

Entropies of kyanite, andalusite, and sillimanite: additional constraints on the pressure and temperature of the Al_2SiO_5 triple point

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Abstract

The low-temperature heat capacities of kyanite (Minas Gerais, Brazil), andalusite (Espírito Santo, Brazil), and sillimanite (Reinbolt Hills, Antarctica) were measured with an automatic, adiabatically shielded calorimeter between approximately 10 and 380 K. At 298.15 K the entropies are 82.30 ± 0.13 , 91.39 ± 0.14 , and 95.79 ± 0.14 J/(mol · K) for kyanite, andalusite, and sillimanite, respectively. Our values are 1.8, 2.0 and 0.4% smaller than those of Todd (1950). Our calculated slope for the andalusite–sillimanite phase boundary is in significantly better agreement with the phase boundaries of Holdaway (1971), than with those of Richardson, Gilbert and Bell (1969) and strongly suggest that Al and Si are ordered in sillimanite to at least 1100 K.

The thermal Debye temperatures, θ_D° , calculated from our heat capacity data in the range $T < 18$ K are 1100, 855, and 730 K for kyanite, andalusite, and sillimanite respectively. For andalusite and sillimanite our values for θ_D° are in moderate agreement with those calculated from the room temperature adiabatic elastic stiffness constants of Vaughan and Weidner (1978), 838 and 800 K, respectively.

Introduction

The usefulness of a mineral system in the interpretation of geologic processes is dependent upon its geologic distribution and upon the confidence that we place in our knowledge of the physical and chemical properties of that system. The Al_2SiO_5 polymorphs, kyanite, andalusite, and sillimanite, commonly occur in metamorphosed pelitic sediments, and because of the relatively simple chemistry of the mineral system, the Al_2SiO_5 polymorphs define one of the most important fixed (invariant) points for establishing a quantitative petrogenetic grid for metamorphic petrology. However, because the Gibbs free energies of the three Al_2SiO_5 polymorphs differ by so little and because of kinetic problems in some areas of the experimental studies of this system, the location of the univariant reaction boundaries and of the invariant (triple) point are not known with the certainty necessary to make this mineral system a fully effective tool for the petrologist.

Most petrologists accept either the phase diagram of Holdaway (1971) or that of Richardson et al. (1969); a few cite the work of Althaus (1967) or Brown and Fyfe (1971). Zen (1969) and Holdaway (1971) have summarized the early work on the stability of the Al_2SiO_5 polymorphs and have provided extensive analyses of the experimental studies, citing the known and potential sources for error. Relatively few studies have been published since Zen's review (e.g., Holdaway, 1971; Anderson et al. 1977;

Winter and Ghose, 1979; and Schneider, 1979; Day and Kumin, 1980).

The phase diagrams of the Al_2SiO_5 system given by Holdaway (1971), Richardson et al. (1969), Althaus (1967), and Brown and Fyfe (1971) differ in the location of the triple point and in the slopes of the univariant reaction boundaries. The univariant reaction boundaries determined from phase-equilibria experiments also differ from the slopes predicted from the calorimetrically derived thermochemical data provided from the low-temperature heat-capacity measurements of Todd (1950), the heat-content measurements of Pankratz and Kelley (1964) and the enthalpy of solution results of Anderson and Kleppa (1969), Navrotsky et al. (1973) and Anderson et al. (1977). Several authors (e.g., Zen, 1969; Holdaway, 1971; and Anderson, Newton, and Kleppa, 1977) have proposed that one or more of the Al_2SiO_5 polymorphs is partially disordered in aluminum and silicon in order to produce general agreement between the calorimetric data and the phase-equilibria data.

The univariant reaction boundaries located by phase-equilibria studies are, in general, based upon only a few experimental phase-reversal brackets through which many reaction curves of varying slopes could be constructed. The reaction boundaries selected in the various studies represent the workers' best estimates of the locations and slopes of the reaction boundaries; however, the choices are not unique.

A combination of (1) the calorimetrically determined

entropies ($S_T^\ddagger - S_0^\ddagger$, where S_0^\ddagger is the zero-point entropy), (2) entropy estimates for various models of order-disorder in Al-Si, and (3) data for the molar volumes (as a function of temperature and pressure) of the Al_2SiO_5 polymorphs can provide estimates of the slopes of the univariant reaction boundaries ($dP/dT = \Delta S/\Delta V$) that have greater precision than those derived solely from phase-reversal brackets. However, the calorimetrically derived entropies at 298.15 K for the Al_2SiO_5 polymorphs that are available in the literature are based upon heat capacity measurements that cover only the range of temperatures from 54.4 to 296.5 K (Todd, 1950) and therefore they have a much larger uncertainty than those available from modern measurements extending down to 5 K. Also, the molar volume data available in the literature are not consistent (e.g., Skinner et al., 1961, and Winter and Ghose, 1979) and consequently increase the uncertainty with which the univariant reaction boundaries may be determined.

We have measured the heat capacities of andalusite, kyanite, and sillimanite between about 6 and 375 K in order to reduce the uncertainty in the calorimetrically determined entropy ($S_T^\ddagger - S_0^\ddagger$). We have combined our results with the heat-content data of Pankratz and Kelley (1964), have calculated heat capacity functions with which we may improve the estimates of the slopes of the univariant reactions, and have compared these results with phase-equilibria data in order to evaluate the contribution of order-disorder in Al/Si and to further restrict the location of the triple point in the Al_2SiO_5 mineral system.

Materials and sample preparation

Kyanite. The kyanite used for our heat capacity studies was obtained from Ward's Natural Science Establishment (Ward's) and came from Minas Gerais, Brazil. The polycrystalline aggregate contained coarse light blue to colorless crystals as much as 2 cm long with a heavy brown (limonite?) stain. The sample was crushed in an alumina mortar and the -10 +20 mesh fraction (-2.0 +0.8 mm) was retained. The material was boiled in a 60/40 HF · HCl solution for 1 hour, rinsed several times with distilled water, dried at 130°C, and then handpicked free of any remaining impurity phases under a binocular microscope. The final sample consisted of transparent needle-shaped crystals, some bent, and ranged from colorless to light blue. The sample was analyzed by atomic absorption and by inductively coupled argon plasma (ICAP) spectroscopy for Fe, Cr, and Mn. The analysis gave $\text{Fe}_2\text{O}_3 = 0.18 \pm 0.05$ wt.%, Cr 90 ppm, and Mn <5 ppm. The sample weight for our calorimetric studies was 42.328 g corrected for buoyancy.

