

Heat capacities and entropies of sillimanite, fibrolite, andalusite, kyanite, and quartz and the Al_2SiO_5 phase diagram

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ABSTRACT

Low-temperature heat capacities for sillimanite, fibrolite, and both fine-grained and coarse-grained quartz have been measured. Superambient heat capacities have been measured for four sillimanite, two andalusite, one kyanite, and two fibrolite samples. The following equations are recommended for the temperature dependence of the heat capacities of kyanite, andalusite, sillimanite, and fibrolite:

C_p^0 (kyanite)

$$= 279.435 - 7.124 \times 10^{-3}T - 2.28936 \times 10^3T^{-0.5} - 2.0556 \times 10^6T^{-2}$$

(valid 298.15–2000 K, average deviation 0.17%)

C_p^0 (andalusite)

$$= 277.306 - 6.588 \times 10^{-3}T - 2.26560 \times 10^3T^{-0.5} - 1.9141 \times 10^6T^{-2}$$

(valid 298.15–2000 K, average deviation 0.24%)

C_p^0 (sillimanite)

$$= 280.190 - 6.900 \times 10^{-3}T - 2.39937 \times 10^3T^{-0.5} - 1.37573 \times 10^6T^{-2}$$

(valid 298.15–2000 K, average deviation 0.52%)

C_p^0 (fibrolite)

$$= 417.596 - 70.2335 \times 10^{-3}T - 5.00119 \times 10^3T^{-0.5} + 1.45450 \times 10^6T^{-2}$$

(valid 298.15–800 K, average deviation 0.25%)

C_p^0 (fibrolite)

$$= 306.108 - 9.99098 \times 10^{-3}T - 3.48957 \times 10^3T^{-0.5} + 7.81586 \times 10^6T^{-2}$$

(valid 800–2000 K, average deviation 0.16%)

The heat capacity functions have been combined with thermal expansion (fibrolite and sillimanite reported here), enthalpy of solution, and phase equilibrium data in order to construct a phase diagram for the Al_2SiO_5 polymorphs. The recommended thermodynamic properties of entropy and enthalpy of formation at 298.15 K consistent with the phase diagram are 95.40 ± 0.52 J/mol·K and -2586.1 ± 3 kJ/mol for sillimanite, 95.43 ± 0.55 J/mol·K and -2586.1 ± 3 kJ/mol for fibrolite, 82.80 ± 0.50 J/mol·K and -2593.8 ± 3 kJ/mol for kyanite, and 91.39 ± 0.52 J/mol·K and -2589.9 ± 3 kJ/mol for andalusite. These values have been derived by minimizing the differences between the experimentally measured and calculated properties. The triple point was located at 3.87 ± 0.3 kbar and 784 ± 20 K.

Anomalous thermal response of a fibrolite sample near room temperature is interpreted as a slow structural change in fibrolite. The heat effect would appear small for the completed transition; however, failure of fibrolite to transform could result in larger measured heat capacities for the sample at temperatures above room temperature than those measured for the transformed sample. This may explain why the heat capacities reported by Salje (1986) for fibrolite are about 2% larger than those reported here.

Lack of a demonstrated excess heat capacity for novaculite at low temperatures suggests

that aggregates of cemented or intergrown small crystals do not have the same degree of surface lattice distortion and degrees of freedom for surface atoms and consequently have smaller surface energies than powders of the same mineral. The chemically similar quartz grains and quartz cement of the novaculite represent one limit on the excess properties that fine-grained geologic materials may exhibit.

INTRODUCTION

The Al_2SiO_5 polymorphs, kyanite, andalusite, and sillimanite, constitute a fundamental system for a quantitative petrogenetic grid for metamorphic petrology. However, the univariant equilibria of this system are located by only a few experimental phase-reversal brackets and by recent thermochemical data. The equilibrium boundaries selected in recent studies represent the best estimates of the locations and slopes, but the choices are not unique (Day and Kumin, 1980).

A "fibrolite effect" was postulated by Holdaway (1971) to explain the observed difference between phase equilibria results he obtained for the Al_2SiO_5 polymorphs and those of Richardson et al. (1968a, 1968b, 1969). Fibrolite, a fine-grained acicular variety of sillimanite, was considered by Holdaway (1971) to have formed metastably through rapid crystallization that resulted in possible Al-Si disorder and possible excess silica. The sillimanite sample used by Richardson et al. (1968a, 1968b, 1969) was considered by Holdaway (1971) to be less stable than coarse-grained sillimanite because it contained fibrolite. However, Cameron and Ashworth (1972) found no evidence for Al-Si disorder from electron diffraction and infrared spectroscopic studies of a sample they considered to be a typical fibrolite, and they concluded that both fibrolite and sillimanite are ordered. Salje (1986) has revived the concept of a fibrolite effect that, if shown to be correct, would greatly modify our understanding of the phase diagram for the Al_2SiO_5 polymorphs.

The entropy and volume changes of the reactions between the polymorphs (Clapeyron equation) may be used as additional constraints on the slopes of the reaction boundaries estimated from phase equilibrium data. Recent measurements of the low-temperature heat capacities of kyanite (Minas Gerais, Brazil), andalusite (Espírito Santo, Brazil), and sillimanite (Reinbolt Hills, Antarctica) by Robie and Hemingway (1984) were used to calculate revised values for the entropies of these phases and to make slight modifications to the Al_2SiO_5 phase diagram. Salje (1986) has concluded that the entropy for sillimanite reported by Robie and Hemingway (1984) is too low. Salje (1986) calculated the entropy of sillimanite using the method of Salje and Werneke (1982) and combined this value with new differential scanning calorimetric heat capacity measurements for superambient temperatures for sillimanite and fibrolite to calculate revised boundaries for the andalusite = sillimanite and andalusite = fibrolite equilibria.

We have obtained gem quality sillimanite (Sri Lanka) and an excellent fibrolite (Lewiston, Idaho) to reevaluate

the sillimanite heat capacities reported by Robie and Hemingway (1984) and the hypothesis and calculations of Salje (1986). The low-temperature heat capacities for these samples are reported in this study. Additionally, we have measured the heat capacities by differential scanning calorimetry (DSC) between 340 and 1000 K of sillimanite from Sri Lanka, Antarctica, Benson Mines (New York), and Brandywine Springs (Delaware); of fibrolite from Lewiston (Idaho) and South Australia; of andalusite from Espírito Santo (Brazil) and Standish (Maine); and kyanite from Minas Gerais (Brazil).

Differences in the apparent stability of fibrolite and sillimanite have been attributed to surface energy contributions arising from the small crystallites in fibrolite (Cameron and Ashworth, 1972; Salje, 1986; Kerrick, 1987). Using HF solution calorimetry, Hemingway and Robie (1977) have shown that surface energy contributions to the enthalpy of solution of quartz can be measured for powders of quartz grains $<2 \mu m$ in size. Giauque and Archibald (1937) have shown that powders of fine-grained crystals show excess heat capacity at subambient temperatures and have attributed the excess heat capacity to surface energy contributions. Salje (1986) has shown that sillimanite ground to a fine particle size will exhibit excess heat capacity at superambient temperatures. It is not clear whether small crystallites cemented together or intergrown, as would be the case for geologic materials in general and fibrolite in this case, would show the same magnitude of contribution to the thermodynamic properties arising from surface energy that free powders of the same material would show. Consequently, we have chosen to model this problem using Arkansas novaculite that contains quartz crystallites of $<2 \mu m$ that are cemented with quartz. Low-temperature heat capacity measurements of Arkansas novaculite and Brazilian quartz are reported here and are compared with heat capacity measurements of quartz obtained from the literature.

MATERIALS

Sillimanite. Gem quality sillimanite from Sri Lanka was kindly provided by Carl Francis, Curator, Harvard University Mineral Museum. The calorimetric sample mass was 31.8267 g corrected for buoyancy. The average of microprobe analyses of four crystals is Al_2O_3 63.08, SiO_2 36.68, MgO 0.06, K_2O 0.00, TiO_2 0.00, V_2O_5 0.02, Cr_2O_3 0.02, MnO 0.02, and Fe_2O_3 0.26 wt% as compared with Al_2O_3 62.93 and SiO_2 37.07 wt% for Al_2SiO_5 . The sample chemistry was also determined by J. B. Bodkin

and N. H. Suhr of the Mineral Constitution Laboratory at the Pennsylvania State University using quantitative spectrochemical analysis. Their analysis (number 89-67) gives Al_2O_3 62.41, SiO_2 37.10, MgO 0.055, CaO 0.11, K_2O 0.017, Na_2O <0.01, TiO_2 0.008, V_2O_5 0.01, BeO 0.027, Fe_2O_3 0.20 wt%, and H_2O^- and H_2O^+ looked for but not found. The sample was analyzed by modern X-ray diffraction and NMR methods at the Pennsylvania State University (Kerrick, 1990).

Fibrolite. Fibrolite from Lewiston, Idaho, was also analyzed by quantitative spectrochemical analysis at the Mineral Constitution Laboratory of the Pennsylvania State University. The resulting analysis gives Al_2O_3 61.5, SiO_2 37.9, MgO 0.03, CaO 0.12, K_2O 0.47, Na_2O 0.11, TiO_2 <0.01, and Fe_2O_3 0.14 wt%. The analysis for H_2O is H_2O^- 0.11 and H_2O^+ 0.61. The impurities (largely in the form of muscovite and quartz) were not homogeneously distributed, so the H_2O analysis may have a large sampling error. The calorimetric sample mass was 30.0013 g corrected for buoyancy. A second sample from South Australia was obtained for comparison with the Lewiston sample. No chemical analysis of this sample was made. The fibrolite samples were analyzed by modern X-ray diffraction, optical and electron microscopy, and NMR methods at the Pennsylvania State University (Kerrick, 1990).

Samples for differential scanning calorimetric study were obtained from the materials discussed above and from portions of samples used in other studies: sillimanite or fibrolite from Robie and Hemingway (1984, Antarctica), Richardson et al. (1968a, 1968b, 1969; Brandywine Springs, Delaware), and Skinner et al. (1961, Benson Mines, New York); andalusite from Robie and Hemingway (1984, Espirito Santo, Brazil) and Skinner et al. (1961, Standish, Maine); and kyanite from Robie and Hemingway (1984, Minas Gerais, Brazil). DSC samples weighed from 29 to 42 mg. The Sri Lanka, Antarctica, and Espirito Santo and Minas Gerais, Brazil, samples consisted of one to three coarse crystals. The remaining samples were powders.

Novaculite. Arkansas novaculite obtained from the Whetstone quarry was analyzed by quantitative and qualitative spectrochemical analysis at the Pennsylvania State University. Trace (<0.01%) amounts of B, Fe, Mg, Ca, and Ti were detected. Al_2O_3 is 0.11 wt%. No other impurities were detected in this nearly pure SiO_2 . The calorimetric sample mass was 28.4817 g corrected for buoyancy.

