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Heat capacities and thermodynamic properties of annite (aluminous iron biotite)

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ABSTRACT

Thermodynamic data are reported for a natural sample of annite (aluminous iron biotite) having the composition

$$(Na_{0.025}K_{0.998}Ca_{0.001})Fe_{1.517}Al_{0.865}Mn_{0.110}Ti_{0.034}Mg_{0.005}Sn_{0.002}[Al_{1.027}Si_{2.973}O_{9.656}]F_{0.971}OH_{1.728}.$$

The heat capacities have been measured between 7 and 650 K by quasi-adiabatic calorimetry and differential scanning calorimetry. At 298.15 K and 1 bar, the calorimetric entropy for our sample is 354.9 ± 0.7 J/(mol·K). A minimum configurational entropy of 18.7 J/(mol·K) for full disorder of Al/Si in the tetrahedral sites should be added to the calorimetric entropy for third-law calculations.

The heat capacity equation [C_P in units of J/mol·K)]

$$C_P^0 = 583.586 + 0.075246T - 3420.60T^{-0.5} - (4.4551 \times 10^6)T^{-2}$$

fits the experimental and estimated heat capacities for our sample (valid range 250 to 1000 K) with an average deviation of 0.37%.

INTRODUCTION

Annites are a potential source of petrologic information regarding conditions of oxygen fugacity and temperature (e.g., Wones and Eugster, 1965, and Rutherford, 1973). The stability of biotite to higher temperatures increases as Al substitution for Fe increases. The substitution of Al in biotite and magnetite increases as the oxygen fugacity increases (Rutherford, 1973).

Complicating the development of a geobarometer-geothermometer is the lack of thermodynamic data for aluminous iron biotites and for Al-bearing magnetite-hercynite solid solutions that in part limit biotite stability through reactions of the following type: oxygen + biotite = $magnetite_{ss}$ + sanidine + leucite + corundum + water; oxygen + biotite = $magnetite_{ss}$ + $hercynite_{ss}$ + sanidine + leucite + water; and oxygen + biotite + corundum = $hercynite_{ss}$ + sanidine + leucite + water. Direct determination of the stability of biotites of varying compositions of Fe, Mg, and Al represents an enormous experimental program that may be sharply reduced when augmented with thermodynamic data. We report here heat-capacity data for annite (aluminous iron biotite) as part of a continuing study of the thermodynamic properties of sheet-structure silicates by our laboratory (talc, Robie and Stout, 1963; muscovite and pyrophyllite, Robie et al., 1976, and Krupka et al., 1979; chlorite, Hemingway et al., 1984; and phlogopite and paragonite, Robie and Hemingway, 1984).

SAMPLE AND APPARATUS

Several large blocks of Lost Creek Granite (Wanek and Barclay, 1966) were crushed and sieved to between −60 and +100 mesh. The granite was collected from James Elliott's (USGS) site E0189 on Lost Creek at lat 46°12′17″N and long 112°59′58″W in Deer Lodge County in southwestern Montana. The green high-Al annite crystals were separated by use of a shaker table operated within a strong magnetic field. The sample was further cleaned by hand picking and by repeated washes in a ultrasonic bath containing isopropyl alcohol. The resulting calorimetric sample contained less than 0.5% of contaminating mineral phases, largely quartz and feldspar with some hematite.

Nine microprobe analyses by Steve Ludington (USGS) of a hand-picked sample of annite from the same general location provided the following average chemistry (in weight percent): SiO_2 36.71, Al_2O_3 19.82, TiO_2 0.55, total Fe as FeO 22.40, MgO 0.04, MnO 1.60, CaO 0.01, Na_2O 0.16, K_2O 9.66, SnO_2 0.06, F 3.79, and Cl <0.01. Ba was not detected and Fe^{3+}/Fe^{2+}, Li, Zn, and Nb were not analyzed. Subsequent EDX analyses on a scanning electron microscope by Joan Fitzpatrick (USGS) verified the absence of significant quantities of additional heavier elements. The concentration of H, reported as total water, was 3.2 wt%, as determined by Floyd Brown (USGS) using a Perkin-Elmer 240B elemental analyzer[1] with PbO as the flux.

