressions in the GE0-CALC program.

#### Standard entropy and enthalpy

Room-temperature *S* and *H* for aluminum silicates are given in Table 10. For each mineral there are multiple entries, as explained in the footnote. *S<sub>3</sub>* and *H<sub>2</sub>* are values based on the present study.

The accepted reversals and half-reversals for this study are shown in Figures 1-3. It can be seen that all the reversals are self-consistent, that is, none violates any other. Using our *V* data (Table 9), the *C<sub>p</sub>* data of Hemingway et al. (1991), and thermal expansion and compressibility data of Berman (1988), we modified the values of *S* and *H* to fit the experimental reversals. Our procedure involved first the determination of standard Δ*S* and Δ*H* from the reversals and half-reversals (Figs. 1-3). This was done by assuming that *S* and *H* of kyanite were as determined by Hemingway et al. (1991), then adjusting *S* and

**TABLE 9.** Determinations of  $V$  for aluminum silicates

Mineral	Locality	Mol% $\text{Fe}_2\text{O}_3^*$	$V$ (J/bar)	$V_c$ (J/bar)**	Ref.†
Kyanite	Burnsville, NC	0.06	4.4101	4.4098	1
Andalusite	Standish, ME	0.41	5.1516	5.1488	1
Sillimanite	Brandyw. Spgs., DE	0.03	4.9828	4.9826	1
Sillimanite	Williamstown, Aus.	0.40	4.9851	4.9818	1
Kyanite	Burnsville, NC	0.06	4.4067	4.4064	2
Andalusite	Standish, ME	0.41	5.1504	5.1476	2
Sillimanite	Brandyw. Spgs., DE	0.03	4.9833	4.9831	2
Kyanite	Yancy Co., NC	0.41	4.4293	4.4274‡	3
Andalusite	Minas Gerais, Bra.	0.39	5.1474	5.1447	3
Sillimanite	Williamstown, Aus.	0.40	4.9848	4.9815	3
Sillimanite	Jefferson Co., CO	0.13	4.9878	4.9872	3
Sillimanite§	NE Dalradian, Scot.	0.30	4.9882	4.9858	4
Andalusite	Minas Gerais, Bra.	0.41	5.1508	5.1481	5
Kyanite	Burnsville, NC	0.06	4.4202	4.4199‡	6
Andalusite	Minas Gerais, Bra.	0.39	5.1557	5.1530‡	6
Sillimanite	Brandyw. Spgs., DE	0.03	5.0027	5.0025‡	6
Andalusite	Andalusia, Sp.	0.18	5.1454	5.1442	7
Andalusite	Minas Gerais, Bra.	0.23	5.1477	5.1461	7
Andalusite	Brazil	0.23	5.1465	5.1449	7
Andalusite	Minas Gerais, Bra.	0.30	5.1450	5.1430	7
Andalusite	Oreville, SD	0.41	5.1469	5.1441	7
Andalusite	Minas Novas, Bra.	0.47	5.1469	5.1437	7
Andalusite	Minas Gerais, Bra.	0.41	5.1488	5.1460	8
Sillimanite	New Hampshire	0.18	4.9865	4.9850	8
Sillimanite§	Harcujuela, Spa.	0.16	4.9849	4.9836	9
Sillimanite	Träskbole, Fin.	0.36	4.9788	4.9758‡	9
Sillimanite	Waldeck, Ger.	0.08	4.9839	4.9832	9
Sillimanite	Sri Lanka	0.26	4.9864	4.9842	10
Sillimanite§	Lewiston, ID	0.14	4.9881	4.9862	10
Sillimanite§	Brittany, Fr.	0.25	4.9884	4.9863	11
Kyanite	Average	0.06	4.408(2)	4.408(2)	
Andalusite	Average	0.35	5.148(2)	5.146(2)	
Sillimanite	Average	0.20	4.986(2)	4.984(2)	