Brazilian quartz. A crystal of water-clear quartz was crushed and sieved to +18 mesh. The sample was washed with dilute HCl. No chemical analysis of the sample was made. The calorimetric sample mass was 39.466 g corrected for buoyancy.

The formula weights are based upon the 1975 values for the atomic weights (Commission on Atomic Weights, 1976). The formula weight for pure stoichiometric kyanite, andalusite, fibrolite, and sillimanite is 162.047 g and for novaculite and quartz is 60.085 g.

TABLE 1. Experimental low-temperature molar heat capacities of natural sillimanite (Sri Lanka, molar mass = 162.047 g)

Temp. K	Heat capacity J/mol·K	Temp. K	Heat capacity J/mol·K	Temp. K	Heat capacity J/mol·K
Series 1		Series 3		Series 4	
300.37	124.3	60.03	11.41	197.80	85.10
305.17	125.8	64.73	13.43	203.14	87.56
310.47	127.5	69.32	15.63	208.49	89.93
315.80	129.0	74.30	18.11	213.84	92.38
321.17	130.3	80.10	21.09	219.22	94.73
326.54	131.8	85.78	24.14	224.66	96.99
331.88	132.9	91.51	27.36	230.16	99.31
337.21	134.7	97.24	30.65	235.75	101.5
342.53	136.3	102.87	33.88	241.39	103.9
347.88	137.5	108.43	37.07	247.07	106.0
Series 2					
8.70	0.0078	113.92	40.25	252.78	108.1
9.91	0.0130	119.33	43.36	258.51	110.2
10.98	0.0048	124.68	46.48	264.24	112.3
12.21	0.0263	129.97	49.52	270.00	114.4
13.66	0.0508	135.20	52.44	Series 5	
15.20	0.0847	140.38	55.43	261.92	111.2
16.91	0.1393	145.53	58.27	Series 6	
18.80	0.2210	150.64	61.05	257.18	109.8
20.88	0.3419	155.71	63.78	263.05	111.9
23.21	0.5084	160.74	66.51	268.92	113.9
25.79	0.7616	165.75	69.15	274.80	116.0
28.68	1.156	170.72	71.72	280.75	118.1
31.91	1.744	Series 4		286.68	120.2
35.54	2.572	176.00	74.34	292.60	122.2
39.63	3.504	181.57	77.19	298.50	124.0
44.18	5.122	186.98	79.90	304.39	125.8
49.24	6.946	192.44	82.54	310.26	127.3
54.93	9.394				

APPARATUS AND EXPERIMENTAL HEAT-CAPACITY RESULTS

Low-temperature heat capacities were measured using the intermittent heating method under quasi-adiabatic conditions. The cryostat and general experimental procedures are described by Robie and Hemingway (1972), the provisional temperature scales by Robie et al. (1978), and the electrical measurement system by Hemingway et al. (1984). Samples were sealed in the calorimeter under a small pressure of pure He gas (about 5 kPa).

Heat capacities were measured between 7 and 350 K for samples of the Sri Lanka sillimanite, Lewiston fibrolite, and Arkansas novaculite and between 50 and 315 K for Brazilian quartz. The tabulated heat capacities are given in Tables 1–4 in chronological order and have been corrected for curvature (e.g., Robie and Hemingway, 1972). No corrections were made for deviations of the sample compositions from the ideal compositions Al_2SiO_5 or SiO_2 .

Low-temperature heat capacities were smoothed using cubic spline smoothing procedures (Robie et al., 1982). For temperatures below 30 K (excluding the Brazilian quartz) the smoothed heat capacities and the experimental values were plotted as C_p/T vs. T^2 and extrapolated to 0 K. Smoothed values of the heat capacities and thermodynamic properties were calculated from the spline equations and extrapolations for Sri Lanka sillimanite,

TABLE 2. Experimental low-temperature molar heat capacities of natural fibrolite (Lewiston, molar mass = 162.047 g)

Temp. K	Heat capacity J/mol·K	Temp. K	Heat capacity J/mol·K	Temp. K	Heat capacity J/mol·K
Series 1		Series 3		Series 4	
335.64	136.5	100.39	33.36	241.21	105.0
340.15	137.6	105.76	36.44	245.97	107.1
344.95	139.1	111.04	39.49	250.77	108.8
Series 2		116.24	42.47	255.60	110.6
8.94	0.0521	121.36	45.43	260.44	112.4
10.16	0.0529	126.42	48.39	265.33	114.2
11.21	0.0731	131.44	51.28	270.25	116.0
12.41	0.0827	136.39	54.07	275.15	117.8
13.89	0.1049	141.30	56.92	280.03	119.6
15.45	0.1354	146.17	59.64	284.90	121.2
17.17	0.1909	151.00	62.29	289.76	122.9
19.07	0.2801	155.81	64.89	294.59	124.3
21.15	0.4114	160.58	67.40	299.40	126.1
23.47	0.6064	165.33	69.98	304.20	127.7
26.07	0.9006	170.05	72.50	308.98	129.1
28.97	1.338	174.76	74.92	Series 5	
32.22	1.992	179.45	77.22	314.34	130.3
35.86	2.904	184.12	79.54	319.25	132.3
39.95	4.074	188.79	81.76	323.97	133.9
44.52	5.610	Series 4		328.69	135.6
49.62	7.440	190.27	82.54	333.32	136.8
55.30	9.739	194.99	84.78	337.92	137.9
61.34	12.58	199.70	86.90	Series 6	
Series 3		204.47	89.23	342.81	139.2
67.72	15.52	208.99	91.50	347.76	140.6
73.57	18.50	213.52	93.26	352.47	141.6
78.47	21.05	218.06	95.20	357.20	143.0
83.74	23.86	222.61	97.30	361.79	144.1
89.42	27.03	227.20	99.21	366.36	145.4
94.93	30.21	231.82	101.1	370.91	146.6
		236.50	103.0		

Lewiston fibrolite, and Arkansas novaculite and are listed in Tables 5–7.

The entropy changes, $S_T^0 - S_0^0$, at 298.15 K are 95.77 ± 0.29 , 97.65 ± 0.29 , and 41.51 ± 0.15 J/mol·K for sillimanite, fibrolite, and novaculite, respectively. Our value for the entropy of the Sri Lanka sillimanite is essentially identical to the value of 95.79 ± 0.14 J/mol·K reported by Robie and Hemingway (1984) for a sillimanite sample from Reinbolt Hills, Antarctica. Also our value for the entropy of novaculite is essentially identical to the entropy of quartz of 41.46 ± 0.13 J/mol·K reported by Westrum (unpublished data cited in Stull and Prophet, 1971) and that of 41.43 ± 0.03 J/mol·K from Gurevich and Khlyustov (1979). The entropy change $S_{298.15}^0 - S_0^0$ calculated from our measurements on Brazilian quartz differs by 0.02 J/mol·K from the equivalent value calculated from the heat capacities of the novaculite sample. Smoothed values for Brazilian quartz measured in this study differ by from 0.3 to -0.3% from the smoothed values for novaculite.

The observed entropy for fibrolite may be corrected for impurities by assuming that the principle of additivity holds and that 1 mol of the natural fibrolite sample is composed of Al_2SiO_5 , 0.0167 of muscovite, 0.0009 of hematite, and 0.0274 of quartz. Muscovite is estimated from total alkali and alkaline earth cations. The corrected

TABLE 3. Experimental low-temperature molar heat capacities of Arkansas novaculite (quartz, molar mass = 60.085 g)

Temp. K	Heat capacity J/mol·K	Temp. K	Heat capacity J/mol·K	Temp. K	Heat capacity J/mol·K
Series 1		Series 3		Series 4	
346.35	49.12	205.84	33.64	302.80	45.05
Series 2		210.60	34.17	308.48	45.65
52.20	6.309	215.37	34.84	314.34	46.22
57.56	7.354	220.18	35.49	320.21	46.74
62.19	8.256	225.04	35.99	326.22	47.36
67.37	9.275	229.98	36.68	Series 7	
73.53	10.49	235.00	37.37	301.98	44.97
79.48	11.64	240.08	38.05	307.62	45.54
85.40	12.81	245.20	38.49	313.40	46.13
91.31	14.00	250.34	39.19	319.19	46.70
97.18	15.18	255.51	39.75	325.12	47.24
102.95	16.27	260.68	40.30	Series 8	
108.63	17.39	265.89	40.99	297.44	44.41
114.23	18.44	271.11	41.58	303.09	45.04
119.78	19.50	276.31	42.13	308.87	45.69
125.27	20.51	281.51	42.81	Series 9	
130.71	21.50	286.70	43.33	8.02	0.0157
136.10	22.49	291.87	43.85	8.96	0.0121
141.45	23.42	297.03	44.24	9.91	0.0189
146.75	24.38	302.18	45.11	11.09	0.0489
152.02	25.29	307.32	45.66	12.47	0.0944
Series 3		312.46	45.96	13.91	0.1523
152.78	25.47	Series 4		15.52	0.2497
157.98	26.40	317.25	46.40	17.28	0.3836
162.83	27.16	322.37	47.03	19.21	0.5687
167.72	27.95	327.30	47.49	21.39	0.8122
172.53	28.74	332.23	47.94	23.83	1.126
177.32	29.41	337.28	48.44	26.55	1.521
182.08	30.13	342.32	48.75	29.60	2.005
186.84	30.98	347.35	49.37	33.01	2.609
191.60	31.62	352.40	49.70	36.83	3.329
196.36	32.26	Series 5		41.14	4.135
201.10	32.89	311.93	45.69	45.97	5.082
				51.35	6.114
				57.31	7.279

TABLE 4. Experimental low-temperature molar heat capacities of natural quartz (Brazil, molar mass = 60.085 g)

Temp. K	Heat capacity J/mol·K	Temp. K	Heat capacity J/mol·K	Temp. K	Heat capacity J/mol·K
Series 1		Series 1		Series 1	
51.84	6.256	143.37	23.81	226.96	36.36
56.64	7.185	147.89	24.63	231.60	36.94
60.74	7.990	152.37	25.37	236.33	37.55
65.29	8.873	156.83	26.10	Series 2	
70.64	9.930	161.27	26.83	240.74	38.05
75.82	10.95	165.68	27.55	245.40	38.66
80.97	11.97	170.08	28.24	250.43	39.25
86.04	12.97	174.45	28.92	256.02	39.90
91.09	13.98	178.81	29.60	261.80	40.57
96.12	14.96	183.16	30.27	267.60	41.25
101.08	15.93	187.50	30.93	273.40	41.94
106.97	16.89	191.84	31.56	279.18	42.58
110.80	17.83	196.17	32.17	284.95	43.20
115.38	18.74	200.50	32.81	290.71	43.85
120.31	19.63	204.84	33.45	296.46	44.47
124.99	20.51	209.19	34.05	302.23	45.05
129.64	21.36	213.56	34.63	307.98	45.63
134.25	22.20	217.97	35.19	313.71	46.20
138.83	23.00	222.42	35.78		