Thermodynamic properties are reported for the composition $(Na_{0.025}K_{0.998}Ca_{0.001})Fe_{1.517}Al_{0.865}Mn_{0.110}Ti_{0.034}Mg_{0.005}Sn_{0.002}[Al_{1.027}Si_{2.973}O_{9.656}]F_{0.971}OH_{1.728}$ for which the calculated formula weight is 469.259 g, based upon the 1975 values for the atomic weights (Commission on

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[1] The use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

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TABLE 1. Experimental low-temperature molar heat capacities for natural annite (an aluminous iron biotite with a molar mass = 469.259 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 3**	
302.15	360.6	27.94	21.33	220.30	291.1
Series 2		30.98	25.18	225.78	296.6
18.09	10.84	34.40	29.76	231.28	301.9
19.22	11.92	38.21	35.39	236.80	307.2
20.77	13.43	42.48	40.82	242.33	312.1
22.55	15.17	47.26	46.90	247.85	317.1
24.92	17.79	52.58	54.42	253.36	321.9
27.54	20.85	58.49	63.38	258.87	326.7
30.51	24.56	64.72	73.41	264.37	331.5
33.86	29.02	70.97	83.98	269.89	336.1
37.60	34.56	77.22	94.87	275.39	340.5
41.79	39.95	83.39	105.6	280.87	345.0
46.50	45.74	89.48	115.8	286.33	349.3
51.75	53.11	95.52	125.6	291.78	353.1
57.58	61.97	101.52	135.1	297.21	357.0
63.78	71.89	107.47	144.5	302.62	360.9
Series 3		113.37	153.6	308.02	364.9
7.26	0.9928	119.22	162.7	313.39	368.6
7.44	0.9871	125.03	171.7	318.74	371.7
7.61	1.385	130.81	180.4	**Series 4**	
7.97	2.694	136.57	188.9	313.43	367.2
8.52	3.939	142.29	197.2	318.64	371.1
9.62	5.066	147.98	205.2	323.62	374.3
10.84	5.824	153.65	212.9	328.61	377.6
11.83	6.349	159.30	220.6	333.75	381.4
12.71	6.881	164.92	227.8	338.89	384.1
13.53	7.408	170.53	234.8	344.02	386.6
14.33	7.987	176.12	241.8	349.16	389.4
15.12	8.487	181.69	248.7	354.29	392.4
15.89	9.025	187.25	255.4	359.40	395.3
16.67	9.665	192.79	261.7	364.51	397.8
18.79	11.52	198.32	267.8	369.60	400.9
20.71	13.34	203.83	274.0	374.67	404.4
22.80	15.45	209.33	279.7	379.73	407.2
25.22	18.13	214.82	285.5	384.77	408.8

TABLE 2. Molar thermodynamic properties of natural annite

Temp. T	Heat capacity C_P^0	Entropy $S_T^0 - S_0^0$	Enthalpy function $(H_T^0 - H_0^0)/T$	Gibbs energy function $-(G_T^0 - H_0^0)/T$
(K)	[J/(mol·K)]			
5	0.260	0.085	0.060	0.025
10	5.293	1.372	1.123	0.249
15	8.421	4.090	3.017	1.073
20	12.66	7.059	4.868	2.191
25	17.87	10.43	6.932	3.496
30	23.90	14.21	9.248	4.963
35	30.69	18.39	11.82	6.578
40	37.68	22.96	14.62	8.337
45	43.96	27.76	17.53	10.23
50	50.64	32.73	20.50	12.23
60	65.76	43.27	26.76	16.51
70	82.33	54.64	33.50	21.14
80	99.69	66.77	40.69	26.08
90	116.6	79.50	48.20	31.30
100	132.8	92.62	55.85	36.77
110	148.5	106.0	63.56	42.46
120	163.9	119.6	71.28	48.32
130	179.2	133.3	78.99	54.33
140	193.9	147.1	86.68	60.47
150	208.0	161.0	94.30	66.71
160	221.4	174.9	101.8	73.03
170	234.2	188.7	109.2	79.43
180	246.6	202.4	116.5	85.88
190	258.5	216.1	123.7	92.37
200	269.7	229.6	130.7	98.90
210	280.5	243.0	137.6	105.4
220	290.8	256.3	144.3	112.0
230	300.7	269.5	150.9	118.6
240	310.0	282.5	157.3	125.1
250	319.0	295.3	163.6	131.7
260	327.7	308.0	169.8	138.2
270	336.2	320.5	175.8	144.7
280	344.3	332.9	181.7	151.2
290	351.9	345.1	187.4	157.7
300	359.1	357.2	193.0	164.2
310	365.8	369.0	198.5	170.6
320	372.3	380.8	203.8	177.0
330	378.6	392.3	209.0	183.3
340	384.5	403.7	214.1	189.6
350	390.1	414.9	219.0	195.9
360	395.6	426.0	223.9	202.1
370	401.3	436.9	228.6	208.3
380	406.8	447.7	233.2	214.5
273.15	338.8	324.4	177.7	146.8
298.15	357.8	354.9	192.0	163.0

