

UNITED STATES DEPARTMENT OF THE INTERIOR
U.S. GEOLOGICAL SURVEY

Heat capacity and thermodynamic properties for two samples of prismatic¹

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Open-file Report 96-508

¹ This report is preliminary and has not been edited or reviewed for conformity with U.S. Geological Survey editorial standards.

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Abstract

Heat capacities of two prismatine samples have been measured by low-temperature quasi-adiabatic calorimetry. Australian prismatine was measured between 18 and 350 K and Greenland prismatine was measured between 50 and 350 K. At 298.15 K the heat capacity and entropy are 589.8 ± 0.9 and 476.7 ± 1.2 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and 593.8 ± 0.8 and 476.4 ± 3.0 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively, for the Australian and Greenland prismatine samples. Tables of thermodynamic properties are included for each phase.

Introduction

Preliminary results are presented here for the heat capacity and other thermodynamic properties of two prismatine samples. Failure of the system heat exchange tank (see Robie and Hemingway, 1972) prevented measurement of what we generally consider to be a complete set of heat-capacity data for these phases (measurements from about 5 to 350 K). Measurements were completed from about 18 to 350 K for the Australian prismatine and from about 50 to 350 K for the Greenland sample. It is hoped that time will permit completion of these data sets.

Samples

Grew et al. (1996) have divided the kornerupine group into two compositional ranges which they call kornerupine and prismatine. The kornerupine group represent complex borosilicates, with boron-free members known (Schreyer and Abraham, 1976). Boron is confined to the one T3 site. Where the boron content is <0.5 , Grew et al. (1996) recommend the use of the name kornerupine. For larger boron content, they recommend the name prismatine. The samples used in this study would be classified as prismatine following the Grew et al. (1996) nomenclature.

The first sample of prismatine acquired for this study is from Mt. Riddock Station, Harts Range, NT, Australia. The sample consisted of large porphyroblasts of prismatine (up to about 6 cm in length), rimmed by plagioclase and embedded in a coarse biotite gneiss. Individual crystals were removed from the matrix using a pneumatic drill. The crystals were crushed to pass a 28 micrometer screen. The sample was cleaned using floatation in heavy liquids followed by hand picking. Visual inspection of the concentrate showed less than 1 percent by volume of impurities. Microprobe analyses (23) of the sample yielded a practical chemical formula of $(\text{Mg}_{2.80}\text{Al}_{0.18})(\text{Al}_{4.95}\text{Fe}_{1.05})(\text{Al}_{0.36}\text{Si}_{3.68}\text{B}_{1.05})\text{O}_{21}(\text{OH}_{0.84}\text{F}_{0.08})$ based on the averaged chemical data given in Table 1. The results presented in Tables 2 and 3 are based on the practical chemical formula for which the molar mass is 741.322 g.

The second sample of prismatine is from Fiskenaeset, Greenland. This material has been described by Ackermann et al. (1984). The material was obtained from the U.S. National Museum of Natural History (#133772), but was labeled as sapphirine. Both X-ray and microprobe analyses showed the sample to be in the kornerupine group. Microprobe analyses (11) of the sample were made and the average values are listed in Table 1. The experimental results presented in Tables 4 and 5 are based on the practical chemical formula of $(\text{Mg}_{2.98}\text{Na}_{0.01}\text{Ca}_{0.01})(\text{Al}_{5.27}\text{Fe}_{0.25}\text{Cr}_{0.10}\text{Mg}_{0.37}\text{Ti}_{0.01})(\text{Al}_{0.85}\text{Si}_{3.53}\text{B}_{0.62})\text{O}_{21}(\text{OH})_1$ for which the

molar mass is 725.658 g.

Experimental results

Heat-capacity measurements were made using the quasi-adiabatic calorimeter described by Hemingway et al. (1984) and Robie and Hemingway (1972). The helium heat exchange tank failed during a measurement series at temperatures below 50 K, with the Australian prismatic in the calorimeter. Measurements from 18 to 50 K were completed, however, measurements at lower temperature could not be completed until the damage to the exchange tank was repaired. Following repairs, heat capacities of the Greenland prismatic were measured from 50 K (the lowest temperature to which the system will cool with nitrogen as the cryogenic material) to 350 K to test the system. These measurements are reported here.