TABLE 5. Molar thermodynamic properties for sillimanite (Sri Lanka)

Temp. (T) Kelvin	Heat capacity C _p	Entropy S _T - S ₀ J/mol·K	Enthalpy function (H _T - H ₀)/T	Gibbs energy function -(G _T - H ₀)/T
5	0.002	0.001	0.000	0.000
10	0.015	0.005	0.003	0.002
15	0.084	0.020	0.016	0.004
20	0.298	0.069	0.056	0.013
25	0.756	0.178	0.144	0.034
30	1.380	0.358	0.286	0.072
35	2.423	0.645	0.514	0.132
40	3.665	1.046	0.826	0.220
45	5.367	1.573	1.233	0.340
50	7.283	2.236	1.741	0.495
60	11.43	3.928	3.007	0.920
70	15.96	6.021	4.526	1.495
80	21.04	8.479	6.268	2.211
90	25.60	11.27	8.210	3.059
100	32.20	14.36	10.32	4.032
110	37.98	17.70	12.57	5.121
120	43.77	21.25	14.93	6.315
130	49.51	24.98	17.37	7.607
140	55.17	28.86	19.87	8.985
150	60.71	32.85	22.41	10.44
160	66.10	36.94	24.97	11.97
170	71.34	41.11	27.55	13.56
180	76.42	45.33	30.12	15.21
190	81.35	49.60	32.69	16.91
200	86.09	53.89	35.24	18.65
210	90.65	58.20	37.77	20.43
220	95.03	62.52	40.28	22.24
230	99.22	66.84	42.75	24.09
240	103.2	71.15	45.19	25.96
250	107.1	75.44	47.58	27.85
260	110.8	79.71	49.94	29.77
270	114.4	83.96	52.26	31.69
280	117.9	88.18	54.54	33.64
290	121.2	92.38	56.79	35.59
300	124.3	96.54	58.99	37.55
310	127.3	100.7	61.14	39.52
320	130.1	104.7	63.25	41.50
330	132.8	108.8	65.32	43.47
340	135.5	112.8	67.34	45.45
273.15	115.5	85.29	52.99	32.30
298.15	123.7	95.77	58.58	37.19

Note: The results are not corrected for chemical deviations from stoichiometric Al₂SiO₅. Molar mass = 162.047 g.

value for S_T-S₀ of fibrolite at 298.15 K is 95.93 ± 0.55 J/mol·K. Corrections for these impurities are reasonable because most of the correction results from the adjustment for muscovite, a trace of which was observed in an X-ray pattern of the sample. The uncertainties here and elsewhere in the paper have been expanded to include the estimated uncertainty in the chemical analyses. We consider that most or all such deviations result from analytical error.

A comparison can be made of the heat capacity and entropy data for the Sri Lanka and Reinbolt Hills sillimanite samples. The heat capacities from the two data sets are in good agreement except at temperatures less than 50 K, where the heat capacities reported for the Reinbolt Hills sillimanite show a significant excess heat capacity. Robie and Hemingway (1984) suggested that the heat capacities measured in this temperature region are in excess because the Reinbolt Hills sillimanite con-

TABLE 6. Molar thermodynamic properties for fibrolite (Lewiston, Idaho)

Temp. (T) Kelvin	Heat capacity C _p	Entropy S _T - S ₀ J/mol·K	Enthalpy function (H _T - H ₀)/T	Gibbs energy function -(G _T - H ₀)/T
5	0.005	0.002	0.001	0.000
10	0.038	0.012	0.009	0.003
15	0.126	0.042	0.031	0.011
20	0.335	0.102	0.076	0.025
25	0.769	0.218	0.167	0.051
30	1.532	0.420	0.325	0.094
35	2.667	0.737	0.575	0.162
40	4.094	1.183	0.923	0.261
45	5.753	1.759	1.365	0.394
50	7.606	2.460	1.895	0.565
60	11.87	4.213	3.192	1.020
70	16.67	6.397	4.770	1.628
80	21.87	8.958	6.578	2.380
90	27.37	11.85	8.580	3.269
100	33.07	15.03	10.74	4.284
110	38.86	18.45	13.04	5.414
120	44.66	22.08	15.43	6.650
130	50.43	25.88	17.90	7.983
140	56.12	29.83	20.43	9.401
150	61.70	33.89	22.99	10.90
160	67.13	38.05	25.58	12.46
170	72.39	42.28	28.18	14.09
180	77.48	46.56	30.78	15.78
190	82.40	50.88	33.37	17.51
200	87.14	55.23	35.94	19.29
210	91.72	59.59	38.49	21.10
220	96.14	63.96	41.01	22.95
230	100.4	68.33	43.50	24.83
240	104.5	72.69	45.96	26.73
250	108.5	77.04	48.38	28.66
260	112.3	81.37	50.76	30.60
270	115.9	85.67	53.11	32.56
280	119.5	89.95	55.42	34.54
290	122.9	94.21	57.69	36.52
300	126.2	98.43	59.91	38.51
310	129.3	102.6	62.10	40.51
320	132.4	106.8	64.25	42.52
330	135.4	110.9	66.36	44.53
340	138.2	115.0	68.43	46.54
350	141.0	119.0	70.47	48.56
360	143.8	123.0	72.47	50.57
370	146.6	127.0	74.43	52.58
273.15	117.1	87.02	53.84	33.18
298.15	125.6	97.65	59.50	38.15

Note: The results are not corrected for chemical deviations from stoichiometric Al₂SiO₅. Molar mass = 162.047 g/mol.

tains about 1.2% of Fe₂O₃; such small concentrations of Fe in minerals usually produce Schottky contributions (Gopal, 1966) to the heat capacities measured below about 50 K. Between 130 and 340 K, heat capacities for the Reinbolt Hills sillimanite systematically average 0.27% less than those of the Sri Lanka sillimanite. Approximately half the observed difference may be accounted for by correcting the Reinbolt Hills sillimanite heat capacities for the Fe impurity. Correcting the entropy reported by Robie and Hemingway (1984) for Fe₂O₃ (Reinbolt Hills sillimanite, see Grew, 1980, p. 44) yields 95.85 ± 0.55 J/mol·K at 298.15 K. Correcting the entropy of the Sri Lanka sillimanite for deviations of the sample chemistry from Al₂SiO₅ yields 95.90 ± 0.52 J/mol·K.

Debye temperatures, θ_D, may be calculated from heat capacities measured at less than θ_D/50 or less than about

TABLE 7. Molar thermodynamic properties for Arkansas novaculite (quartz)

Temp. (T) Kelvin	Heat capacity C_p°	Entropy $S_p^\circ - S_0^\circ$ J/mol·K	Enthalpy function $(H_p^\circ - H_0^\circ)/T$	Gibbs energy function $-(G_p^\circ - H_0^\circ)/T$
5	0.001	0.000	0.000	0.000
10	0.028	0.006	0.005	0.001
15	0.216	0.044	0.036	0.007
20	0.655	0.160	0.131	0.029
25	1.289	0.371	0.296	0.075
30	2.077	0.674	0.525	0.148
35	2.972	1.060	0.810	0.250
40	3.917	1.518	1.139	0.379
45	4.885	2.036	1.501	0.534
50	5.861	2.601	1.888	0.712
60	7.823	3.843	2.714	1.129
70	9.789	5.196	3.584	1.612
80	11.76	6.632	4.483	2.149
90	13.74	8.131	5.401	2.730
100	15.71	9.681	6.334	3.347
110	17.64	11.27	7.274	3.995
120	19.53	12.89	8.217	4.668
130	21.38	14.52	9.159	5.363
140	23.19	16.17	10.10	6.076
150	24.96	17.83	11.03	6.805
160	26.68	19.50	11.95	7.546
170	28.31	21.17	12.87	8.298
180	29.87	22.83	13.77	9.059
190	31.36	24.48	14.66	9.828
200	32.78	26.13	15.53	10.60
210	34.13	27.76	16.38	11.38
220	35.44	29.38	17.22	12.16
230	36.70	30.98	18.04	12.94
240	37.93	32.57	18.84	13.73
250	39.13	34.14	19.63	14.51
260	40.30	35.70	20.40	15.30
270	41.45	37.24	21.16	16.08
280	42.57	38.77	21.90	16.87
290	43.67	40.29	22.64	17.65
300	44.73	41.78	23.36	18.43
310	45.76	43.27	24.06	19.21
320	46.75	44.74	24.76	19.98
330	47.70	46.19	25.44	20.75
340	48.63	47.63	26.10	21.52
350	49.54	49.05	26.76	22.29
273.15	41.80	37.73	21.40	16.33
298.15	44.54	41.51	23.22	18.28

Note: The results are not corrected for chemical deviations from stoichiometric SiO_2 . Molar mass = 60.085 g/mol.

20 K. The resulting Debye temperatures are 900 ± 50 and 750 ± 50 K for the Sri Lanka sillimanite and Lewiston fibrolite data, respectively. Robie and Hemingway (1984) calculated Debye temperatures for the Reinbolt Hills sillimanite of 730 ± 50 and 800 K, respectively, from their low-temperature heat capacities and from the single-crystal elastic constants of Vaughan and Weidner (1978). The smaller Debye temperature calculated for the Reinbolt Hills sillimanite is consistent with the contribution of an Fe impurity to the heat capacity as discussed by Robie and Hemingway (1984). Debye temperatures calculated from low-temperature heat capacities are extremely sensitive to both impurities and to the total heat capacity of the sample measured. The presence of Fe, for example, can cause an excess heat capacity contribution of the order of 100% in heat capacities below 15 K. Therefore, the agreement between the Debye tempera-

tures calculated for the two sillimanite samples from low-temperature heat capacities and that calculated from the elastic constants for sillimanite is as good as can be expected for natural samples.

DSC measurements were made using the procedures described by Hemingway et al. (1981). Measurements were made continuously and in overlapping segments between 340 and 680 K. At higher temperatures, measurements were made only at selected temperatures. DSC heat capacities for the four sillimanite, two fibrolite, two andalusite, and one kyanite samples are listed in Table 8. For temperatures above 1000 K, the heat capacities have been estimated based upon a corresponding states model with reference to mean heat capacities calculated from the data of Pankratz and Kelley (1964). The DSC data for sillimanite, kyanite, and andalusite have not been corrected for deviations of the sample chemistry from Al_2SiO_5 . The uncertainty of the DSC method is considered to be about 1%, significantly larger than the estimated effect of deviations in sample chemistry.