Note: The entropy values do not include the addition of a zero-point entropy contribution.

Atomic Weights, 1976). The low- and high-temperature heat-capacity samples weighed 36.5282 g and 17.911 mg, respectively.

The polytype of the natural annite is *1M* as determined from a single crystal using a Buerger X-ray precision camera. However, the annite exhibits a significant number of intermixed dioctahedral layers and stacking faults consistent with the low assignment of cation occupancies in the octahedral layer that have been made based upon the microprobe analyses. X-ray diffraction data from 13 reflections collected with an automated diffractometer using Cu radiation were indexed on a slightly distorted cell. The cell parameters are $a = 5.313(3)$ Å, $b = 9.224(12)$ Å, $c = 10.101(7)$ Å, $\beta = 99.91(5)°$, and $V = 487.6(4)$ Å^3. The cell parameters observed for this annite are smaller than those reported by Rutherford (1973). Rutherford (1973) noted that the cell parameters decreased as the Al content increased, suggesting that the changes reflected an increase in Fe^{3+} and the coupled creation of octahedral vacancies.

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

High-temperature heat capacities were measured with a Perkin-Elmer DSC-2 differential scanning calorimeter following the procedures outlined by Hemingway et al. (1981). The sample was enclosed in an unsealed Au pan.

LOW-TEMPERATURE HEAT CAPACITIES AND THERMODYNAMIC FUNCTIONS

The experimental heat capacities of the annite sample are listed in the chronological order of measurement in Table 1. Smoothed values of the heat capacities calculated from cubic-spline smoothing functions and of the entropy, enthalpy, and Gibbs energy functions are listed in Table 2. At 298.15 K and 1 bar, the heat capacity and calorimetric entropy values for our sample are 357.8 ± 0.7 and 354.9 ± 0.7 J/(mol·K), respectively.

The low-temperature heat capacities rise through a small peak near 10 K. Anomalous low-temperature heat capacities likely result from a Schottky (magnetic) contribution to the heat capacity from the zero-field splitting of spin states in the transition elements Fe and Mn (e.g., Hemingway and Robie, 1984, and Robie and Hemingway, 1984) and/or antiferromagnetic ordering (Robie et al., 1982). On the basis of the composition of our sample, we may estimate a theoretical magnetic contribution to the entropy (e.g., Gopal, 1966) of our annite sample of 21.9 ± 2.0 J/(mol·K).

The observed magnetic entropy may be estimated from the difference between the lattice heat capacities and the observed heat capacities. Lattice heat capacities may be estimated from procedures such as those discussed by Hemingway and Robie (1984). A corresponding-states model was developed for the lattice heat capacities of annite at low-temperature based upon the temperature-dependent ratio $[1.1206 - (4.1333 \times 10^{-4})T]$ of the heat capacities of annite divided by those of hydroxyphlogopite from Robie and Hemingway (1984). The function was derived for heat capacities in the interval 180 to 260 K. A magnetic entropy of 23.8 ± 3.0 J/(mol·K) estimated in this manner is somewhat larger than the estimate based upon the chemical composition of our sample, but the two values are in agreement within the estimated errors.