Tables 2 and 3, and 4 and 5 contain the experimental heat capacities and smoothed thermodynamic properties, respectively, for the Australian and Greenland prismatic samples, respectively.

Discussion

Tables 3 and 5 contain smoothed thermodynamic properties for the Australian and Greenland prismatic samples based on the combination of estimated and measured values. The heat capacities and entropies of the two prismatic samples were estimated for temperatures below the lowest measured values for each phase.

For the Australian sample, the heat capacities were estimated from a Debye function evaluated at about 19 K and based on the smoothed experimental data. The smoothed thermodynamic properties listed in Table 3 at 20 K and below are based on this function ($C_P^0 = 5.0062 \times 10^{-4} T^3$). Based upon this extrapolation, the entropy at 298.15 K is $476.7 \pm 1.2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

For the Greenland prismatic sample, the entropy and heat content at 60 K were estimated by a summation procedure. Heat capacities were estimated for the temperature interval 50 to 150 K from the following summation; the heat capacities of pyrope (Téqui et al., 1991), plus 2.5 times the heat capacity of sillimanite (Hemingway et al., 1991), and 0.25 times the heat capacity of danburite (unpublished data) less the heat capacities of 0.25 times enstatite (Krupka et al., 1985) and 2.25 quartz (Hemingway et al., 1991). The summation yielded values within about 0.5 percent of the measured heat capacities for the Greenland sample from 60 to 110 K. Similar summations were made to estimate the entropy and heat content of the sample at 60 K. Using this estimation procedure for the contribution at 60 K and below (entropy, $23.92 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and enthalpy function, $17.81 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), the entropy of the Greenland prismatic at 298.15 K was estimated to be $476.4 \pm 3.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

Acknowledgements

This work was partially supported by Interagency Agreements No. DE-AI01-91CE31020 and DE-AI01-93CE31020 between the Department of Energy, Geothermal Division and the Department of the Interior, U.S. Geological Survey. We thank our US Geological Survey colleague Howard T. Evans, Jr. for his x-ray analysis of the Greenland sample and identification of the material as a member of the

kornerupine group.

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Table 1. Chemical analyses for prismatine¹ from Australia and Greenland.

Sample	Australia	Greenland
SiO ₂	30.1328	29.912
TiO ₂	0.1607	0.055
Al ₂ O ₃	38.1981	44.060
B ₂ O ₃	4.3537	3.033
Cr ₂ O ₃	0.0616	1.102
Fe ₂ O ₃	11.4399	2.493
FeO	n.a.	n.a.
MnO	0.0413	0.022
MgO	15.4075	19.070
CaO	0.0095	0.085
Na ₂ O	0.1544	0.043
K ₂ O	0.0108	0.001
H ₂ O	1.0500	n.a.
F	0.2736	0.061
Cl	0.0097	0.004
(-O=(F+Cl))	-0.1174	-0.027
Total	101.1862	99.960

¹ Members of the kornerupine group may contain Li and Be that were not analysed here. Values represent the averaged results from microprobe analyses. Total Fe assumed to be Fe³⁺. H₂O is estimated.

n.a. not analysed

Table 2. Experimental heat capacities of Australian prismatine corrected for curvature.
Values are listed for a sample mass of 741.322 g.