Andalusite. Andalusite was also purchased from Ward's. The source was listed as Santa Theresa, Espirito Santo, Brazil. The material was in the form of water-rounded, transparent single crystals 0.5 to 1 cm in diame-

ter and were either bottle green or pink. The individual crystals were examined under a binocular microscope, and those crystals showing rutile or other inclusions were discarded. Analysis by atomic absorption and ICAP gave $\text{Fe}_2\text{O}_3 = 0.36 \pm 0.05$ wt.%, and less than 5 ppm for Cr and Mn. The sample weight corrected for buoyancy was 44.598 g.

Sillimanite. The sillimanite sample was separated from a pegmatite lens in a granulite-facies rock from the Reinbolt Hills, Antarctica (Sample number 556, also Smithsonian NMNH #137011, Grew, 1980). The source material was first crushed to -20 mesh (0.83 mm), soaked for 14 hours in 40 percent HF(aq), and the larger grains of sillimanite were picked free. The remaining material was crushed to -48 mesh (0.29 mm), passed thru tetrabromoethane to remove feldspars and quartz, passed several times thru a Franz¹ magnetic separator to remove ilmenite, sieved to remove material smaller than 0.10 mm (150 mesh), boiled in 25% HF(aq) for 3 hours, and finally handpicked under a binocular microscope. Grew (1980) reported a range of 0.76 to 1.30 wt.% Fe_2O_3 for various grains of sillimanite from sample 556 with an average of 1.23. A complete analysis of sample 556 is given by Grew (1980).

Apparatus and experimental results

The heat capacity measurements were made by means of the calorimeter and cryostat described by Robie and Hemingway (1972), Robie, Hemingway, and Wilson (1976). Our experimental results are listed in their chronological order of measurement in Tables 1 through 3 for kyanite, andalusite and sillimanite respectively. Figure 1 shows values for kyanite, and Figure 2 shows the differences $C_p^\circ(\text{andalusite}) - C_p^\circ(\text{kyanite})$, and $C_p^\circ(\text{sillimanite}) - C_p^\circ(\text{kyanite})$. Our experimental measurements below 30 K were plotted as C_p°/T versus T^2 and extrapolated smoothly to 0 K. Figure 3 gives examples for kyanite and andalusite. The heat capacities measured between 20 and ~385 K were smoothed by computer, using the smoothing spline procedure described by Robie, Finch, and Hemingway (1982). The two data sets were joined smoothly and used to produce tables of the thermodynamic properties (Tables 4, 5, and 6). No corrections were made to our data for deviation from the exact composition Al_2SiO_5 . Over the range of temperatures common to our results and those of Todd (1950), 51 to 298 K, our values for $S_{298}^\circ - S_{51}^\circ$ agree within 1.3% for kyanite, 0.9% for andalusite, and 0.2% for sillimanite. At 298.15 K, the entropies of kyanite, andalusite, and sillimanite are 83.20 ± 0.13 , 91.39 ± 0.14 , and 95.79 ± 0.14 J/(mol · K), respectively. The correction for Fe_2O_3 for each phase would be less than 0.1%.

¹ Any use of trade names in this report is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table 1. Experimental molar heat capacities of kyanite from Minas Gerais, Brazil

Temp.	Heat capacity	Temp.	Heat capacity	Temp.	Heat capacity
K	J/(mol·K)	K	J/(mol·K)	K	J/(mol·K)
Series 1		Series 4		Series 6	
304.28	124.2	159.16	58.46	8.16	0.0242
308.89	125.5	164.83	61.80	9.00	0.0109
313.88	127.1	170.08	64.81	11.20	0.0066
318.90	128.7	175.42	67.81	12.38	0.0113
324.17	130.3	181.09	70.98	15.32	0.0362
329.45	131.8	186.74	73.97	17.02	0.0526
334.71	133.5	192.38	77.00	18.91	0.0843
339.97	134.9	198.02	79.95	20.97	0.1224
345.21	136.6	203.66	82.89	23.27	0.1674
		209.28	85.72	25.85	0.2375
		214.90	88.48	28.72	0.3550
		220.50	91.07	31.94	0.5677
350.33	137.6			35.53	0.9429
355.52	138.9	Series 5		39.56	1.400
360.48	140.1			44.09	2.085
365.46	141.3	225.76	93.52	49.16	2.853
370.63	142.5	230.95	95.86	54.80	4.043
		236.08	98.29	60.96	5.884
		241.27	100.5	67.34	8.175
		246.74	103.1		
52.76	3.579	252.20	105.1	Series 7	
65.41	7.464	257.66	107.2		
73.66	10.77	263.10	109.4	7.42	0.0167
80.49	13.85	268.54	111.5	10.21	0.0154
87.03	16.99	273.96	113.6		
93.38	20.16	279.35	115.8	Series 8	
99.54	23.42	284.75	117.5		
105.63	26.80	290.12	119.4	8.37	0.0172
111.65	30.30	295.49	121.5	9.06	0.0088
117.64	33.82	300.84	123.2	9.85	0.0141
123.60	37.27	306.20	124.9	10.35	0.0173
129.52	40.86	311.54	126.5	10.84	0.0183
135.42	44.44			11.35	0.0103
141.31	47.89			12.29	0.0129
147.17	51.33			12.77	0.0144
153.01	54.83			13.27	0.0131
158.83	58.20			13.77	0.0249
164.64	61.60			14.27	0.0332

The agreement between the thermal and the elastic values for the Debye temperature is excellent (within 2%) for andalusite but is less satisfactory for sillimanite. This is probably due to the greater amount of iron in solid solution in the sillimanite as compared with the andalusite sample, which would lead to a larger specific heat at low temperatures, as compared with pure Al_2SiO_5 , and thus to a smaller value of θ_D^0 . Our values for the Debye temperatures differ significantly from those given by Kieffer (1982). Her values were calculated from *estimated* mean sound velocities.