DSC heat capacities for the two andalusite samples were equivalent within the uncertainty of DSC method. The heat capacities from the two data sets (including estimated values) were combined with the smoothed heat capacities reported by Robie and Hemingway (1984) for the Espirito Santo andalusite and fitted with the following equation (Haas and Fisher, 1976) with an average deviation of 0.24%.

C_p° (andalusite)

$$= 277.306 - 6.588 \times 10^{-3}T \\ - 2.26560 \times 10^3 T^{-0.5} - 1.9141 \times 10^6 T^{-2} \\ \text{(valid from 298.15 to 2000 K).}$$

DSC heat capacities (and estimated values) for kyanite were combined with the smoothed heat capacities reported by Robie and Hemingway (1984) for the Minas Gerais kyanite sample and fitted to the following equation with an average deviation of 0.17%.

C_p° (kyanite)

$$= 279.435 - 7.124 \times 10^{-3}T \\ - 2.28936 \times 10^3 T^{-0.5} - 2.0556 \times 10^6 T^{-2} \\ \text{(valid from 298.15 to 2000 K).}$$

DSC heat capacities for sillimanite are not as smooth as those for kyanite and andalusite. The data sets (including estimated values) were smoothed individually and together as one data set. The average deviations of the data sets from the smooth analytical curves varied from about 0.45 to 0.52%. Local deviations from the smooth curve in excess of 1% were seen in the data sets for each sillimanite and fibrolite sample. Although the differences observed may represent real differences in the heat capacities of the samples (arising from differences in sample chemistry), the smooth analytical expressions are not statistically different. Therefore, the data for the four silli-

TABLE 8. Experimental molar heat capacities of fibrolite, sillimanite, andalusite, and kyanite from DSC measurements in the temperature interval 340 to 1000 K

Temp. K	Fibrolite			Sillimanite			Andalusite		Kyanite
	Lewiston	South Australia	Sri Lanka	Antarctica	Benson Mine	Brandywine Springs	Espirito Santo	Standish	Minas Gerais
349.0	137.5	137.1	138.5	136.1	136.8	138.0	137.3	138.2	136.9
359.1	140.1	139.4	140.2	138.5	138.9	140.1	139.7	140.6	139.6
369.1	142.6	141.6	142.4	140.9	141.0	142.2	142.2	143.0	142.0
379.2	145.0	143.6	144.4	143.5	143.2	144.4	144.6	145.4	144.7
389.3	147.2	145.3	146.4	145.7	145.0	146.4	146.6	147.7	146.8
399.3	149.4	147.6	148.3	147.9	147.0	148.0	148.7	149.6	149.0
409.4	151.2	149.4	150.2	150.0	148.7	149.9	150.8	151.4	151.2
419.5	153.1	151.1	152.1	151.7	150.5	151.7	152.6	153.3	153.0
429.5	155.0	153.1	153.9	153.6	152.1	153.2	154.5	154.8	155.0
439.6	156.7	154.7	155.5	155.3	154.1	154.9	156.2	156.8	156.7
449.6	158.3	156.3	157.0	156.7	155.6	156.6	157.7	158.2	158.3
459.7	159.9	157.9	158.7	158.6	157.1	158.0	159.5	159.8	159.9
469.8	161.3	159.6	160.3	159.9	158.4	159.4	160.9	161.0	161.6
479.8	162.6	160.9	161.6	161.1	160.1	160.9	162.3	162.4	163.1
489.9	164.2	162.6	163.4	162.5	161.4	162.4	163.8	164.1	164.4
499.0		163.8							
500.0	165.1	163.2	164.6	163.7	162.8	164.0	165.0	165.3	165.5
510.0	166.2	164.5	165.9	164.8	164.4	165.9	166.4	166.8	166.9
520.1	167.3	165.1	167.2	166.2	166.4	167.1	167.4	167.9	167.8
530.2	168.3	166.9	169.0	167.6	167.6	168.5	168.6	169.1	169.0
540.2	169.4	168.1	169.8	168.6	169.3	169.9	169.6	170.4	170.0
549.3	170.0		170.9	169.7	170.2	171.2	170.5	171.1	170.8
550.3	170.2	169.0	170.9	170.4	170.7	170.3	171.2	170.7	171.2
560.4	171.4	170.0	172.2	171.0	171.4	171.4	172.2	172.2	172.3
570.4	172.1	171.6	173.0	171.8	172.1	172.0	173.3	172.7	173.0
580.5	173.5	172.8	174.2	173.2	173.5	173.4	174.4	173.8	174.4
590.6	174.6	174.5	175.4	174.0	174.2	174.0	174.7	174.8	175.0
599.6	175.5	175.3	175.7	174.5	174.6	175.1	175.1	175.8	175.7
600.6	175.8		175.1	174.0	173.4	173.9	175.7	175.8	175.9
610.7	175.9		176.4	174.6	174.6	175.2	177.4	176.1	176.9
620.8	177.1		177.6	175.0	175.1	175.4	178.1	177.0	177.7
630.8	177.8		178.0	175.7	176.2	176.0	178.9	177.8	178.4
640.9	178.5		178.9	176.2	176.5	176.4	179.8	178.4	179.4
651.0	180.0		179.7	177.1	177.7	176.9	180.8	178.8	180.6
661.0	180.4		180.7	177.8	178.7	177.5	181.6	179.5	181.6
671.1	181.0		180.9	178.5	179.4	178.3	181.9	180.9	182.2
680.1	182.4		181.1	179.0	179.6	179.4	182.6	181.6	182.8
700.3		179.6							
750.6		183.9							
760.7	185.5		185.9	183.0	185.4	183.3	185.7	185.8	186.9
800.9	188.6		188.7	184.8	187.0	185.8	188.8	187.9	189.1
851.0		186.6							
899.7	191.1	189.9	192.8	189.3	191.6	192.0	192.3	192.4	193.6
996.2	193.9	193.3	196.1	194.5	195.7	196.7	197.7	197.4	197.7

Note: The results are not corrected for chemical deviations from stoichiometric Al₂SiO₅. Molar mass = 162.047 g.

manite samples were combined with the heat capacities of the fibrolite sample (for temperatures less than 850 K) and fitted with the following equation with an average deviation of 0.52%.

$$C_p^{\circ}(\text{sillimanite}) = 280.190 - 6.900 \times 10^{-3}T - 2.39937 \times 10^3 T^{-0.5} - 1.37573 \times 10^6 T^{-2}$$

(valid from 298.15 to 2000 K).

The DSC heat capacities for the fibrolite were corrected for deviations of sample chemistry from Al₂SiO₅ using the plan outlined earlier and data from Robie et al. (1979). At temperatures above 800 K, the slope of the heat capacity data was not consistent with that at lower temper-

atures, therefore, the data (including estimated values) were fitted in two segments. The resulting equations are

$$C_p^{\circ}(\text{fibrolite}) = 417.596 - 70.2335 \times 10^{-3}T - 5.00119 \times 10^3 T^{-0.5} + 1.45450 \times 10^6 T^{-2}$$

(valid 298.15–800 K, average deviation 0.25%)

$$C_p^{\circ}(\text{fibrolite}) = 306.108 - 9.99098 \times 10^{-3}T - 3.48957 \times 10^3 T^{-0.5} + 7.81586 \times 10^6 T^{-2}$$

(valid 800–2000 K, average deviation 0.16%).

TABLE 9. Molar thermodynamic properties for fibrolite

Temp. (T) Kelvin	Heat capacity C _p	Entropy S _T ^o - S ₂₉₈ ^o	Enthalpy function (H _T ^o - H ₂₉₈ ^o)/T J/mol·K	Gibbs energy function -(G _T ^o - H ₂₉₈ ^o)/T	Formation from the elements	
					Enthalpy	Gibbs free energy kJ/mol
298.15	123.380	95.430	0.000	95.430	-2586.06	-2439.08
300	123.943	96.195	0.763	95.432	-2586.08	-2438.16
350	137.563	116.362	19.368	96.994	-2586.51	-2413.43
400	148.534	135.473	34.852	100.621	-2586.94	-2388.69
450	157.415	153.499	47.994	105.504	-2586.68	-2363.94
500	164.637	170.471	59.310	111.161	-2586.41	-2339.18
550	170.524	186.448	69.162	117.286	-2585.78	-2314.51
600	175.323	201.499	77.815	123.683	-2585.14	-2289.84
650	179.224	215.691	85.471	130.220	-2584.34	-2265.29
700	182.374	229.093	92.285	136.808	-2583.54	-2240.74
750	184.889	241.764	98.378	143.387	-2582.74	-2216.31
800	186.863	253.763	103.849	149.914	-2581.95	-2191.88
850	188.742	265.151	108.790	156.361	-2581.23	-2167.54
900	190.446	275.988	113.280	162.708	-2580.51	-2143.21
950	192.060	286.328	117.384	168.944	-2601.45	-2118.48
1000	193.583	296.219	121.156	175.062	-2600.60	-2093.15
1100	196.363	314.803	127.870	186.933	-2598.90	-2042.50
1200	198.811	331.996	133.682	198.314	-2597.04	-1991.97
1300	200.961	347.996	138.776	209.220	-2595.10	-1941.61
1400	202.846	362.959	143.287	219.672	-2593.10	-1891.47
1500	204.495	377.011	147.314	229.698	-2590.98	-1841.42
1600	205.936	390.256	150.933	239.323	-2588.81	-1791.53
1700	207.193	402.780	154.207	248.573	-2637.07	-1741.35
1800	208.287	414.654	157.181	257.473	-2634.52	-1688.72

Note: Short dashed lines indicate transitions in the reference elements.

The DSC data were not combined with the low-temperature data because there appears to be a small transition in fibrolite near room temperature (see discussion below).

Smoothed values of the thermodynamic properties of fibrolite, sillimanite, andalusite, and kyanite derived from these equations are listed in Tables 9–12. The heat contents calculated from the data recommended in this report are about 3% larger at 1600 K for andalusite and sillimanite and about 1.6% larger for kyanite than the equivalent values reported by Kelley (1960). The smooth heat content data reported by Kelley (1960) are based on drop calorimetric data that were obtained prior to 1930. These data have not been used directly because average heat capacities calculated from the heat content data at temperatures greater than 800 K appear to flatten abnormally and, in the case of sillimanite, pass through a maximum and minimum. The results are systematically larger than the experimental heat contents reported by Pankratz and Kelley (1964) and the tabulated heat contents reported by Robie et al. (1979) that were based on the results of Pankratz and Kelley (1964). At 1000 K, the heat contents for sillimanite and andalusite are about 1% larger and for kyanite about 0.5% larger. The calculated heat contents for sillimanite reported here are also about 0.5% larger than those derived from the equations given by Salje (1986) at 1000 K but are in excellent agreement at 700 K, the upper limit of Salje's (1986) experimental data.