Temp.	Heat capacity	Temp.	Heat capacity	Temp.	Heat capacity
K	J·mol ⁻¹ ·K ⁻¹	K	J·mol ⁻¹ ·K ⁻¹	K	J·mol ⁻¹ ·K ⁻¹
Series 1		Series 3		Series 4	
307.29	602.5	19.13	3.474	229.55	481.3
Series 2		20.97	4.339	235.19	491.6
		23.08	5.369	240.83	501.4
		24.42	6.023	Series 5	
58.71	58.66	27.46	8.201		
63.36	67.93	29.45	9.744		
68.75	80.05	32.19	12.05	236.21	492.8
75.17	95.60	35.78	15.56	242.17	503.7
81.42	112.3	39.55	22.77	247.56	513.1
87.77	130.2	44.16	26.32	252.98	522.1
94.13	147.8	49.50	37.26	258.64	530.6
100.45	165.7	55.28	49.11	264.33	539.7
106.72	183.3	61.58	62.65	270.04	550.0
112.92	200.9	Series 4		275.76	558.1
119.08	218.4			281.48	565.4
125.19	235.9			287.18	574.6
131.29	252.7	161.16	330.9	292.86	583.7
137.34	269.2	167.23	346.1	298.51	591.0
143.36	285.1	172.66	359.4	304.17	598.4
149.33	301.4	178.16	372.7	309.81	605.8
155.28	316.3	183.94	386.2	315.42	612.9
161.20	331.3	189.69	399.2	321.02	619.5
167.10	346.2	195.43	412.2	326.60	626.9
		201.15	424.6	332.17	633.8
		206.86	436.5	337.71	641.4
		212.56	448.8	343.25	647.9
		218.24	460.2	348.81	654.1
		223.90	470.7		

Table 3. Thermodynamic properties for Australian prismatine.

Temp.	Heat Capacity	Entropy	Enthalpy function	Gibbs energy function
K	-----	J·mol ⁻¹ ·K ⁻¹	-----	-----
5	0.062	0.021	0.017	0.004
10	0.495	0.164	0.129	0.035
15	1.670	0.556	0.431	0.125
20	3.956	1.318	1.014	0.304
25	6.464	2.446	1.830	0.616
30	10.16	3.933	2.894	1.041
35	15.13	5.852	4.268	1.584
40	21.63	8.284	6.020	2.264
45	29.15	11.25	8.160	3.090
50	38.21	14.78	10.70	4.081
60	59.62	23.59	17.02	6.566
70	83.31	34.54	24.78	9.757
80	108.9	47.31	33.68	13.63
90	136.0	61.68	43.52	18.16
100	164.0	77.46	54.16	23.30
110	192.4	94.42	65.44	28.98
120	220.7	112.4	77.20	35.18
130	248.6	131.2	89.31	41.83
140	275.9	150.5	101.7	48.90
150	302.5	170.5	114.2	56.34
160	328.3	190.9	126.7	64.11
170	353.1	211.5	139.4	72.17
180	377.0	232.3	151.9	80.49
190	400.0	253.4	164.4	89.04
200	421.9	274.4	176.6	97.79
210	442.9	295.6	188.9	106.7
220	462.8	316.6	200.8	115.8
230	481.8	337.6	212.7	124.9
240	499.9	358.5	224.2	134.3
250	517.0	379.2	235.6	143.6
260	533.3	400.0	246.8	153.2
270	549.1	420.3	257.6	162.7
280	564.1	440.5	268.3	172.2
290	578.5	460.5	278.8	181.7
300	592.4	480.4	289.0	191.4
310	606.0	500.1	299.0	201.1
320	619.1	519.5	308.8	210.7
330	632.0	538.8	318.4	220.4
340	645.0	557.8	327.9	229.9
273.15	553.9	426.7	261.1	165.6
298.15	589.8	476.7	287.2	189.5
	±0.9	±1.2	±0.9	±1.2

Table 4. Experimental heat capacities of Greenland prismatine corrected for curvature.
Values are listed for a sample mass of 725.658 g.