Molar volumes of Al_2SiO_5 polymorphs

In Table 7, we have summarized the available unit-cell parameters and molar volume data at 25°C for sillimanite from Brandywine Springs, Delaware, for andalusite from Minas Gerais, Brazil, and for kyanite from Burnsville, North Carolina. These materials are the most widely studied and demonstrate only too well the difference between precision and accuracy in X-ray unit-cell data. For each of these materials, the single-crystal cell parameters of Winter and Ghose (1979) are significantly larger than are the other values, which have been obtained primarily from power diffractometry using an internal standard. It is tempting to conclude that the difference in the cell parameters is related to determination procedures, i.e., single-crystal or powder techniques. However

Table 2. Experimental molar heat capacities of andalusite from Santa Theresa, Espirito Santo, Brazil

Temp.	Heat capacity	Temp.	Heat capacity	Temp.	Heat capacity
K	J/(mol·K)	K	J/(mol·K)	K	J/(mol·K)
Series 1		Series 1		Series 2	
55.09	7.449	226.39	96.47	5.88	0.0124
59.96	9.438	231.91	98.85	6.46	0.0216
64.71	11.58	237.46	101.1	6.96	0.0305
70.00	14.13	243.00	103.3	7.57	0.0213
76.13	17.24	248.53	105.6	8.40	0.0223
82.19	20.47	254.05	107.8	9.28	0.0316
88.31	23.71	259.57	109.8	10.23	0.0390
94.44	27.06	265.06	111.9	11.33	0.0375
100.51	30.46	270.54	113.7		
106.53	33.89	276.01	115.7	Series 3	
112.51	37.30	281.47	118.0		
118.45	40.85	286.93	119.6	13.55	0.0514
124.35	44.29	292.38	121.4	14.68	0.0740
130.22	47.58	297.80	123.2	15.72	0.0951
136.05	50.93	303.20	124.9	17.02	0.1226
141.85	54.22	308.59	126.4	18.76	0.1803
147.62	57.35	313.95	128.1	20.65	0.2574
153.37	60.51	319.32	129.6	22.84	0.3652
159.10	63.70	324.66	131.1	25.31	0.5332
164.81	66.74	330.00	132.9	28.08	0.7893
170.49	69.68	335.31	134.3	31.20	1.197
176.16	72.70	340.60	135.7	34.69	1.799
181.80	75.57	345.89	136.7	38.61	2.689
187.42	78.50	351.16	138.1	42.99	3.774
193.03	81.33	356.42	139.3	47.92	5.098
198.63	83.92	361.67	140.6	53.43	6.841
204.21	86.50	366.92	141.9	59.50	9.233
209.77	89.02	372.14	143.2		
215.32	91.62	377.36	144.4		
220.86	94.11				

Debye temperatures of kyanite, andalusite, and sillimanite

We have calculated the Debye temperatures θ_D^0 , from our heat capacity data for temperatures below approximately 18 K for the three Al_2SiO_5 polymorphs. The resultant values are 1100 ± 25 , 855 ± 20 , and 730 ± 50 K for kyanite, andalusite, and sillimanite, respectively. Figure 3 gives a comparison between our observed heat capacities and those calculated from the above values of θ_D^0 for kyanite and andalusite. The excessively large scatter of the C_p^0 data below 20 K is a consequence of the very small heat capacities of the Al_2SiO_5 polymorphs and the fact that the sample is only a very small percentage of the total heat capacity (calorimeter plus sample). For example, at 20 K the heat capacity of the kyanite sample was only 5.1% of the total measured heat capacity.

We have also calculated the Debye temperature of andalusite and sillimanite from the single-crystal elastic constant data of Vaughan and Weidner (1978), using the methods described by Robie and Edwards (1966). These calculations yield 838 and 800 K for the elastic Debye temperature of andalusite and sillimanite, respectively.

Table 3. Experimental molar heat capacities of sillimanite from Reinbolt Hills, Antarctica

Temp.	Heat capacity	Temp.	Heat capacity	Temp.	Heat capacity
K	J/(mol·K)	K	J/(mol·K)	K	J/(mol·K)
Series 1		Series 3 (cont)		Series 4	
303.06	124.5	152.80	62.06	6.47	0.046
307.86	125.9	158.52	65.15	7.29	0.050
312.82	127.3	164.23	68.13	8.09	0.066
317.80	128.4	169.92	71.06	9.01	0.056
323.00	130.0	175.59	74.04	10.11	0.053
328.19	131.4	181.24	76.90	11.24	0.060
333.36	132.7	186.89	79.68	12.50	0.068
338.52	134.4	192.53	82.35	13.88	0.082
343.70	135.6	198.16	84.92	15.38	0.119
348.86	136.7	203.78	87.43	17.05	0.177
		209.37	89.84	18.91	0.265
		214.96	92.45	20.97	0.394
		220.53	94.83	23.26	0.564
Series 2		226.11	97.17	25.82	0.820
352.80	137.7	231.69	99.48	28.67	1.198
357.93	138.6	237.27	101.7	31.87	1.766
362.88	140.1	242.85	103.9	35.45	2.564
367.84	141.5	248.42	106.1	39.45	3.707
372.96	142.7	253.98	108.2	43.94	5.014
378.06	143.6	259.52	110.1	48.99	6.520
		265.07	112.2	54.61	8.553
		270.63	114.1	60.70	11.21
Series 3		276.16	115.8	67.02	14.29
55.09	8.723	281.68	117.6	73.36	17.60
59.98	10.84	287.18	119.5	79.63	20.95
64.73	13.12	292.65	121.4	85.80	24.30
70.01	15.80	298.11	122.9	91.90	27.61
76.10	19.03	303.56	124.5	97.92	30.97
82.11	22.29				
88.17	25.60	308.99	126.1		
94.23	28.93				
100.25	32.32				
106.22	35.72			Series 5	
112.14	39.16			175.24	73.93
118.03	42.62			180.61	76.62
123.89	46.00			185.73	79.12
129.72	49.32			190.90	81.63
135.53	52.58			196.34	84.16
141.31	55.82			201.75	86.60
147.07	58.93			207.15	89.00
				212.54	91.39
				217.91	93.65
				223.28	96.02
				228.63	98.29
				233.98	100.5
				239.32	102.7

the data for the Burnsville, North Carolina, kyanite include single-crystal data by Skinner et al. (1961) and Burnham (1963) that agree closely with one another and with the powder data but that are significantly less than the values of Winter and Ghose (1979).

Furthermore, based on the work of Hubbard et al. (1975) one might expect systematic differences between single crystal and powder measurements at the level of a few parts in 10^5 , not the 60 parts in 10^5 observed between the Winter and Ghose (1979) and Skinner et al. (1961) data.

The molar volumes at 298 K that we have adopted for use in our calculations are 44.15 ± 0.05 , 51.52 ± 0.05 , and 49.86 ± 0.05 cm^3/mol for kyanite, andalusite, and sillimanite, respectively, and were obtained from unit-cell volumes of Table 7 and using a value for Avogadro's number = $(6.022094 \pm 0.000008) \times 10^{23}$ mol^{-1} (Deslattes et al., 1974).