THERMAL EXPANSION OF SILLIMANITE AND FIBROLITE

The unit-cell parameters of sillimanite (Sri Lanka) and fibrolite (Lewiston) were measured at 298.15 K by the

Guinier-Hägg method from powder patterns made with monochromatized CuK α_1 radiation ($\lambda = 1.540562 \text{ \AA}$). Bragg angles were measured (43 lines for each sample) and scaled by a quadratic function determined by an internal standard (Si, NBS SRM640, $a = 5.43075 \text{ \AA}$). The following unit-cell edges and volumes were determined:

	$a, \text{ \AA}$	$b, \text{ \AA}$	$c, \text{ \AA}$	$V, \text{ \AA}^3$
sillimanite (Sri Lanka)	7.4845(10)	7.6713(11)	5.7686(7)	331.21(5)
fibrolite (Lewiston)	7.4830(7)	7.6754(10)	5.7685(5)	331.32(4)

The unit-cell parameters agree closely with those previously determined for sillimanite by Cameron (1976), but the b value for fibrolite is somewhat larger.

The change in the cell constants of sillimanite (Sri Lanka) and fibrolite (Lewiston) were measured by the Guinier-Lenné method over the temperature interval 298–1473 K using monochromatized CuK α radiation. The 2 θ values of 24–35 lines for sillimanite and 24–36 lines for fibrolite were measured at intervals of 100 K, and these values were used to derive for each temperature the corresponding unit-cell parameters (by least-squares analysis). The results of this analysis are listed in Table 13. No unusual heating effects in either sillimanite or fibrolite can be conclusively demonstrated. Although the agreement between the unit-cell parameters calculated for heating and cooling experiments do deviate somewhat, tests on sapphire suggest that the differences arise from equipment problems rather than changes in the samples.

Thermal expansion curves constructed from the data for fibrolite in Table 13 are in good agreement in slope

TABLE 10. Molar thermodynamic properties for sillimanite

Temp. (T) Kelvin	Heat capacity C_p	Entropy $S_p^\circ - S_0^\circ$	Enthalpy function $(H_p^\circ - H_{298}^\circ)/T$ J/mol·K	Gibbs energy function $-(G_p^\circ - H_{298}^\circ)/T$	Formation from the elements	
					Enthalpy	Gibbs free energy kJ/mol
298.15	123.700	95.400	0.000	95.400	-2586.09	-2439.11
300	124.306	96.167	0.765	95.402	-2586.11	-2438.20
350	138.293	116.434	19.463	96.971	-2586.50	-2413.45
400	148.863	135.621	35.006	100.615	-2586.90	-2388.71
450	157.184	153.653	48.136	105.517	-2586.65	-2363.96
500	163.934	170.575	59.389	111.185	-2586.40	-2339.22
550	169.538	186.470	69.156	117.314	-2585.81	-2314.55
600	174.275	201.430	77.723	123.707	-2585.22	-2289.88
650	178.338	215.544	85.310	130.234	-2584.47	-2265.33
700	181.865	228.892	92.084	136.808	-2583.72	-2240.78
750	184.957	241.547	98.175	143.373	-2582.92	-2216.34
800	187.690	253.573	103.686	149.887	-2582.11	-2191.89
850	190.123	265.026	108.700	156.326	-2581.32	-2167.55
900	192.303	275.956	113.285	162.671	-2580.54	-2143.21
950	194.265	286.407	117.496	168.910	-2601.38	-2118.46
1000	196.040	296.417	121.380	175.037	-2600.40	-2093.15
1100	199.119	315.251	128.312	186.939	-2598.45	-2042.54
1200	201.691	332.690	134.322	198.367	-2596.30	-1992.06
1300	203.859	348.922	139.590	209.331	-2594.06	-1941.78
1400	205.702	364.099	144.249	219.850	-2591.78	-1891.75
1500	207.277	378.346	148.399	229.946	-2589.38	-1841.82
1600	208.628	391.767	152.122	239.645	-2586.93	-1792.07
1700	209.791	404.451	155.481	248.970	-2634.94	-1742.06
1800	210.792	416.472	158.527	257.944	-2632.13	-1689.60

Note: Short dashed lines indicate transitions in the reference elements.

with those found in Winter and Ghose (1979) for sillimanite. Those for sillimanite are less consistent, both internally (two sets of measurements) and with the data of Winter and Ghose (1979). The lack of internal agreement may be a consequence of the preparation of the sillimanite powder, which may have been too coarse. The significantly larger unit-cell values published by Winter and

Ghose (1979) may be a consequence of a zero error (initial calibration). The largest source of error in the Guinier-Lenné patterns obtained in this study arose from the zero error. Elimination of this error was accomplished by adjustment of the Guinier-Lenné data to the Guinier-Hägg data at 25 °C.

The molar volumes of sillimanite and fibrolite as a

TABLE 11. Molar thermodynamic properties for andalusite

Temp. (T) Kelvin	Heat capacity C_p	Entropy $S_p^\circ - S_0^\circ$	Enthalpy function $(H_p^\circ - H_{298}^\circ)/T$ J/mol·K	Gibbs energy function $-(G_p^\circ - H_{298}^\circ)/T$	Formation from the elements	
					Enthalpy	Gibbs free energy kJ/mol
298.15	122.600	91.390	0.000	91.390	-2589.90	-2441.72
300	123.258	92.150	0.758	91.392	-2589.92	-2440.80
350	136.274	112.341	19.388	92.952	-2590.32	-2415.85
400	149.428	131.566	34.978	96.589	-2590.72	-2390.91
450	158.088	149.686	48.194	101.492	-2590.43	-2365.97
500	165.035	166.715	59.543	107.172	-2590.14	-2341.03
550	170.750	182.721	69.401	113.320	-2589.49	-2316.17
600	175.544	197.789	78.052	119.737	-2588.84	-2291.31
650	179.629	212.006	85.712	126.293	-2588.02	-2266.58
700	183.157	225.450	92.550	132.900	-2587.20	-2241.85
750	186.234	238.194	98.695	139.499	-2586.33	-2217.24
800	188.944	250.301	104.253	146.048	-2585.46	-2192.63
850	191.348	261.829	109.307	152.523	-2584.62	-2168.13
900	193.494	272.828	113.925	158.903	-2583.78	-2143.63
950	195.421	283.343	118.165	165.178	-2604.56	-2118.72
1000	197.160	293.411	122.072	171.340	-2603.52	-2093.27
1100	200.167	312.348	129.039	183.309	-2601.45	-2042.35
1200	202.669	329.876	135.073	194.802	-2599.21	-1991.59
1300	204.773	346.183	140.356	205.827	-2596.89	-1941.04
1400	206.556	361.426	145.023	216.403	-2594.50	-1890.73
1500	208.076	375.730	149.177	226.552	-2592.02	-1840.54
1600	209.378	389.201	152.900	236.301	-2589.50	-1790.53
1700	210.496	401.929	156.256	245.673	-2637.43	-1740.26
1800	211.457	413.989	159.297	254.692	-2634.56	-1687.56

Note: Short dashed lines indicate transitions in the reference elements.

TABLE 12. Molar thermodynamic properties for kyanite

Temp. (T) Kelvin	Heat capacity C_p°	Entropy $S_p^\circ - S_0^\circ$	Enthalpy function $(H_p^\circ - H_{298}^\circ)/T$ J/mol·K	Gibbs energy function $-(G_p^\circ - H_{298}^\circ)/T$	Formation from the elements	
					Enthalpy	Gibbs free energy kJ/mol
298.15	121.601	82.800	0.000	82.800	-2593.77	-2443.03
300	122.282	83.554	0.752	82.802	-2593.79	-2442.09
350	137.790	103.634	19.281	84.352	-2594.22	-2416.72
400	149.270	122.818	34.845	87.972	-2594.65	-2391.34
450	158.157	140.933	48.072	92.860	-2594.36	-2365.96
500	165.267	157.977	59.449	98.529	-2594.06	-2340.58
550	171.103	174.011	69.342	104.669	-2593.39	-2315.28
600	175.988	189.115	78.031	111.083	-2592.72	-2289.99
650	180.143	203.370	85.730	117.639	-2591.88	-2264.82
700	183.723	216.854	92.605	124.249	-2591.03	-2239.66
750	186.842	229.638	98.786	130.852	-2590.14	-2214.62
800	189.583	241.786	104.377	137.409	-2589.24	-2189.59
850	192.010	253.354	109.462	143.892	-2588.36	-2164.66
900	194.174	264.391	114.109	150.282	-2587.48	-2139.74
950	196.113	274.942	118.375	156.567	-2608.23	-2114.42
1000	197.859	285.047	122.306	162.741	-2607.16	-2088.54
1100	200.873	304.051	129.316	174.735	-2605.02	-2036.79
1200	203.371	321.639	135.386	186.253	-2602.71	-1985.21
1300	205.462	338.003	140.699	197.304	-2600.31	-1933.83
1400	207.227	353.295	145.389	207.906	-2597.86	-1882.70
1500	208.724	367.645	149.563	218.082	-2595.32	-1831.71
1600	210.000	381.158	153.302	227.856	-2592.72	-1780.89
1700	211.088	393.922	156.670	237.253	-2640.60	-1729.82
1800	212.017	406.015	159.719	246.295	-2637.66	-1676.31

Note: Short dashed lines indicate transitions in the reference elements.

function of temperature may be calculated from the following equations (in units of cm^3).

$$V(\text{sillimanite}) = 49.732 + 3.4647 \times 10^{-4}T + 3.323 \times 10^{-7}T^2$$

$$V(\text{fibrolite}) = 49.746 + 3.9337 \times 10^{-4}T + 2.029 \times 10^{-7}T^2.$$

The molar volume of fibrolite is slightly larger than that of sillimanite at 298.15 K. At 1373 K, the molar volume of fibrolite is 0.3% smaller than that for sillimanite.

SELECTION OF HEAT CAPACITY AND ENTROPY DATA FOR SILLIMANITE

Using the data presented in this report, we may examine Salje's (1986) argument for the use of calculated (Salje and Werneke, 1982) rather than measured (Robie and Hemingway, 1984) heat capacity data for sillimanite. Salje's (1986) estimated entropies at 298.15 K are 2–4% larger than the calorimetrically determined values. Salje (1986) found good agreement (within 1%) for calculated and measured heat capacities for sillimanite for temperatures greater than 80 K. Based on a comparison with the calculated heat capacities for temperatures less than 80 K, Salje (1986) concluded that the measurements of Robie and Hemingway (1984) were anomalously low. The heat capacities reported here support the values reported by Robie and Hemingway (1984). Salje (personal communication, 1991) now believes that his earlier calculations may be in error because he did not know the dispersion curves for sillimanite.