Ballet and Coey (1982) have studied the magnetic properties of 2:1 layer-silicate minerals, including a high-Fe biotite that may be an adequate model for our natural annite sample studied here. Ballet and Coey (1982) have reported susceptibility, magnetization, and Mössbauer results for biotite of the composition $(K_{0.94})Mg_{0.10}Fe^{2+}_{2.08}Fe^{3+}_{0.32}Al_{0.10}Ti_{0.10}\,[Si_{2.82}Al_{1.18}O_{10}](OH)_2$. Both the susceptibility and Mössbauer results suggest that high-Fe biotite undergoes an antiferromagnetic transition at about 7 K. The Mössbauer spectra at 4.2 and 1.6 K were virtually identical, suggesting that there were no additional sources of magnetic entropy that arise from transitions below about 5 K. Below 7 K, high-Fe biotite has an ordered magnetic structure in which the Fe ions in the octahedral sheets are ferromagnetically coupled with the magnetic moments lying in the sheets, and the successive octahedral sheets are coupled antiferromagnetically. The inverse susceptibility data deviate from a Curie-Weiss law below 100 K. This suggests that above 100 K, the magnetic exchange interactions that align the magnetic moments of neighboring Fe ions are weak (i.e., most of the long-range magnetic ordering is developed below 100 K and consequently, most of the magnetic entropy would be developed by about 100 K).

Beausoleil et al. (1983) have studied the magnetic properties of eight biotite samples with compositions that ranged from high Mg to high Fe. They have shown that the Néel temperature decreases as the Fe content of the octahedral layer decreases in trioctahedral biotite and that the theoretical percolation concentration (the minimum concentration of magnetic cations required to develop magnetic order at low temperatures) is 33% for trioctahedral layers and 50% for dioctahedral layers. Based upon the findings of Beausoleil et al. (1983), the Néel temperature for the annite sample studied here would be about 5 K. However, the low occupancy of blocking cations in the octahedral layer in the annite would allow greater development of super-exchange interactions and, consequently, a higher Néel temperature than predicted from the data of Beausoleil et al. (1983).

TABLE 3. Experimental superambient molar heat capacities for natural annite

Temp. (K)	Heat capacity [J/(mol·K)]	Temp. (K)	Heat capacity [J/(mol·K)]	Temp. (K)	Heat capacity [J/(mol·K)]
Series 1		**Series 2**		**Series 3**	
339.3	384.8	468.6	444.9	468.6	448.0
349.3	391.1	478.6	447.7	478.6	450.7
359.2	396.1	488.5	449.4	488.5	452.8
369.2	401.0	498.5	452.4	498.5	451.8
379.2	406.0	508.5	455.4	508.5	454.9
389.1	411.0	518.4	457.0	518.4	455.9
399.1	415.2	528.4	459.5	528.4	458.9
409.1	419.2	538.3	460.6	538.3	460.9
419.0	422.0	548.3	461.3	548.3	461.7
429.0	427.5	558.3	466.2	558.3	464.5
439.0	430.0	568.2	468.5	568.2	466.5
448.9	433.0	578.2	469.5	578.2	469.3
458.9	436.2	588.2	469.0	588.2	471.0
468.9	440.3	598.1	472.4	598.1	472.1
478.8	446.2	608.1	475.8	608.1	475.7
488.8	450.8	618.1	478.3	618.1	480.3
497.8	545.9	628.0	481.7	628.0	483.0
		638.0	487.2	638.0	491.0
		647.0	490.5	647.0	497.4

The results presented by Ballet and Coey (1982) and Beausoleil et al. (1983) are consistent with the model presented above and support a conclusion that the experimental heat capacities reported here fully account for the magnetic contributions of the transition elements in the annite sample.

HIGH-TEMPERATURE HEAT CAPACITIES AND THERMODYNAMIC FUNCTIONS

Heat capacities were measured from near room temperature to about 650 K using differential scanning calorimetry. Heat-capacity measurements were terminated at about 650 K because small quantities of volatiles escaping from the annite sample caused a baseline shift in the calorimeter that resulted in the calculation of spurious heat-capacity values. The experimental heat-capacity values are listed in Table 3.

Estimates of the heat capacity of annite were made for the temperature interval 700 to 1000 K using a pseudo-corresponding-states model based upon the heat capacities of phlogopite, $KMg_3[AlSi_3O_{10}](OH_{1.22}F_{0.78})$, given by Robie and Hemingway (1984). The ratio of the specific