Skinner et al. (1961) and Winter and Ghose (1979) have both measured the unit-cell parameters of kyanite, anda-

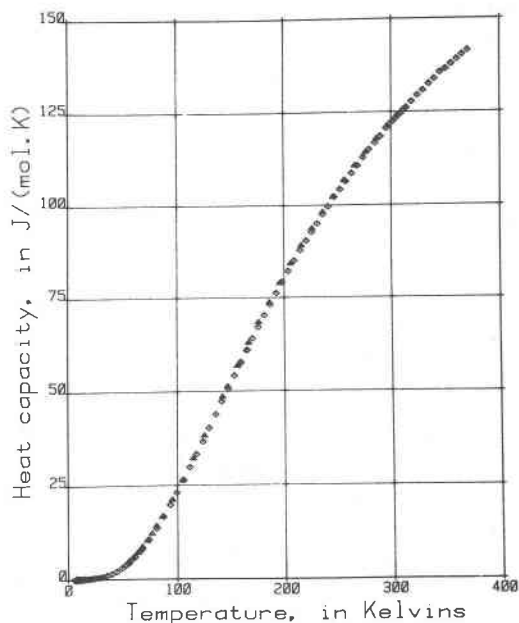


Fig. 1. Experimental molar heat capacities (open diamonds) of kyanite from Minas Gerais, Brazil. Solid triangles, data of Todd (1950).

lusite, and sillimanite at high temperatures, and Schneider (1979) has measured the cell parameters of andalusite to 1000°C . The results of the three investigations for andalusite are shown in Figure 4. The agreement between the three investigations is unsatisfactory.

The effect of pressure upon the molar volume can be estimated from the compressibilities at 298 K, ($\beta = 1/V(dV/dP)_T$). Brace et al. (1969) obtained 0.70, 0.67, and 0.65 Mbar^{-1} for kyanite, andalusite, and sillimanite, respectively. The compressibilities (adiabatic) of andalusite and sillimanite are 0.63 and 0.60 Mbar^{-1} obtained

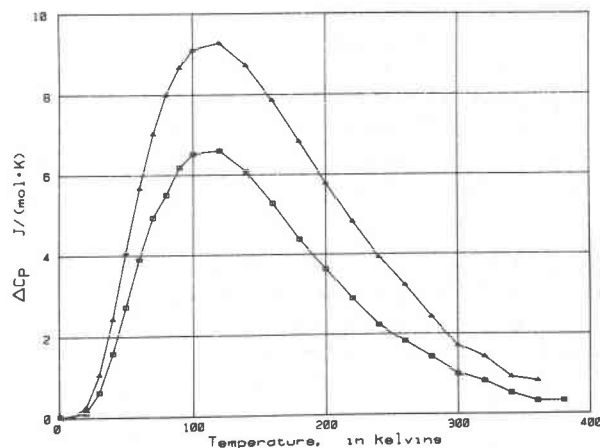


Fig. 2. ΔC_p for andalusite - kyanite (circles) and for sillimanite - kyanite (triangles) versus temperature.

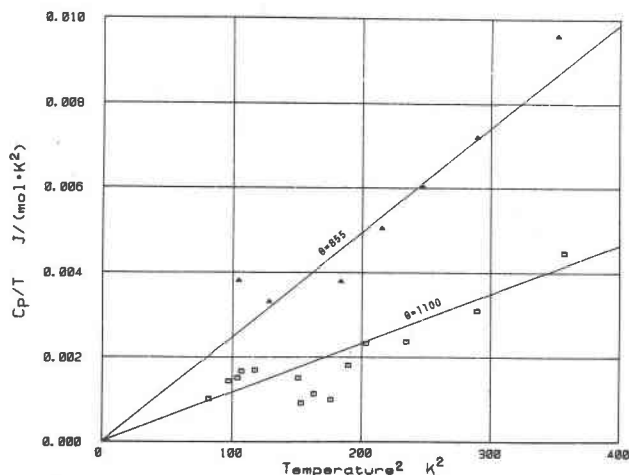


Fig. 3. C_p/T versus T^2 for Al_2SiO_5 polymorphs. Straight lines are calculated using the indicated Debye temperatures (θ_D). Squares, data for kyanite; triangles, data for andalusite.

from the elastic constant data of Vaughan and Weidner (1978), and 0.90 to 0.70 $Mbar^{-1}$ for andalusite (isothermal) obtained from the unit-cell parameters of Ralph, Finger, and Ghose (1981). From these data and the assumption that β is independent of temperature, or at least that the temperature dependence of β is essentially the same for each Al_2SiO_5 polymorph, it is easily seen that below 10 kbar, pressure will have negligible effect upon the molar volumes, that is $\Delta V_p - \Delta V^0$ is less than 0.03 cm^3 (i.e., smaller than the uncertainties in ΔV^0) and can therefore be safely neglected.

The Al_2SiO_5 triple point

We wish to use our new entropy data together with the existing high-temperature heat content values of Pankratz and Kelley (1964) and the high-temperature molar volume data of Skinner et al. (1961), Winter and Ghose (1979), and Schneider (1979) to see whether we can distinguish which of the proposed triple points (or phase diagrams) gives the best agreement.

In order to calculate the entropy changes at high temperature, we have combined our heat-capacity data above 250 K with the heat content data of Pankratz and Kelley (1964) and have fit these combined data sets to an extended Maier-Kelley equation (Haas and Fisher, 1976)

$$C_p^0 = a + bT + cT^{-2} + dT^{-1/2} + eT^2$$

by least squares with the constraint that the derived equation joins smoothly with our measured low temperature θ_p^0 and entropy. The T^2 term was not significant and therefore was omitted in the fitting process. The resulting equations, which are valid for the temperature range of 250 to 1600 K, are:

$$C_p^0 \text{ kyanite} = 303.9 - 0.01339T - 2904.3T^{-0.5} - 8.952 \times 10^5 T^{-2} \quad (1)$$

$$C_p^0 \text{ (andalusite)} = 290.4 - 0.01052T - 2627.8T^{-0.5} - 1.109 \times 10^6 T^{-2} \quad (2)$$

$$C_p^0 \text{ (sillimanite)} = 226.1 + 0.01407T - 1376.0T^{-0.5} - 2.440 \times 10^6 T^{-2} \quad (3)$$