MAGNITUDE OF THE DIFFERENCE IN HEAT CAPACITY BETWEEN FIBROLITE AND SILLIMANITE

Salje (1986) measured the heat capacities of several sillimanite samples and of a fibrolite sample using a differential scanning calorimeter. Differences of as much as 4% were observed between the heat capacities of the fibrolite (Harcujuela) and those of the Sri Lanka sillimanite used in Salje's (1986) study at temperatures between 380 and 700 K. Smaller differences (of the order of 1.5%) were observed between the heat capacities of sillimanite from two other localities (Waldeck and Träskbole) and the fibrolite. However, Salje (personal communication, 1990) believes that the heat capacities he reported for the Sri Lanka sillimanite are in error because the sample was too small for his DSC procedure.

There is good agreement between the low-temperature heat capacity data for fibrolite presented here and the DSC data published by Salje (1986) for fibrolite. An equation for the heat capacities of fibrolite was derived by combining these data sets and estimating heat capacities to 1800 K. The resulting equation is:

$$C_p^\circ(\text{fibrolite}) = 258.844 - 4.95 \times 10^{-4}T - 1.82117 \times 10^3 T^{-0.5} - 2.4557 \times 10^6 T^{-2} \quad (\text{valid } 298\text{--}1800 \text{ K}).$$

Also, there is good agreement between the heat capacity data for the Sri Lanka sillimanite reported here and the DSC data reported by Salje (1986) for the Träskbole and Waldeck sillimanite samples.

A small thermal anomaly near room temperature and not seen in the heat capacities for sillimanite is suggested in the heat capacity data for fibrolite. The anomalous heat capacities are not readily reproduced as is the case for a rapid phase change such as the α - β transition in quartz (e.g., Hemingway, 1987). Instead, the anomaly is similar to that observed by Openshaw et al. (1976) for microcline. That is, hysteresis or dependence upon recent thermal history is apparent.

Heat capacities measured with the low-temperature calorimeter provided the first indication of anomalous heat capacities for fibrolite near room temperature. The calorimeter was heated to 335 K and held at that temperature for several hours before three heat capacity measurements were made (series 1 of Table 2). The sample was then cooled to 7 K, and measurements were made over a 2-d interval by incrementally heating the calorimeter to 373 K. The measurements of series 5 and 6 from Table 2 represent data collected by that procedure and include the temperature interval of the initial measurements. The heat capacities from series 5 and 6 may be represented by a curve that is about 0.5% higher than the initially measured heat capacities. The calorimeter was held at about 311 K for 11.5 h before series 5 was initiated. The first measurement of series 5 is also significantly lower than would be predicted from an extrapolation of the measurements of series 4 and the remaining measurements of series 5. In both cases, when the fibrolite was allowed to equilibrate thermally above room temperature for an extended period of time, lower heat capacities were measured.

Initial DSC heat capacities were about 2% lower than heat capacities measured for corresponding temperatures with the low-temperature calorimeter. Following common practice, the sample was heated to and equilibrated thermally at the high-temperature end of the temperature interval for which DSC measurements were about to be made. Further tests were made with other DSC samples that were not preheated. Heat capacities measured from 320 to 400 K agreed with the higher heat capacities on the first scan of the temperature interval and agreed with the lower set of heat capacities on a second scan of that interval. The lower set of heat capacities was very reproducible.

If the thermal anomaly is caused by a small structural change, the data gathered in the experiments discussed in this study are insufficient for determining the temperature of the transition. We can only conclude that the transition should occur below 311 K. From an analysis of the change in slope of the low-temperature heat capacities for fibrolite, we conclude that a transition temperature between 295 and 300 K is likely, and we have chosen 298.15 K for convenience in tabulation of the experimental data.

An extrapolation of the low-temperature heat capacities for the Lewiston fibrolite is in good agreement with the DSC heat capacities for fibrolite (Harcujuela) reported by Salje (1986). We believe that the sample studied by Salje (1986) failed to undergo the transformation ob-

TABLE 13. Cell constants at superambient temperatures for sillimanite (Sri Lanka) and fibrolite (Lewiston)

Temp. (K)	a (Å)	b (Å)	c (Å)	V (Å ³)	n
Sillimanite—heating cycle					
373	7.4873(21)	7.6843(32)	5.7720(24)	332.09(16)	35
473	7.4865(17)	7.6872(25)	5.7725(18)	332.21(13)	35
573	7.4896(20)	7.6926(26)	5.7739(19)	332.67(14)	34
673	7.4914(21)	7.6973(28)	5.7762(21)	333.07(15)	34
773	7.4933(23)	7.7033(31)	5.7781(23)	333.52(16)	34
873	7.4968(24)	7.7086(33)	5.7796(22)	334.01(16)	35
973	7.4991(25)	7.7170(34)	5.7826(22)	334.64(17)	35
1073	7.5012(25)	7.7253(34)	5.7847(23)	335.21(17)	35
1173	7.5034(28)	7.7334(38)	5.7871(25)	335.81(19)	35
1273	7.5064(28)	7.7408(38)	5.7903(25)	336.45(19)	34
1373	7.5158(30)	7.7446(35)	5.7952(25)	337.32(19)	32
Sillimanite—cooling cycle					
373	7.4798(20)	7.6761(29)	5.7703(21)	331.30(15)	26
473	7.4816(20)	7.6812(28)	5.7730(21)	331.76(15)	26
573	7.4826(19)	7.6886(27)	5.7760(20)	332.30(14)	26
673	7.4840(21)	7.6931(29)	5.7801(21)	332.79(15)	26
773	7.4854(21)	7.7001(30)	5.7848(22)	333.43(16)	26
873	7.4874(22)	7.7070(31)	5.7880(23)	334.00(17)	26
973	7.4909(26)	7.7128(36)	5.7913(27)	334.60(19)	26
1073	7.4938(28)	7.7201(39)	5.7956(29)	335.29(21)	26
1173	7.4985(28)	7.7295(39)	5.7997(29)	336.14(21)	26
1273	7.5022(31)	7.7397(41)	5.8034(30)	336.97(22)	26
1373	7.5170(28)	7.7466(30)	5.8065(22)	338.12(17)	24
Fibrolite—heating cycle					
373	7.4825(11)	7.6777(14)	5.7733(9)	331.67(7)	35
473	7.4844(9)	7.6821(12)	5.7751(8)	332.05(6)	35
573	7.4860(10)	7.6873(14)	5.7776(10)	332.48(7)	34
673	7.4875(11)	7.6915(15)	5.7809(10)	332.92(8)	35
773	7.4892(11)	7.6973(15)	5.7827(10)	333.36(8)	33
873	7.4909(12)	7.7025(16)	5.7849(11)	333.78(8)	35
973	7.4924(12)	7.7085(10)	5.7874(11)	334.25(8)	36
1073	7.4948(13)	7.7162(17)	5.7902(12)	334.86(9)	35
1173	7.4961(17)	7.7254(23)	5.7926(15)	335.45(12)	35
1273	7.4991(14)	7.7314(19)	5.7955(12)	336.02(9)	35
1373	7.5018(17)	7.7415(23)	5.7977(15)	336.70(11)	33
Fibrolite—cooling cycle					
373	7.4820(17)	7.6764(19)	5.7736(14)	331.61(10)	24
473	7.4834(12)	7.6803(14)	5.7759(10)	331.97(7)	24
573	7.4850(11)	7.6856(13)	5.7772(10)	332.34(7)	25
673	7.4869(17)	7.6908(19)	5.7788(14)	332.75(10)	25
773	7.4866(15)	7.6959(17)	5.7816(13)	333.12(9)	25
873	7.4884(12)	7.7025(14)	5.7835(11)	333.59(8)	25
973	7.4895(11)	7.7085(13)	5.7845(9)	333.96(7)	24
1073	7.4915(15)	7.7142(18)	5.7868(13)	334.42(9)	24
1173	7.4940(25)	7.7205(29)	5.7915(21)	335.08(15)	25
1273	7.4957(24)	7.7273(13)	5.7958(21)	335.70(15)	25
1373	7.5008(19)	7.7365(22)	5.7982(16)	336.47(12)	24

Note: n = number of X-ray lines used in least-squares fit.

served for the Lewiston fibrolite and that the higher heat capacities he observed are the result. Because we do not know the origin of the thermal anomaly in the Lewiston fibrolite, we cannot speculate on a reason for the difference in sample behavior.

SURFACE ENERGY AND OTHER CONTRIBUTIONS TO EXCESS HEAT CAPACITY

The two commonly considered sources of excess heat capacity in a crystal are surface energy and high defect density. Kerrick (1986) has reviewed the evidence for excess heat capacity arising from dislocation strain energy. Kerrick (1986) concluded that the typical dislocation densities in naturally occurring sillimanite and fibrolite preclude significant perturbation of the P - T phase equi-

librium boundaries of the Al_2SiO_5 polymorphs. No further review of dislocation strain energy is necessary in this study except to note that if fibrolites undergo a small structural change, defects may prevent transformation of the structure and therefore be the cause of differences observed in heat capacity measurements (e.g., Salje, 1988).

Kerrick (1987) and Salje (1986) have suggested that excess heat capacity may result in fibrolite as a consequence of high surface area on and in fibrolite crystals. Holdaway (1971) and Kerrick (1987) suggested that the surface free-energy contribution to fibrolite will destabilize it with respect to sillimanite. Salje (1986) proposed that surface energy contributions to the heat capacity of fibrolite arise from internal and external planes of defects that result from dislocations, stacking faults, and intergrowth of crystals and small crystal size. Such an effect would also be reflected in an excess heat capacity and enthalpy of solution.

We may estimate the contribution of surface energy to the excess heat capacity from the results of several studies. Salje (1986) ground sillimanite to a grain size estimated to be less than 0.0004 mm. Salje (1986) compared the heat capacity of the powder and the coarse-grained sample of sillimanite (temperature interval 400–500 K) and observed that the fine powder had a 2% larger heat capacity. Giaque and Archibald (1937) observed a 1% increase in the heat capacity of fine-grained MgO (grain size unknown) as compared to coarse crystalline MgO at subambient temperatures. The difference in C_p of two size fractions of MgO increased to about 6% at 90 K.

It is well established that fine mineral powders exhibit excesses in thermochemical properties (also see Taylor and Wells, 1938; Hemingway and Robie, 1977); however, the results presented in this study suggest that when such fine crystals are intergrown, as in the case for quartz in novaculite, the surface energy contributions are greatly diminished. Hemingway and Robie (1977) have shown that quartz powder with a grain size less than 0.002 mm shows an excess enthalpy of solution in aqueous HF that they interpreted as a surface energy contribution. Thus the quartz grains in the novaculite (<0.002 mm) should be small enough to exhibit surface energy contributions to the heat capacity. Plots of the heat capacity difference between fine-grained samples or glasses and the coarse crystalline equivalent usually show a strong maximum at temperatures below 150 K (e.g., Richet et al., 1986; Barron et al., 1959). Inspection of the heat capacity data from this report indicates a tendency toward a maximum in the difference plot of the heat capacities of fibrolite and sillimanite somewhere below 60 K; however, this difference may arise from OH in the muscovite contaminant in fibrolite. The low-temperature heat capacities do not support an interpretation of a large excess heat capacity arising from surface energy contributions in interlocking aggregates of fibrolite crystals.