*Note:* Includes only samples with <0.5 mol%  $\text{Fe}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ .  
 \* Calculated from wt%  $\text{Fe}_2\text{O}_3$  assuming ideal stoichiometry, oxides total 100%, and no other oxides present, multiplying wt%  $\text{Fe}_2\text{O}_3$  by 1.016. For some, more recent, higher quality analytical data were added or substituted.  
 \*\*  $V_c$ , corrected for  $\text{Fe}^{3+}$ : 0.0047 J/bar mol%  $\text{Fe}_2\text{O}_3$  for kyanite; 0.0068 for andalusite; 0.0083 for sillimanite (see text).  
 † References: 1 = Skinner et al. (1961); 2 = Richardson et al. (1969); 3 = Holdaway (1971); 4 = Cameron and Ashworth (1972); 5 = Abs-Wurmbach and Langer (1975); 6 = Winter and Ghose (1979); 7 = Gunter and Bloss (1982); 8 = Abs-Wurmbach et al. (1983); 9 = Salje (1986); 10 = Hemingway et al. (1991); 11 = Bish and Burnham (1992).  
 ‡ Excluded from averages (see text).  
 § Fibrous sillimanite; average  $V_c = 4.985(2)$ .  
 || Italicized values recommended for thermochemical calculations.

$H$  for sillimanite to reproduce the kyanite = sillimanite boundary, then adjusting  $S$  and  $H$  for andalusite to fit the andalusite = sillimanite boundary, and then making minor adjustments in  $S$  and  $H$  of kyanite so that the kyanite = andalusite and kyanite = sillimanite boundaries are both fitted as well as possible.

The values of  $\Delta S$  and  $\Delta H$  determined in this way produce the equilibrium curves shown in Figures 1–3. However, the assumption that the  $S$  and  $H$  for kyanite of Hemingway et al. (1991) are more accurate than their  $S$

and  $H$  for sillimanite and andalusite is not valid. In order to produce the best overall agreement with the calorimetric values of Hemingway et al. (1991),  $S$  and  $H$  for each phase were adjusted by an additive constant for  $S$  and an additive constant for  $H$ , so that the average  $S$  and average  $H$  of all three polymorphs are equal to the average  $S$  and  $H$  of Hemingway et al. (1991).

Our standard  $S$  and  $H$  values improve the overall fit of the reversal data with the calculated curves relative to that of Hemingway et al. (1991). We recommend the ad-

**TABLE 10.** Entropy and enthalpy of aluminum silicates

Mineral	$S_1$ (J/mol K)*	$S_2$ (J/mol K)	$S_3$ (J/mol K)	$H_1$ (kJ/mol)	$H_2$ (kJ/mol)
Kyanite	82.30(13)	82.80(50)	82.86(50)**	-2593.8(30)	-2593.70(300)**
Andalusite	91.39(14)	91.39(52)	91.60(52)	-2589.9(30)	-2589.66(300)
Sillimanite	95.87(54)	95.40(52)	95.08(52)	-2586.1(30)	-2586.37(300)

\* $S_1$  = Measurements of Robie and Hemingway (1984) for kyanite and andalusite, and Hemingway et al. (1991) for sillimanite, corrected for impurities where necessary;  $S_2$ ,  $H_1$  = Hemingway et al. (1991), adjusted to fit aluminum silicate reversals and consistent with their  $V$  and  $C_p$ ;  $S_3$ ,  $H_2$  = from our study, adjusted to fit aluminum silicate reversals and consistent with our  $V$  (Table 9) and the  $C_p$  of Hemingway et al. (1991).

\*\* Italicized values are recommended for thermochemical calculations.