Holdaway (1971) pointed out that the Brandywine Springs sillimanite used by Richardson et al. (1969) in their phase-equilibrium studies contained appreciable amounts of fibrolite (fibrous sillimanite) and, as such, might be the cause of the difference in the phase boundaries obtained by Richardson et al. in contrast to his own determinations. Holdaway's premise is supported by the examination of the Brandywine Springs sillimanite by high voltage transmission electron microscopy, which showed that the fibrolite patches contained quartz as a

Table 4. Molar thermodynamic properties of kyanite (Al_2SiO_5). [Formula weight 162.047 g/mol]

Temp. T K	Heat capacity C_p^0	Entropy ($S_T^0 - S_0^0$)	Enthalpy function ($H_T^0 - H_0^0$)/T	Gibbs energy function $-(G_T^0 - H_0^0)/T$
J/(mol·K)				
5	0.0015	0.0005	0.0004	0.0001
10	0.012	0.004	0.003	0.001
15	0.039	0.013	0.010	0.003
20	0.142	0.038	0.032	0.006
25	0.289	0.084	0.067	0.017
30	0.521	0.156	0.122	0.034
35	0.947	0.265	0.207	0.058
40	1.475	0.425	0.331	0.094
45	2.192	0.638	0.496	0.142
50	3.127	0.915	0.710	0.205
60	5.674	1.697	1.313	0.384
70	8.998	2.812	2.165	0.647
80	13.18	4.277	3.272	1.006
90	17.98	6.102	4.635	1.467
100	23.17	8.261	6.225	2.036
110	28.76	10.73	8.017	2.712
120	34.52	13.48	9.985	3.493
130	40.44	16.47	12.10	4.375
140	46.41	19.69	14.34	5.352
150	52.29	23.09	16.67	6.421
160	58.15	26.65	19.08	7.573
170	63.93	30.35	21.55	8.804
180	69.51	34.17	24.06	10.11
190	74.87	38.07	26.59	11.47
200	80.16	42.04	29.14	12.90
210	85.26	46.08	31.69	14.39
220	90.02	50.16	34.24	15.92
230	94.57	54.26	36.76	17.50
240	99.09	58.38	39.26	19.12
250	103.4	62.51	41.74	20.77
260	107.3	66.64	44.19	22.45
270	111.2	70.76	46.60	24.17
280	115.0	74.88	48.97	25.90
290	118.5	78.98	51.31	27.66
300	122.0	83.05	53.61	29.44
310	125.0	87.10	55.86	31.24
320	128.1	91.12	58.07	33.05
330	131.0	95.10	60.24	34.87
340	134.0	99.06	62.37	36.70
350	136.6	103.0	64.45	38.53
360	139.0	106.9	66.49	40.38
370	141.3	110.7	68.48	42.23
380	143.7	114.5	70.43	44.08
390	145.7	118.2	72.35	45.92
400	147.6	121.6	74.23	47.76
410	149.2	125.0	76.07	49.59
420	150.7	128.3	77.87	51.41
430	152.0	131.6	79.63	53.22
440	153.2	134.9	81.36	55.02
450	154.3	138.1	83.05	56.81
460	155.3	141.3	84.71	58.58
470	156.2	144.5	86.34	60.34
480	157.0	147.6	87.94	62.08
490	157.8	150.7	89.51	63.81
500	158.5	153.8	91.05	65.52
510	159.1	156.8	92.57	67.22
520	159.7	159.8	94.06	68.90
530	160.2	162.7	95.53	70.57
540	160.7	165.6	96.97	72.22
550	161.1	168.4	98.39	73.86
560	161.5	171.2	99.79	75.48
570	161.9	174.0	101.17	77.09
580	162.2	176.7	102.53	78.68
590	162.5	179.4	103.87	80.26
600	162.8	182.1	105.19	81.82
610	163.1	184.8	106.49	83.37
620	163.4	187.4	107.77	84.90
630	163.6	190.0	109.03	86.42
640	163.8	192.6	110.27	87.92
650	164.0	195.1	111.49	89.41
660	164.2	197.6	112.69	90.88
670	164.4	200.1	113.87	92.34
680	164.5	202.5	115.03	93.78
690	164.6	204.9	116.17	95.21
700	164.7	207.3	117.29	96.62
710	164.8	209.6	118.39	98.02
720	164.8	211.9	119.47	99.40
730	164.8	214.2	120.53	100.77
740	164.8	216.4	121.57	102.12
750	164.8	218.6	122.59	103.46
760	164.8	220.8	123.59	104.79
770	164.8	222.9	124.57	106.10
780	164.8	225.0	125.53	107.40
790	164.8	227.0	126.47	108.69
800	164.8	229.0	127.39	109.97
810	164.8	231.0	128.29	111.24
820	164.8	232.9	129.17	112.50
830	164.8	234.8	130.03	113.74
840	164.8	236.7	130.87	114.97
850	164.8	238.5	131.69	116.19
860	164.8	240.4	132.49	117.40
870	164.8	242.2	133.27	118.60
880	164.8	244.0	134.03	119.79
890	164.8	245.8	134.77	120.97
900	164.8	247.6	135.50	122.14
910	164.8	249.3	136.21	123.29
920	164.8	251.1	136.91	124.43
930	164.8	252.8	137.59	125.56
940	164.8	254.5	138.25	126.68
950	164.8	256.2	138.89	127.79
960	164.8	257.9	139.52	128.89
970	164.8	259.6	140.13	129.98
980	164.8	261.2	140.73	131.06
990	164.8	262.9	141.31	132.13
1000	164.8	264.5	141.88	133.19

Table 5. Molar thermodynamic properties of andalusite (Al₂SiO₅). [Formula weight 162.047 g/mol]