TABLE 4. Molar thermodynamic properties of natural annite

Temp. T (K)	Heat capacity C_P° [J/(mol·K)]	Entropy $S_T^\circ - S_0^\circ$ [J/(mol·K)]	Enthalpy function $(H_T^\circ - H_0^\circ)/T$ [J/(mol·K)]	Gibbs energy function $-(G_T^\circ - H_0^\circ)/T$ [J/(mol·K)]
298.15	357.8	373.6	0.000	373.6
300	359.2	375.8	2.211	373.6
400	414.8	487.5	99.030	388.5
500	450.4	584.1	165.96	418.1
600	476.7	668.7	215.65	453.0
700	497.9	743.8	254.50	489.3
800	515.9	811.5	286.08	525.4
900	531.8	873.2	312.51	560.7
1000	546.2	929.9	335.17	594.8

Note: The entropy values include the addition of a zero-point entropy of 18.7 J/(mol·K).

heats of Mg-Fe analogue pairs (forsterite-fayalite, geikielite-ilmenite, pichromite-chromite, and magnesium orthotitanate–titanomagnetite) were plotted for the temperature interval 300 to 1200 K. Each curve showed a maximum in the specific heat ratio with the temperature of the maximum decreasing from 850 to 450 K as the ratio of the formula weights of the pure-Fe phase to the pure-Mg phase decreased. Heat-capacity values for annite were estimated from a curve constructed from the phlogopite data and the experimental annite data (to 600 K) and an extrapolation consistent with the shape of the Fe-Mg analogue pairs.

The experimental high-temperature heat capacities were combined with the estimated heat capacities for the temperature interval of 700 to 1000 K and with low-temperature heat capacities for temperatures greater than 250 K, and the combined data set was fit with an equation of the form suggested by Haas and Fisher (1976). The equation [C_P° in J/(mol·K)]

$$C_P^\circ = 583.586 + 0.075246T - 3420.60T^{-0.5} - (4.4551 \times 10^6)T^{-2} \quad (1)$$

fit the data set with an average deviation of 0.37%.

Smoothed values of the thermodynamic properties of annite derived from Equation 1, the calorimetric entropy at 298.15 K of 354.9 J/(mol·K), and a zero-point entropy of 18.7 J/(mol·K) are listed in Table 4 for the interval 298.15 to 1000 K. A zero-point entropy of 18.7 J/(mol·K) has been added as suggested by Ulbrich and Waldbaum (1976) for Al-Si disorder in the tetrahedral sites. This should be considered a minimum value for the configurational entropy of annite. Dyar et al. (1985) and Dyar and Burns (1986) have shown evidence that some Fe^{3+} substitutes for Al^{3+} in tetrahedral sites, even in high-Al annites. In addition, some disorder may be expected in the octahedral sites. Ulbrich and Waldbaum (1976) provided a good discussion of the calculation of a zero-point entropy.

CONCLUSION

Heat capacities measured for a natural annite (aluminous iron biotite) extend our knowledge of the heat capacities and thermodynamic properties of sheet silicates. The calorimetric entropy for the natural annite is 354.9 ± 0.7 J/(mol·K) at 298.15 K. Assuming the tetrahedral sites to be fully disordered between Al and Si yields a minimum configurational (i.e., zero-point) entropy of 18.7 J/(mol·K). Additional disorder may be expected from Fe^{3+} substitution for Al^{3+} in the tetrahedral sites and from substitutions in the octahedral sites.

Natural iron biotites appear to have a large number of their available octahedral sites unoccupied and to have a Fe^{2+} content of less than 2.3 atoms in the three octahedral sites (Foster et al., 1963) in contrast to synthetic iron biotites (Eugster and Wones, 1962, and Rutherford, 1973). The amount of trioctahedral-dioctahedral solid solution can have a significant effect on the stability of iron biotites. Further work including phase equilibrium and/or emf studies and heat-capacity measurements on natural and synthetic iron and aluminous iron biotites will be required to define this dependence. Because most phase-equilibrium experiments have utilized synthetic samples that have occupancies closer to the ideal than those found in natural samples, it is particularly important to determine the effects of these differences on the heat capacity and other thermodynamic properties.

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REFERENCES CITED

Ballet, O., and Coey, J.M.D. (1982) Magnetic properties of sheet silicates: 2:1 layer minerals. Physics and Chemistry of Minerals, 8, 218–229.

Beausoleil, N., Lavallée, P., Yelon, A., Ballet, O., and Coey, J.M.D. (1983) Magnetic properties of biotite micas. Journal of Applied Physics, 54, 906–915.

Commission on Atomic Weights. (1976) Atomic weights of the elements. Pure and Applied Chemistry, 47, 75–95.