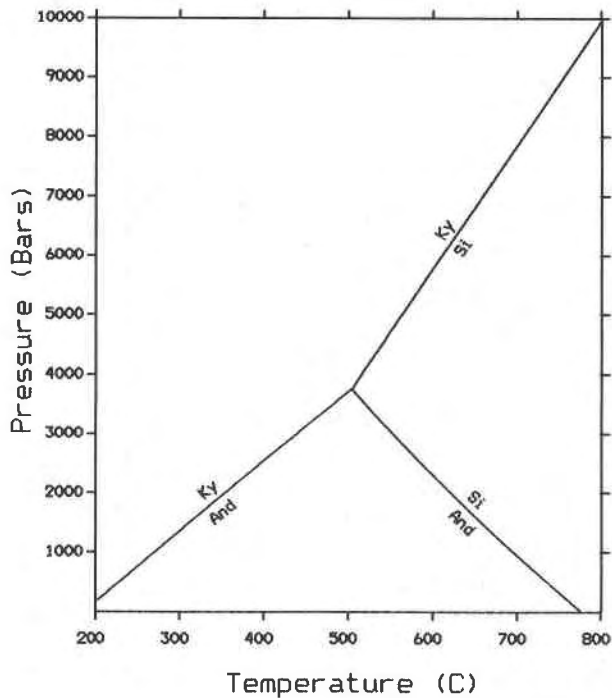


Fig. 5. Aluminum silicate stability diagram calculated using the thermochemical data of Tables 9 and 10 (italicized values), the  $C_p$  expression of Hemingway et al. (1991), and thermal expansion and compressibility formulas of Berman (1988). The equilibrium curves are the same as those of Figures 1–3.

justed calorimetric data in Table 10 ( $S_3$  and  $H_3$ ) as consistent with calorimetric results of Hemingway et al. (1991) and with the molar volumes and reversals determined in this report. The preferred aluminum silicate phase diagram is given in Figure 5 and Table 11 and has a triple point at  $504 \pm 20$  °C,  $3.75 \pm 0.25$  kbar. In our opinion, this is the best possible determination of the aluminum silicate phase boundaries available at present. However, we recall from the discussion on the effect of  $Fe^{3+}$  content that the andalusite = sillimanite phase boundary may still be up to 20 °C higher than that of the pure aluminum silicate system.

The primary causes of the small differences between the  $S$  and  $H$  of Hemingway et al. (1991) and our own values are the differences in  $V$  and the use of compressibility for our determination. The causes of differences between our results and those of Berman (1988) are the updated  $C_p$  expressions of Hemingway et al. (1991) and the differences in  $V$ . We emphasize that differences in  $S$  and  $H$  determined by various methods result from errors in one or more of the following: (1) thermal expansion or compressibility, (2)  $C_p$  expressions, (3)  $V$ , (4) experimental reversals, or (5) calorimetry. Whereas the errors shown in Table 10 are the same as those given by Hemingway et al. (1991), the relative errors among polymorphs are substantially smaller than the errors shown in Table 10. Because the thermodynamic data of Tables 9 and 10 are

TABLE 11. Pressure and temperature values of aluminum silicate phase diagram consistent with all valid experimental reversals and half-reversals

$T$ (°C)	And = kya (kbar)	Kya = sil (kbar)	And = sil (kbar)
200	0.16	—	—
300	1.36	—	—
400	2.54	—	—
500	3.71	3.67	3.82
600	4.86	5.77	2.30
700	6.00	7.86	0.95
800	7.13	9.95	—
900	8.24	12.05	—
1000	9.33	14.16	—

Triple point is  $504 \pm 20$  °C,  $3.75 \pm 0.25$  kbar

Note: Values are calculated with our  $V$  and the  $C_p$  expressions of Hemingway et al. (1991) and are as consistent as possible with calorimetric entropies and enthalpies.

self-consistent and reproduce the aluminum silicate reversals, they can also be expected to serve well in working with reactions involving other silicates, providing appropriate adjustments are made to  $H$  of silicates whose  $H$  depends on that of aluminum silicates.