Temp.	Heat capacity	Entropy	Enthalpy function	Gibbs energy function
T	C _P ^o	(S _T ^o -S ₀ ^o)	(H _T ^o -H ₀ ^o)/T	-(G _T ^o -H ₀ ^o)/T
K	J/(mol·K)			
5	0.0033	0.0010	0.0007	0.0003
10	0.025	0.008	0.006	0.002
15	0.085	0.028	0.021	0.007
20	0.264	0.075	0.058	0.017
25	0.582	0.165	0.128	0.037
30	1.115	0.314	0.245	0.070
35	1.930	0.543	0.423	0.120
40	3.027	0.871	0.678	0.192
45	4.295	1.298	1.008	0.291
50	5.822	1.827	1.410	0.417
60	9.555	3.208	2.446	0.761
70	13.91	5.000	3.766	1.234
80	18.86	7.175	5.338	1.837
90	24.17	9.701	7.134	2.567
100	29.70	12.53	9.112	3.420
110	35.34	15.63	11.24	4.387
120	41.11	18.95	13.49	5.461
130	46.82	22.46	15.83	6.632
140	52.47	26.14	18.25	7.894
150	57.98	29.95	20.71	9.237
160	63.41	33.87	23.21	10.65
170	68.67	37.87	25.73	12.14
180	73.86	41.94	28.26	13.68
190	78.96	46.07	30.80	15.27
200	83.79	50.25	33.33	16.92
210	88.40	54.45	35.84	18.61
220	92.90	58.66	38.33	20.33
230	97.19	62.89	40.80	22.09
240	101.3	67.11	43.24	23.88
250	105.3	71.33	45.64	25.69
260	109.1	75.53	48.01	27.53
270	112.8	79.72	50.34	29.38
280	116.4	83.89	52.63	31.25
290	119.8	88.03	54.89	33.14
300	123.0	92.14	57.11	35.04
310	126.0	96.23	59.28	36.95
320	128.9	100.3	61.41	38.86
330	131.9	104.3	63.50	40.78
340	134.5	108.3	65.55	42.71
350	136.9	112.2	67.55	44.64
360	139.3	116.1	69.51	46.57
370	141.7	119.9	71.43	48.50
380	144.0	123.7	73.31	50.43
273.15	114.2	81.03	51.06	29.97
298.15	122.6	91.39	56.70	34.69

separate phase (Bell and Nord, 1974). Bell and Nord concluded that "parts of the Brandywine Springs sillimanite are technically rocks, not minerals" and that "the existence of quartz makes the Brandywine Springs sillimanite less than desirable for thermochemical studies." However, Holdaway's conclusion that fibrolite is less stable than sillimanite would appear to be the major reason for the discordant results.

The andalusite-sillimanite transition (at 1 bar) takes place at 1048±20 K on the basis of Holdaway's high pressure reversals and the unpublished measurements of Weill as reported by Holdaway (1971). Richardson et al. (1969) placed the andalusite-sillimanite phase boundary intersection with the 1-bar axis at 1123 K. From our heat capacity and entropy data and equations (2) and (3), we get $\Delta S_{1048}^o = 2.84 \pm 0.3$ and $\Delta S_{1123}^o = 2.80 \pm 0.3$ J/(mol · K)

for the andalusite → sillimanite transition. From the data of Skinner et al. (1961), $\Delta V_{1048}^o = -0.232$ and $\Delta V_{1123}^o = -0.240$ J/bar, whereas the data of Winter and Ghose (1979), yield $\Delta V_{1048}^o = -0.193$ and $\Delta V_{1123}^o = 0.197$ J/bar. Above 800 K The measurements by Schneider (1979) on andalusite lie between those by Skinner et al. (1961) and those by Winter and Ghose (1979), as shown in Figure 4; and therefore we have simply taken a graphical average for ΔV_T^o from Skinner et al., Winter and Ghose, and Schneider, i.e., $\Delta V_{1048}^o = 0.213 \pm 0.017$ and $\Delta V_{1123}^o = -0.218 \pm 0.019$ J/bar. Using the Clapeyron equation at 1 bar we get

$$dP/dT = (2.84 \pm 0.30 \text{ J/K})/(-0.213 \pm 0.017 \text{ J/bar}) \\ = -13.3 \pm 2.3 \text{ bar/K at 1048 K, and at 1123 K.}$$

$$dP/dT = (2.80 \pm 0.30 \text{ J/K})/(-0.218 \pm 0.02 \text{ J/bar}) \\ = -12.8 \pm 2.3 \text{ bar/K.}$$

Table 6. Molar thermodynamic properties of sillimanite (Al₂SiO₅). [Formula weight 162.047 g/mol]

Temp.	Heat capacity	Entropy	Enthalpy function	Gibbs energy function
T	C _P ^o	S _T ^o -S ₀ ^o	(H _T ^o -H ₀ ^o)/T	-(G _T ^o -H ₀ ^o)/T
Kelvin	J/(mol·K)			
5	0.006	0.002	0.002	0.001
10	0.042	0.015	0.011	0.004
15	0.142	0.048	0.035	0.012
20	0.376	0.116	0.087	0.029
25	0.822	0.243	0.185	0.058
30	1.552	0.453	0.348	0.105
35	2.559	0.764	0.588	0.176
40	3.873	1.189	0.914	0.275
45	5.414	1.732	1.326	0.406
50	7.182	2.392	1.821	0.570
60	11.31	4.056	3.050	1.006
70	16.01	6.146	4.560	1.587
80	21.18	8.617	6.310	2.307
90	26.64	11.42	8.263	3.161
100	32.28	14.52	10.38	4.140
110	38.02	17.87	12.63	5.235
120	43.78	21.42	14.99	6.434
130	49.50	25.15	17.42	7.730
140	55.12	29.03	19.92	9.112
150	60.62	33.02	22.45	10.57
160	65.99	37.10	25.00	12.10
170	71.23	41.26	27.57	13.69
180	76.32	45.48	30.14	15.34
190	81.23	49.74	32.70	17.04
200	85.94	54.02	35.24	18.78
210	90.46	58.33	37.76	20.56
220	94.81	62.64	40.26	22.38
230	98.98	66.94	42.72	24.22
240	103.0	71.24	45.15	26.09
250	106.8	75.52	47.54	27.98
260	110.5	79.79	49.89	29.89
270	114.0	84.02	52.20	31.82
280	117.4	88.23	54.47	33.76
290	120.7	92.41	56.70	35.71
300	123.7	96.55	58.88	37.67
310	126.7	100.7	61.02	39.64
320	129.5	104.7	63.12	41.61
330	132.2	108.8	65.17	43.58
340	134.8	112.7	67.19	45.56
350	137.3	116.7	69.15	47.53
360	139.8	120.6	71.08	49.51
370	142.2	124.5	72.97	51.48
273.15	115.1	85.35	52.92	32.43
298.15	123.2	95.79	58.48	37.31