Temp.	Heat capacity	Temp.	Heat capacity	Temp.	Heat capacity
K	J·mol ⁻¹ ·K ⁻¹	K	J·mol ⁻¹ ·K ⁻¹	K	J·mol ⁻¹ ·K ⁻¹
Series 1		Series 2		Series 5	
300.86	597.4	223.01	470.4	284.23	570.2
306.31	602.9	227.37	478.8	285.79	574.0
310.99	610.2	231.77	486.8	287.79	578.2
315.67	617.2	236.23	495.1	289.80	582.0
320.39	623.3	240.73	503.1	291.85	586.2
325.10	627.5	245.28	511.3	293.89	589.8
329.80	634.7	249.86	518.4	295.93	591.3
334.49	642.9	253.59	523.7	297.97	593.8
339.17	645.6	258.16	532.7	300.00	595.7
Series 2		262.79	540.7	302.03	598.7
70.76	83.76	267.48	546.9	304.05	602.4
75.12	94.21	272.22	554.2	306.07	604.1
79.60	105.2	276.95	561.0	308.09	608.3
84.24	117.4	281.68	568.7	310.10	611.3
89.38	131.9	286.40	576.8	312.11	611.3
94.50	146.3	291.11	584.5	314.12	614.4
99.59	161.0	295.81	591.3	316.12	617.2
104.63	174.8	300.50	599.3	318.12	619.3
109.61	188.9	Series 3		320.11	622.4
114.53	203.2	305.17	603.1	322.10	626.2
119.40	216.7	309.83	609.2	324.10	628.1
124.22	230.8	314.47	614.0	326.08	629.6
129.00	244.7	319.08	626.7	328.07	631.5
133.74	257.3	Series 4		330.04	633.2
138.43	270.4	298.45	594.0	Series 6	
143.10	283.0	299.84	596.8	329.47	630.4
147.72	296.7	301.52	596.3	331.44	634.0
152.32	307.9	303.21	601.2	333.37	640.3
156.90	319.6	304.91	602.2	335.33	643.1
161.43	331.4	306.61	605.4	337.32	641.8
165.95	343.0	308.31	608.1	339.32	644.3
170.44	354.2	310.01	610.4	341.30	648.1
174.91	364.5	311.70	609.6	343.28	648.8
179.35	375.0	313.39	610.7	345.25	652.3
183.78	386.2	315.08	612.1	347.22	655.1
188.19	396.9	316.77	614.7	Series 7	
192.58	406.6	318.45	623.1	51.44	41.63
196.96	415.0	320.13	626.4	55.84	54.69
201.31	426.6	321.81	622.2	60.27	63.53
205.66	436.3	323.49	623.7	64.99	70.69
210.00	445.8	325.16	631.3		
214.34	453.1	326.83	631.9		
218.67	461.6	328.50	635.7		
		330.17	634.9		

Table 5. Thermodynamic properties for Greenland prismatine.

Temp.	Heat Capacity	Entropy	Enthalpy function	Gibbs energy function
K	-----		J·mol ⁻¹ ·K ⁻¹	-----
60	62.77	23.92	17.81	6.113
70	81.93	34.95	25.54	9.407
80	106.3	47.46	34.07	13.39
90	133.5	61.53	43.60	17.93
100	161.9	77.03	54.01	23.02
110	190.2	93.83	65.11	28.72
120	218.6	111.6	76.71	34.92
130	247.0	130.2	88.72	41.52
140	274.8	149.5	101.1	48.46
150	302.0	169.4	113.6	55.87
160	327.9	189.8	126.1	63.74
170	352.9	210.5	138.7	71.87
180	377.1	231.3	151.3	80.03
190	400.5	252.1	163.8	88.33
200	423.2	273.4	176.2	97.26
210	444.7	294.5	188.5	106.0
220	464.7	315.7	200.6	115.1
230	483.7	336.8	212.4	124.4
240	501.8	357.6	224.2	133.4
250	518.8	378.5	235.5	143.0
260	535.3	399.3	246.9	152.5
270	550.9	419.8	257.7	162.1
280	566.4	440.0	268.6	171.4
290	582.0	460.2	279.1	181.2
300	596.3	480.2	289.5	190.8
310	609.4	500.0	299.5	200.5
320	622.2	519.6	309.5	210.1
330	634.7	538.7	319.1	219.6
340	646.4	557.9	328.6	229.3
273.15	555.7	426.1	261.1	165.0
298.15	593.8	476.4	287.6	188.9
	±0.8	±3.0	±3.0	±3.0