Enthalpy of solution measurement of samples of the Sri Lanka sillimanite and the Lewiston fibrolite have been reported by Topor et al. (1989). These results are also

equivocal. The enthalpies of formation of fibrolite and sillimanite from the oxides quartz and corundum are -2.39 ± 0.75 and -3.04 ± 0.73 kJ/mol, respectively, at 1000 K. These data suggest that fibrolite may be less stable than sillimanite. If fibrolite is less stable than sillimanite, a surface free-energy contribution may be the cause as proposed by Salje (1986) and Kerrick (1987). However, the uncertainties overlap and a correction must be made to the enthalpy of solution of fibrolite for the contribution of impurity phases. Topor et al. (1989) calculated a correction for the muscovite impurity using data for sanidine + corundum + H_2O . This correction represents the largest source of error in the enthalpy of formation of fibrolite. In particular, H_2O released into the molten salt solvent in the dissolution of fibrolite may create systematic differences in solution enthalpies that cannot be properly modeled. Thus, as with the heat capacity data discussed above, the enthalpy of solution results show some differences between fibrolite and sillimanite, but the results do not support an interpretation of a large surface free-energy contribution.

It should be noted that we distinguish free surfaces such as found on grains in a mechanically produced powder from grain boundaries of intergrown crystals or internal surfaces of grains in our analysis of surface energy contributions. We expect fine powders of minerals used in calorimetric or phase equilibria experiments to alter measured results significantly as a consequence of surface energy contributions. However, aggregates of intergrown (or cemented) crystals are not expected to show the same order of lattice distortion and are not expected to have as pronounced an effect on the properties determined by calorimetric or phase equilibrium studies or those properties under geologic conditions. Differences in the preparation of fibrolite samples may be the cause of the observed differences in the behavior of fibrolite in the various experiments.

Salje (1986) investigated several other factors that may cause the thermodynamic properties of fibrolite to differ from sillimanite, but he found no correlation between the observed differences and the Al-Si ratio, chemical impurities, or Al-Si disorder. Results reported by Openshaw et al. (1976) support the latter point as these authors found only minor differences between the low-temperature heat capacities and the calculated calorimetric entropies for ordered and disordered alkali feldspars.

THE Al_2SiO_5 PHASE DIAGRAM

A phase diagram for the Al_2SiO_5 polymorphs can be constructed by combining calorimetrically determined enthalpies of reaction, entropies, and heat capacity functions with volumes, expansivities, and phase equilibrium data for the Al_2SiO_5 polymorphs. Phase equilibrium data place constraints on both the location and slope of equilibria in P - T space. In a similar manner, the enthalpies of formation and entropies at 298.15 K place constraints on the P - T location; the volume, thermal expansivity, entropy at 298.15 K, and the heat capacity functions place

constraints on the slope of the equilibrium reaction boundary.

In addition to the calorimetric data presented earlier, the data set used to construct a phase diagram for Al_2SiO_5 consists of the results from the following studies. Minor differences between the reported results for molar volume and expansivity for kyanite and andalusite were not resolved (Skinner et al., 1961; Winter and Ghose, 1979). The average values calculated from the results of the two reports were utilized for kyanite and andalusite. Molar volumes and thermal expansivities for sillimanite and fibrolite were taken from the results presented in this study. Enthalpies of reaction were taken from Topor et al. (1989). Equilibrium reactions were taken from the following studies: Evans (1965), Newton (1966a, 1966b), Weill (1966), Althaus (1967), Richardson et al. (1968a, 1968b, 1969), Newton (1969), Holdaway (1971), Newton (cited in Holdaway, 1971), Kerrick and Heninger (1984), and Bohlen et al. (1989).

If the results reported by Evans (1965) for the reaction kyanite = sillimanite, by Richardson et al. (1969) for the reaction andalusite = sillimanite, and by Althaus (1967) for the reactions kyanite = sillimanite and andalusite = sillimanite are excluded, the phase equilibrium experiments provide reasonably consistent data from which the slopes of the equilibrium reactions involving the three Al_2SiO_5 polymorphs, kyanite, sillimanite, and andalusite, may be estimated. These slopes may be compared with the slopes of the equilibrium reactions calculated by the third-law method (e.g., Robie, 1965) using the equation

$$\Delta_r H_{298}^0 = T\Delta \left[\frac{(G_T^0 - H_{298}^0)}{T} \right] + \int_1^P \Delta V_T dP$$

where $\Delta_r H_{298}^0$ is the enthalpy of the reaction at 298.15 K, T is the temperature in kelvins, $\Delta[(G_T^0 - H_{298}^0)/T]$ is the difference in Gibbs functions, and ΔV_T is the volume change at T .

An attempt was made to construct a phase diagram consistent with experimental phase equilibrium brackets using the enthalpies of reaction calculated from the molten salt calorimetry of Topor et al. (1989) and the Gibbs functions from this study. These results were inconsistent with the results from the phase equilibrium data. If we assume that the molar volume data are basically correct, then the enthalpy of reaction at 298.15 K, the Gibbs functions, or both may be altered in order to yield agreement with phase equilibrium data. The enthalpies of reaction calculated from the data of Topor et al. (1989) were first held constant, and adjustments to the Gibbs function were calculated. The Gibbs function is defined as

$$\frac{(G_T^0 - H_{298}^0)}{T} = \frac{1}{T} \int_{298}^T C_P^0 dT - \int_{298}^T \frac{C_P^0}{T} dT - S_{298}^0.$$

Adjustment to the Gibbs function may be easily visualized as a change to the third-law entropy at 298.15 K (the last term) or as a change in the heat capacity function. The results of such calculations required that the entropy

at 298.15 K for one phase be both increased and decreased when considering the two equilibria involving the phase. Thus, the enthalpies of reaction calculated from the data obtained by Topor et al. (1989) are not directly consistent with the phase equilibrium data and the thermodynamic functions presented in this study. However, it should be noted that the enthalpies of reaction are the differences between two values of nearly equal size, each having an uncertainty of 15–25% of the calculated difference (see Table 14). Thus a deviation of 30% or more may yet represent good agreement with the data of Topor et al. (1989).

In a second set of calculations, the Gibbs functions were initially held constant and the enthalpies of reaction at 298.15 K were estimated through iteration and comparison with the experimental equilibrium bracketing data. Good agreement was obtained for the kyanite = andalusite and andalusite = sillimanite equilibria. These equilibria establish the triple point at their intersection in P - T space. The kyanite = sillimanite equilibrium constructed to be consistent with this triple point was not consistent with the phase equilibrium data for this reaction. Good agreement was obtained for the three equilibrium reactions if the entropy of kyanite at 298.15 K was increased by 0.5 J/mol·K and the entropy of sillimanite was decreased by 0.5 J/mol·K, both changes within the uncertainty of the values. The resulting enthalpies of reaction at 298.15 K were -3.867 kJ for andalusite = kyanite, $+3.809$ kJ for andalusite = sillimanite, and -7.676 kJ for sillimanite = kyanite, which may be compared with the results listed in Table 14. The estimated uncertainties in the adjusted values are of the same magnitude as those of the calorimetrically measured values. The adjusted enthalpies of reaction at 298.15 K agree within the respective uncertainties with the results of Topor et al. (1989). The triple point resulting from these calculations is at 784 ± 20 K and 3.87 ± 0.3 kbar. Selected values of temperatures and pressures calculated for the equilibrium reactions from the recommended thermodynamic properties are listed in Table 15. The phase diagram derived from these results is shown in Figure 1.

Bohlen et al. (1989) have proposed that significant curvature is required in the univariant kyanite-sillimanite equilibria between 1075 and 1275 K. That degree of curvature is not predicted from the volume and entropy changes for kyanite and sillimanite. Bohlen et al. (1989) have suggested that increasing Al-Si disorder in sillimanite with increasing temperature (and consequent increase in entropy) could explain the curvature. Navrotsky et al. (1973) studied Al-Si disorder in sillimanite prepared at temperatures greater than 1475 K and pressures greater than 16 kbar. Navrotsky et al. (1973) concluded that Al-Si disorder was not important at temperatures below about 1675 K. The argument of Bohlen et al. (1989) in support of curvature rests largely on acceptance of the reversal bracket at 1173 K and 11.4–11.7 kbar (Fig. 1). This reversal is at a somewhat lower pressure than the other reversal bracket of 11.8–12.2 kbar also reported by these

TABLE 14. Enthalpies of solution and reaction of Al_2SiO_5 polymorphs and related phases

Phase/reaction	Enthalpy of solution/reaction		Reference
	at about 970 K kJ/mol	at 298.15 K kJ/mol	
Fibrolite	28.95 ± 0.72		Topor et al. (1989)
Sillimanite	29.60 ± 0.70		Topor et al. (1989)
	29.75 ± 1.21		Navrotsky et al. (1973)
	29.00 ± 0.29		Anderson and Kleppa (1969)
	28.58 ± 0.63		Anderson and Kleppa (1969)
Andalusite	31.44 ± 0.92		Topor et al. (1989)
	31.59 ± 0.84		Anderson et al. (1977)
	33.51 ± 1.26		Topor et al. (1976)
Kyanite	34.14 ± 0.59		Topor et al. (1989)
	35.06 ± 0.96		Topor et al. (1976)
	34.94 ± 0.71		Anderson and Kleppa (1969)
Andalusite-kyanite		-3.867 ± 1.10	This study
	-2.70 ± 1.09	-2.93 ± 1.09	Topor et al. (1989)
	-1.55 ± 1.58	-1.78 ± 1.58	Topor et al. (1976)
	-3.35 ± 1.10	-3.58 ± 1.10	Anderson et al. (1977), Anderson and Kleppa (1969)
		-4.11 ± 2.42	Robie and Hemingway (1984)
		-4.25	Berman (1988)
		-4.06	Holland and Powell (1990)
Andalusite-sillimanite		3.809 ± 1.10	This study
	1.84 ± 1.16	2.53 ± 1.16	Topor et al. (1989)
	2.59 ± 0.89	3.28 ± 0.89	Anderson et al. (1977), Anderson and Kleppa (1969)
	3.01 ± 1.05	3.70 ± 1.05	Anderson et al. (1977), Anderson and Kleppa (1969)
		4.13 ± 2.42	Robie and Hemingway (1984)
		3.88	Berman (1988)
		4.60	Holland and Powell (1990)
Sillimanite-kyanite		-7.676 ± 1.10	This study
	-4.54 ± 0.92	-5.47 ± 0.92	Topor et al. (1989)
	-5.94 ± 0.95	-6.87 ± 0.95	Anderson et al. (1977), Anderson and Kleppa (1969)
	-5.19 ± 0.77	-6.12 ± 0.77	Anderson et al. (1977), Anderson and Kleppa (1969)
		-8.24 ± 2.42	Robie and Hemingway (1984)
		-8.13	Berman (1988)
		-8.66	Holland and Powell (1990)
Andalusite-fibrolite		3.838 ± 1.10	This study
Fibrolite-kyanite		-7.706 ± 1.10	This study
Quartz + corundum	28.62 ± 1.05		Shearer and Kleppa (1973)
	27.20 ± 0.45		Charlu et al. (1975)
	28.66 ± 1.66		Topor et al. (1976)
	26.56 ± 0.22		Topor et al. (1989)

authors for the same temperature. If the former reversal bracket is given little weight in a fit to the total set of reversal brackets, then a nearly linear curve fits the data set.