Table 7. X-ray unit-cell parameters and molar volumes of kyanite from Burnsville, North Carolina; andalusite from Minas Gerais, Brazil; and sillimanite from Brandywine Springs, Delaware

a nm	b nm	c nm	α deg	β deg	γ deg	V 10^{-24} cm^3	V^0 cm^3	Source
Kyanite, Burnsville, North Carolina								
† 0.7121 0.0002	0.7846 0.0002	0.5577 0.0005	89.97 0.08	101.15 0.08	106.00 0.08	293.41 0.32	44.17 0.05	Skinner et al. (1961)
0.7123 0.0002	0.7844 0.0002	0.5568 0.0002	89.90 0.08	101.22 0.08	105.98 0.09	292.92 0.21	44.10 0.03	Skinner et al. (1961)
† 0.71192 0.00005	0.78473 0.00004	0.55724 0.00006	89.977 0.005	101.121 0.005	106.006 0.003	293.16 0.04	44.14 0.01	Burnham (1963)
0.7124 0.0001	0.7843 0.0002	0.5566 0.0005	89.92 0.05	101.32 0.03	105.97 0.03	292.7 0.3	44.07 0.05	Richardson et al. (1968)
* 0.7121 0.0002	0.7851 0.0002	0.5588 0.0002	90.13	101.10	105.99	294.2 0.2	44.29 0.03	Holdaway (1971)
† 0.71262 0.00012	0.78520 0.00010	0.55724 0.00010	89.99 0.02	101.11 0.02	106.03 0.01	293.60 0.09	44.20 0.01	Winter and Ghose (1979)
Andalusite, Minas Gerais, Brazil								
0.77950 0.0001	0.78996 0.0001	0.55580 0.0001				342.25 0.09	51.53 0.04	Skinner et al. (1961)
† 0.77942 0.00002	0.78985 0.00002	0.5559 0.0002				342.23 0.12	51.52 0.02	Burnham and Buerger (1961)
0.7795 0.0002	0.7901 0.0002	0.5551 0.0002				341.9 0.2	51.47 0.03	Holdaway (1971)
† 0.77980 0.00007	0.79031 0.00010	0.55566 0.00005				342.44 0.06	51.56 0.01	Winter and Ghose (1979)
0.78003 0.00012	0.79012 0.00014	0.55547 0.00007				342.35 0.09	51.54 0.01	Brace et al. (1969)
Sillimanite, Brandywine Springs, Delaware								
0.74806 0.0002	0.76709 0.0002	0.57678 0.0002				330.97 0.17	49.83 0.03	Skinner et al. (1961)
0.7481 0.0002	0.7672 0.0002	0.5769 0.0002				331.1 0.2	49.85 0.03	Aramaki and Roy (1963)
0.7479 0.0002	0.7670 0.0001	0.5770 0.0001				331.0 0.1	49.83 0.02	Richardson et al. (1969)
0.7485 0.0002	0.7673 0.0002	0.5769 0.0002				331.33 0.17	49.87 0.03	Navrotsky et al. (1973)
0.74831 0.00004	0.76710 0.00004	0.57700 0.00004				331.22 0.03	49.87 0.01	Cameron (1976)
† 0.74883 0.00007	0.76808 0.00007	0.57774 0.00005				332.29 0.05	50.03 0.01	Winter and Ghose (1979)

† Single-crystal measurements

* Yancey County, North Carolina--probably Burnsville, NC

Our calculated slope (at 1 bar) for the temperature range covered by the Richardson et al. and the Holdaway data is thus in excellent agreement with Holdaway's (1971) experimental value, -13.9 bar/K. However, if we calculate the slope at Holdaway's triple point (774 K and 3.76 kbar) we get $dP/dT = [(3.44 - (-7.75 \times 10^{-5}) (3760)]/(-0.191) = -19.5 \pm 3.8$ bar/K where the second term in the numerator is the change in ΔS_{774} between 1 and 3.76 kbar. The additional ± 0.5 bar/K uncertainty in the slope at the triple point arises because of the uncertainty in $d\Delta V/dT$. To be compatible with the measured heat capacity and molar volume data the andalusite-

sillimanite phase boundary must exhibit substantial curvature. The slope from Richardson et al., (1969) is approximately -24.1 bars/K. Our slope calculation (-14.1 ± 2.4 bar/K at 973 K and 1 bar) provides a completely independent check of the value, -12 ± 4 bar/K, obtained by Anderson, Newton, and Kleppa (1977) on the basis of the difference in the enthalpies of solution of andalusite and sillimanite in $2\text{PbO} \cdot \text{B}_2\text{O}_3$ at 973 K. The general agreement between our results and those of Anderson et al. (1977), together with the direct measurements of Holdaway, appear to be sufficient grounds for concluding that the andalusite-sillimanite phase boundary of Richardson et al., is incorrect. In our calculations we assumed that $S_0^0 = 0$, i.e., there was no frozen-in disorder in sillimanite at low temperatures (see also the neutron structural refinement of Peterson and McMullen, 1980). Our data strongly suggest that sillimanite is Al/Si ordered at least below 1100 K.

The kyanite-andalusite boundary has been reversed by Newton (1966b) (hydrothermally) at 6.6 ± 0.4 kbar and 1023 K. Holdaway (1971) has also reversed this boundary at 666 ± 16 K and 2.4 kbar, 746 ± 26 K and 3.6 kbar, and gives an "apparent" reversal at 847 ± 17 K and 4.8 kbar. From our entropy data and equations (1) and (2) we calculate $\Delta S_{1023}^0 = 8.20 \pm 0.3$ J/(mol · K). The correction necessary to calculate ΔS_{1023}^0 at 6.6 kbar is quite uncertain, because of the large differences between the values of $d\Delta V^0/dT$ obtainable from the measurements of Skinner et al. (1960), and those of Winter and Ghose (1979). Again we have averaged the two different sets of $V(T)$ data to get ΔS_{1023}^0 (6.6 kbar) = $(8.20 \pm 0.3) + 0.34 \pm 0.26 = 8.54 \pm 0.40$ J/(mol · K). The average value for ΔV_{1023}^0 is 0.763 ± 0.003 J/bar. The calculated slope is 11.2 bar/K at 1023 K and 6.6 kbar. If we assume a constant slope the kyanite-andalusite boundary would occur at 434 K and 1 bar pressure. At 434 K and 1 bar $\Delta S_{434}^0 = 9.26 \pm 0.3$ J/(mol · K) and

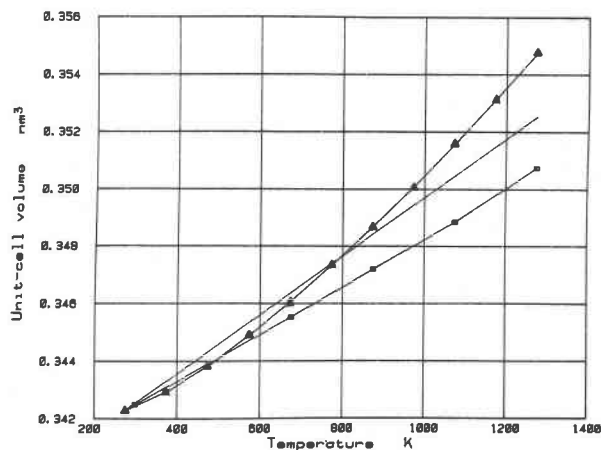


Fig. 4. Unit-cell volumes of andalusite at high temperatures. Sources of experimental data: circles, Winter and Ghose (1979); solid line Schneider (1979); inverted triangles, Skinner, Clark, and Appleman (1961).