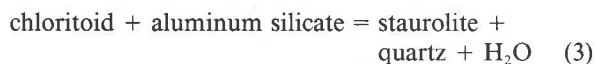
## DISCUSSION

We wish to emphasize that phase equilibrium studies should be judged primarily on their merits: on the basis of experimental technique, nature of starting materials, method of detecting reaction, thermodynamic logic, and consistency with calorimetric data, and only secondarily on the basis of natural occurrence, unless the occurrence depends in no way on the accuracy of other experimental studies. Extreme care is necessary to calibrate a phase boundary on the basis of natural occurrences. In some instances it may be possible to use petrologic occurrences to reject certain phase diagrams, and perhaps to support others. Here we contrast two examples of comparison with nature, one of which supports the aluminum silicate diagram of this report and one of which does not.

A low-variance assemblage that, if stable, occupies only a small area of  $P$ - $T$  space, and for this reason is rare in nature, is ideal for secondary comparison with an experimentally determined phase diagram, provided the limiting phase boundaries for the other parts of the assemblage are well known. The assemblages sillimanite + chloritoid + quartz and sillimanite + paragonite + quartz commonly seen in the Picuris (Holdaway and Goodge, 1990) and Truchas (Grambling, 1981, 1983, 1984) Ranges in New Mexico provide such a possibility. Even though these assemblages are relatively rare elsewhere, their occurrence is common enough in northern New Mexico for them to be regarded as equilibrium assemblages. Textural evidence strongly supports this conclusion. Absence of graphite and carbonates indicates that the fluid phase was relatively pure  $H_2O$ . Both assemblages require that the  $P$ - $T$  conditions lie in a small space at higher  $T$  than the aluminum silicate triple point. The assemblages also require unusually high  $Al_2O_3$  content, and chloritoid re-

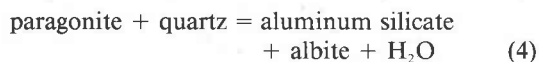
quires high Fe/Mg whereas paragonite requires high Na/(K + Ca). Most normal pelites do not have these characteristics. In New Mexico, the occurrences are in aluminous Ortega quartzite, which was metamorphosed at the requisite  $P$  and  $T$  over a range of  $f_{O_2}$ . Garnet-biotite geothermometry in both areas indicates  $T$  near 530 °C (Holdaway and Goodge, 1990; Grambling, 1986).  $Fe^{3+}$  in the aluminum silicates increases the triple point  $T$  by about 20 °C above its value in a pure  $Al_2SiO_5$  system (Holdaway and Goodge, 1990).

Occurrences of sillimanite + chloritoid + quartz in the Picuris Range were studied by Holdaway and Goodge (1990). The reaction



takes place at 547 °C at 4 kbar in the pure system (Richardson, 1968). Holdaway and Goodge (1990) estimate that compositional effects lower this equilibrium to 526 °C. The pure  $Al_2SiO_5$  triple point must lie at  $T$  below 506 °C (526 - 20) for sillimanite to occur. The combined error of the experimental determination of Reaction 3 and estimation of compositional effects is about 25 °C. Thus the pure aluminum silicate triple point lies below some  $T$  between 480 and 530 °C.

Grambling (1984) observed the assemblage sillimanite + paragonite + quartz in the Truchas Range. The reaction



takes place at 560 °C at 4 kbar (Chatterjee, 1972). Corrections for composition made using the GE0-CALC program (Brown et al., 1988) with the Berman (1988) data base increase the  $T$  by about 20 °C. Thus the pure  $Al_2SiO_5$  triple point must lie at  $T$  below 560 °C, or, with the 20 °C error, below some  $T$  between 540 and 580 °C. The rareness of this assemblage is very much associated with bulk composition; Grambling found it in only two specimens of mica-bearing rocks, and found the products of Reaction 4 in none.

These conclusions depend critically on the accuracy of the chloritoid aluminum silicate stability determination of Richardson (1968) and the paragonite-quartz stability determination of Chatterjee (1972), each assumed to be within 15 °C of the correct value for these estimates. If these experimental determinations were substantially too low in  $T$ , the above restrictions would not be correct.