As noted above, the Gibbs function may be adjusted in two ways. The previous example demonstrates the effect of lowering the entropy for sillimanite at 298.15 K. The effect of such a change is greatest at the lower temperatures and decreases at higher temperatures. The rationale for this selection as opposed to the alternative

TABLE 15. Calculated pressures and temperatures for the equilibrium reactions

T/K	P/kbar				
	A ≈ K	A ≈ S	S ≈ K	A ≈ F	F ≈ K
500	0.61	—	—	—	—
600	1.78	—	—	—	—
700	2.92	5.40	2.12	5.50	1.98
800	4.05	3.59	4.20	3.58	4.23
900	5.15	1.96	6.28	1.90	6.46
1000	6.21	0.51	8.36	0.51	8.64
1100	—	—	10.45	—	10.79
1200	8.31	—	12.54	—	12.89
1300	—	—	14.62	—	14.94

Note: The triple point is 784 K and 3.87 kbar. A = andalusite, K = kyanite, S = sillimanite, F = fibrolite.

choice is as follows. The heat capacity function must be adjusted toward lower values to produce a decrease in the Gibbs function. The effect of such a change is smallest at the lower temperatures, with the effect increasing with temperature. However, because the Gibbs function represents the difference between the heat content of the phase and the entropy of the phase at the same temperature, fairly large changes in the heat capacity produce only small changes in the Gibbs function. For example, lowering the heat capacity function by 0.3% at 1000 K lowers the Gibbs function by only 0.01%, or only 3% of the change produced by lowering the entropy at 298.15 K. Thus, when using the third-law method, small adjustments to the entropy at 298.15 K maintained the greatest consistency with the measured data set.

Similar calculations were made using the thermodynamic functions calculated from the Lewiston-South Australia fibrolite data set in place of the data for sillimanite. Using the triple point and data for the andalusite ≈ kyanite reaction established above, similar results were obtained for the fibrolite ≈ kyanite and andalusite ≈ fibrolite equilibrium reaction boundaries and enthalpies of reaction at 298.15 K after an adjustment of -0.5 J/mol·K in the entropy of fibrolite at 298.15 K. The curve calculated for the andalusite ≈ fibrolite reaction has

greater curvature than that calculated for the andalusite \rightleftharpoons sillimanite reaction; however, deviations between the two curves at constant temperature do not exceed 0.1 kbar between 700 and 1050 K. The slope of the kyanite \rightleftharpoons fibrolite reaction boundary is slightly steeper than that for the kyanite \rightleftharpoons sillimanite reaction. The difference at constant temperature between these curves increases to about 0.3 kbar at 1300 K. The enthalpies of reaction were +3.838 and -7.706 kJ, respectively, for the andalusite \rightleftharpoons fibrolite and fibrolite \rightleftharpoons kyanite reactions at 298.15 K. Thus, unlike the results presented by Salje (1986), we find little difference between these fibrolite samples and the sillimanite samples. Selected values of temperature and pressure calculated for the equilibrium reactions are listed in Table 15.

It is possible that some fibrolites have higher heat capacities and, consequently, larger entropies in the superambient region because they fail to undergo a solid-solid transition, perhaps because of sample preparation techniques (also see Zen, 1969; Holdaway, 1971). This may be the cause of the disparate results of Althaus (1967). We calculated the slopes of the reaction boundaries for the kyanite \rightleftharpoons fibrolite and andalusite \rightleftharpoons fibrolite using the equation developed from the heat capacity data for fibrolite given by Salje (1986), that is, values that are about 2% higher than those recommended in this study. The resulting P - T slopes of the reactions andalusite \rightleftharpoons fibrolite and kyanite \rightleftharpoons fibrolite were considerably steeper than those discussed above. The slopes calculated in this final exercise were in general agreement with the slopes that may be estimated from the phase equilibrium data of Althaus (1967). In the temperature interval of 700 to 900 K, the slope of the andalusite \rightleftharpoons fibrolite reaction calculated in this study is -35 kbar/K; the slope estimated from all of the data of Althaus (1967) is -34 bar/K. In the temperature interval of 800 to 1000 K the slope of the fibrolite \rightleftharpoons kyanite reaction calculated herein is 30 bar/K and that estimated from the data of Althaus (1967) is 28 bar/K.

We have presented examples of how small adjustments in the various thermodynamic parameters affect the calculated phase diagram. The recommended values derived above were based on an iterative calculation to produce consistency between the selected phase equilibrium data and the recommended calorimetric data, with the minimum adjustment to the stated measured values. This procedure is similar to the process that computer algorithms utilize to fit data sets such as these simultaneously (e.g., Haas and Fisher, 1976; Day and Kumin, 1980; Haas et al., 1981; Berman, 1988); that is, adjustments of measured values are allowed within the uncertainty of the measurement and within the applied weighting scheme utilized.

ENTHALPIES AND GIBBS FREE ENERGIES OF FORMATION OF THE Al_2SiO_5 POLYMORPHS FROM THE ELEMENTS AT 298.15 K

The enthalpies and Gibbs free energies of formation of the Al_2SiO_5 polymorphs can be calculated from enthalpy

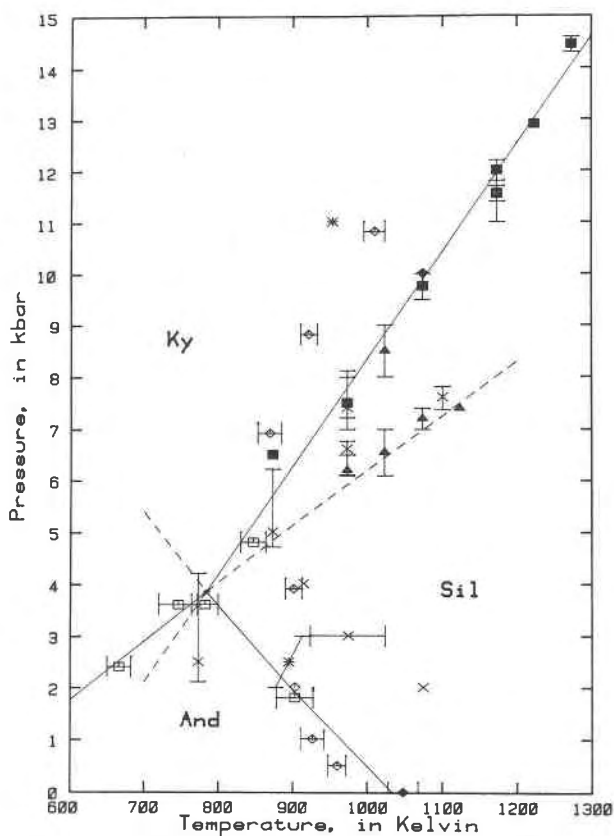


Fig. 1. Aluminum silicate phase diagram calculated from the thermodynamic properties recommended in the text. Experimental data from Evans (stars, 1965), Weill (solid diamonds, 1966), Newton (open triangles, 1966a, 1966b, 1969, and in Holdaway, 1971), Richardson et al. (X's, 1968a, 1968b, 1969), Holdaway (open squares, 1971), Althaus (open diamonds, 1967), and Bohlen et al. (solid squares, 1989) are included for comparison.

pies of solution of the polymorphs and reference oxides and ancillary thermodynamic data for the Al_2SiO_5 polymorphs, quartz, corundum, and the elements Al, Si, and O_2 . The thermodynamic properties for the elements are taken from Robie et al. (1979), and those for the Al_2SiO_5 polymorphs are taken from the recommended values given previously in this study. The Al_2SiO_5 polymorphs are refractory phases that completely dissolve only in molten salt solutions. Enthalpies of dissolution of the Al_2SiO_5 polymorphs and of the reference oxides quartz and corundum in lead borate melts at about 970 K are listed in Table 14.

A lack of agreement between the enthalpies of reaction calculated from the molten salt enthalpies of solution and those calculated from the phase equilibrium and heat capacity data by the third-law method was discussed in a previous section together with the consequences of changes in the various types of thermodynamic data. The method of resolving the differences will affect the enthalpies and Gibbs free energies of formation that are calculated for the Al_2SiO_5 polymorphs.

Because there is no clear reason to accept the enthalpy

of solution results for one Al_2SiO_5 polymorph as being better than the others, the minimum adjustment was achieved by raising the enthalpy of solution for kyanite and lowering that of sillimanite with respect to that for andalusite in order to match the enthalpies of reaction calculated earlier. The enthalpies of formation at 298.15 K calculated from this procedure and the enthalpy of solution of quartz and corundum reported by Topor et al. (1989) are -2589.90 ± 3.0 , -2593.77 ± 3.0 , and -2586.09 ± 3.0 kJ/mol for andalusite, kyanite, and sillimanite, respectively. These values together with the selected triple point are in good agreement with those derived by Berman (1988) and Robie and Hemingway (1984) but less so with those of Holland and Powell (1990). The enthalpy of formation of fibrolite is essentially identical to that calculated for sillimanite. The enthalpies and Gibbs free energies of formation are also given in Tables 9–12 at selected temperatures.

CONCLUSION

The triple point chosen in this study was derived through minimum adjustments of the experimental data. It was assumed that each experimental technique had equally valid results, but as noted, enthalpy of solution results were considered to be subject to larger uncertainties than heat capacity and perhaps phase equilibrium results. The triple point could be moved to higher pressure and temperature along the line of the kyanite = sillimanite equilibria if greater emphasis is placed on results for the reaction andalusite = kyanite conducted in the metastable region at temperatures and pressures above the triple point. This would, however, require the andalusite = sillimanite boundary to miss completely the reversal for this reaction provided by Holdaway (1971) near the chosen triple point and the andalusite = kyanite reaction to miss the 2.4 kbar reversal of Holdaway (1971) determined in the stable region below the triple point. With these constraints in mind, a triple point at 3.87 ± 0.3 kbar and 784 ± 20 K was selected.

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