Table 8. Selected thermodynamic properties of kyanite, andalusite, and sillimanite at 298.15 K and a comparison of the enthalpies of reaction ($\Delta H_{r,970}^{\circ}$) at 970 K calculated from data given in this study with the results from molten salt calorimetry.

Property	Kyanite	Andalusite	Sillimanite
$\Delta H_{f,298}^{\circ}$ kJ	-2596.01 ± 1.70	-2591.90 ± 1.72	-2587.77 ± 1.73
$\Delta G_{f,298}^{\circ}$ kJ	-2445.12 ± 1.69	-2443.72 ± 1.71	-2440.90 ± 1.72
$\Delta S_{f,298}^{\circ}$ J/(mol.K)	-506.08 ± 0.24	-497.00 ± 0.25	-492.60 ± 0.25
S_{298}° J/(mol.K)	82.30 ± 0.13	91.39 ± 0.14	95.79 ± 0.14
$\Delta H_{r,970}^{\circ}$ kJ	0	3.46 (3.34) ^{a,b}	6.52 (5.94) ^a (6.36) ^b
	0	0	3.06 (2.80) ^b

a. Anderson and Kleppa (1969)
b. Anderson, Newton, and Kleppa (1977)

$\Delta V_{434}^{\circ} = 0.740 \pm 0.003$ J/bar from which the calculated slope is 12.5 bar/K. Based on a combination of the equilibrium measurements and the calorimetric and molar volume data we adopt 450 ± 15 K as the 1 bar intercept and 11.8 ± 0.7 bar/K as the slope for the kyanite-andalusite boundary.

Newton (1966a, 1969) has also reversed (hydrothermally) the kyanite-sillimanite equilibrium at 1023 K and 8.5 \pm 0.4 kbar. The Clapeyron slope (at 1023 K and 1 bar) calculated from our entropy data and the average of the ΔV_T° measurements of Skinner et al. (1961) and of Winter and Ghose (1979) for this reaction is

$$\begin{aligned} dP/dT &= (11.08 \pm 0.30 \text{ J/K}) / (0.551 \pm 0.005 \text{ J/bar}) \\ &= 20.1 \pm 0.4 \text{ bar/K} \end{aligned}$$

At 8.5 kbar $\Delta S_{1023} = 11.05$ J/K and the calculated slope is essentially unchanged and the 1 bar intercept for the kyanite-sillimanite boundary would thus be 600 ± 15 K. Above 1100 K we might expect a slight positive curvature of this phase boundary as a consequence of the Al-Si disordering in sillimanite. The reaction boundary calculated from our data shows reasonable agreement with the results of Richardson et al. (1969), and Newton (1966a, 1969).

In Table 8, we summarize the values for the thermodynamic properties of the Al_2SiO_5 polymorphs derived from our measurements and calculations. These values are in agreement with the equilibrium reversals of Newton (1966a,b, 1969), and Holdaway (1971), the solubility measurements of Weill (1966), and the calorimetrically determined enthalpy change of the kyanite \rightarrow sillimanite transition (Anderson and Kleppa, 1969), the andalusite \rightarrow sillimanite transition (Anderson et al. 1977), and for the kyanite \rightarrow andalusite change obtained by combining data in these last two named studies.

The phase-equilibrium data only provide information on the differences in ΔG_T° and do not fix the absolute values. To be consistent with the work of Haas, Robinson, and Hemingway (1981), we have arbitrarily adopted their value of $\Delta H_{f,298}^{\circ}$ for sillimanite as our reference value.

The phase diagram calculated from the data in Table 8 together with the high-temperature heat capacity functions and the average of the ΔV_T° values of Skinner et al. (1961), and of Winter and Ghose (1979) is shown in Figure 5, together with selected phase-equilibria results. The calculated triple point is at 790 ± 25 K and 4.0 ± 0.5 kbar.

Acknowledgments

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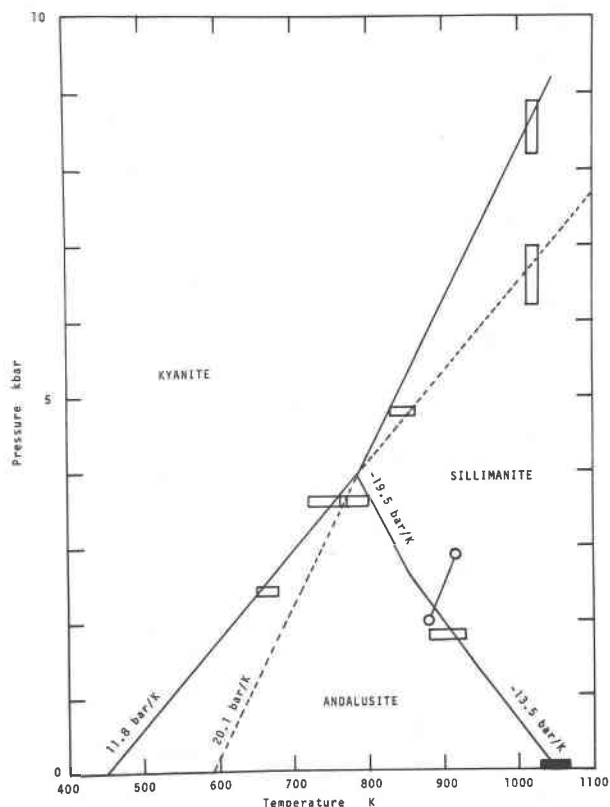


Fig. 5. Phase diagram Al_2SiO_5 . Phase boundaries calculated from (1) data in Table 8; (2) molar volume data of Skinner, Clark, and Appleman (1961) and of Winter and Ghose (1979); (3) heat-capacity equations listed in text. Experimental results are from Holdaway (1971, open horizontal rectangles); Newton (1966a,b, 1969, vertical rectangles); and Evans, 1965, open circles). The filled horizontal rectangle is the unpublished data of Weill reported by Holdaway (1971).

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