Pattison (1992) has used a number of geobarometers and geothermometers, including cordierite-bearing assemblages, to estimate a point at 3 kbar, 650 °C, on the andalusite-sillimanite boundary in the Ballachulish aureole. Using this point, he suggests that the andalusite-sillimanite boundary is 50 to 100 °C above the boundary we propose here. We suggest that some of the geobarometers used by Pattison (1992) were either in error or had low precision and that the andalusite breakdown at Ballachulish was closer to 2.1 kbar, 610 °C, based on the

intersection of the present andalusite = sillimanite phase diagram with the muscovite-quartz breakdown curve calculated with the GE0-CALC program. We argue against Pattison's (1992) conditions partly because Mukhopadhyay et al. (1991) have recently redetermined the iron cordierite stability relations in the reaction



and find that iron cordierite is less stable by about 1 kbar at 600 °C than originally determined by Holdaway and Lee (1977). This should come as no surprise to petrologists who have criticized the Holdaway and Lee determination (Martignole and Sisi, 1981; Aranovich and Podlesskii, 1983). (The other iron cordierite stability boundaries, especially those based on thermodynamic data for iron cordierite, may well shift down in  $P$  also, requiring a reevaluation of all the  $P$ -sensitive iron magnesium cordierite reactions.)

The important conclusion to be drawn is that it is extremely difficult to use petrologic occurrences to locate or verify equilibrium phase boundaries. The secondary nature of such determinations should always be emphasized. Perhaps when most petrologists can agree on an accurate petrogenetic grid, such estimates will be more meaningful.

## CONCLUSIONS

1. Many previous experimental studies on the kyanite = andalusite and andalusite = sillimanite equilibria provide significant input into solving the enigma of the aluminum silicate system if the studies are evaluated carefully.
2. The main experimental difficulties with this system involve (1) the detection of small amounts of reaction, (2) the presence of reactive fibrous sillimanite or intergrown quartz in sillimanite starting materials, and (3) the effects of  $Fe^{3+}$  impurities.
3. The kyanite = andalusite equilibrium is well bracketed by four of the five studies since 1966. Small adjustments in the standard  $S$  and  $H$  of the aluminum silicates (Hemingway et al., 1991) steepen the curve slightly and produce an overall better fit of experiments.
4. The andalusite = sillimanite equilibrium is bracketed by reversals and half-reversals from five experimental studies since 1966. Andalusite-stable apparent half-reversals of Richardson et al. (1969) must be rejected because they used fine fibrous sillimanite and repeated grinding during the experiments; crystal growth reversals of Bowman (1975) must be enlarged to remove ambiguities; cryolite melt experiments of Weill (1966) and Bowman (1975) must be regarded as sillimanite-stable half-reversals; and andalusite-stable data points of Heninger (1984) must be rejected because weight gains were not more than weighing error. Many of the experiments of Holdaway (1971) must be regarded as upper limits because the 1.15%  $Fe_2O_3$  in the sillimanite may have raised the  $T$  of the curve by up to 20 °C. Small adjustments of the aluminum silicate  $S$  and  $H$  improve the overall fit.

5.  $\text{Fe}_2\text{O}_3$ -corrected data are provided for  $V$  of each of the aluminum silicates. These are recommended for future calculations. The Hemingway et al. (1991)  $C_p$  expressions were used for calculations.

6. Our suggested equilibrium curves meet in a triple point at  $504 \pm 20$  °C,  $3.75 \pm 0.25$  kbar, with the present determinations of  $V$ , the  $C_p$ ,  $S$  (adjusted by us), and  $H$  (adjusted by us) of Hemingway et al. (1991), and fit very well the accepted reversals. This triple point is consistent with that of Berman (1988; 503 °C, 3.73 kbar), and that of Hemingway et al. (1991; 511 °C, 3.87 kbar).

7. We emphasize that petrologic occurrences should, as much as possible, be used only for secondary comparison with experiments. There are risks associated with basing equilibrium curves on natural occurrences because experimental error and experimental mistakes of determining  $P$ - $T$  conditions are compounded.

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