Dyar, M.D., and Burns, R.B. (1986) Mössbauer spectral study of ferruginous one-layer trioctahedral micas. American Mineralogist, 71, 955–965.

Dyar, M.D., Burns, R.G., and Rossman, G.R. (1985) Is there tetrahedral Fe^{3+} in biotite? Geological Society of America Abstracts with Programs, 17, 571.

Eugster, H.P., and Wones, D.R. (1962) Stability relations of the ferruginous biotite, annite. Journal of Petrology, 3, 82–125.

Foster, M.D., Wones, D.R., and Eugster, H.P. (1963) The atomic ratios of natural ferruginous biotites with reference to "The stability relations of the ferruginous biotite, annite." Journal of Petrology, 4, 302–306.

Gopal, E.S.R. (1966) Specific heats at low temperatures. Plenum, New York.

Haas, J.L., Jr., and Fisher, J.R. (1976) Simultaneous evaluation and correlation of thermodynamic data. American Journal of Science, 276, 525–545.

Hemingway, B.S., and Robie, R.A. (1984) Heat capacity and thermodynamic functions for gehlenite and staurolite: With comments on the Schottky anomaly in the heat capacity of staurolite. American Mineralogist, 69, 307–318.

Hemingway, B.S., Krupka, K.M., and Robie, R.A. (1981) Heat capacities of the alkali feldspars between 350 and 1000 K from differential scanning calorimetry, the thermodynamic functions of the alkali feldspars from 298.15 to 1400 K, and the reaction quartz + jadeite = analbite. American Mineralogist, 66, 1205–1215.

Hemingway, B.S., Robie R.A., Kittrick, J.A., Grew, E.S., Nelen, J.A., and London, D. (1984) The heat capacities of osumilite from 298.15 to 1000 K, the thermodynamic properties of two natural chlorites to 500 K, and the thermodynamic properties of petalite to 1800 K. American Mineralogist, 69, 701–710.

Krupka, K.M., Robie, R.A., and Hemingway, B.S. (1979) High-temperature heat capacities of corundum, periclase, anorthite, $CaAl_2Si_2O_8$ glass, muscovite, pyrophyllite, $KAlSi_3O_8$ glass, grossular and $NaAlSi_3O_8$ glass. American Mineralogist, 64, 86–101.

Robie, R.A., and Hemingway, B.S. (1972) Calorimeters for heat of solution and low-temperature heat capacity measurements. U.S. Geological Survey Professional Paper 755.

——— (1984) Heat capacities and entropies of phlogopite ($KMg_3[AlSi_3O_{10}](OH)_2$) and paragonite ($NaAl_2[AlSi_3O_{10}](OH)_2$) between 5 and 900 K and estimates of the enthalpies and Gibbs free energies of formation. American Mineralogist, 69, 858–868.

Robie, R.A., and Stout, J.W. (1963) Heat capacity from 12 to 305 K and entropy of talc and tremolite. Journal of Physical Chemistry, 67, 2252–2256.

Robie, R.A., Hemingway, B.S., and Wilson, W.H. (1976) The heat capacities of Calorimetry Conference copper and of muscovite $KAl_2(AlSi_3)O_{10}(OH)_2$, pyrophyllite $Al_2Si_4O_{10}(OH)_2$, and illite $K_3(Al_7Mg)(Si_{14}Al_2)O_{40}(OH)_8$ between 15 and 375 K and their standard entropies at 298.15 K. U.S. Geological Survey Journal of Research, 4, 631–644.

——— (1978) Low-temperature heat capacities and entropies of feldspar glasses and of anorthite. American Mineralogist, 63, 109–123.

Robie, R.A., Hemingway, B.S., and Takei, H. (1982) Heat capacities and entropies of Mg_2SiO_4, Mn_2SiO_4, and Co_2SiO_4 between 5 and 380 K. American Mineralogist, 67, 470–482.

Rutherford, M.J. (1973) The phase relations of aluminous iron biotites in the system $KAlSi_3O_8$-$KAlSiO_4$-Al_2O_3-Fe-O-H. Journal of Petrology, 14, 158–180.

Ulbrich, H.H., and Waldbaum, D.R. (1976) Structural and other contributions to the third-law entropies of silicates. Geochimica et Cosmochimica Acta, 40, 1–24.

Wanek, A.A., and Barclay, C.S.V. (1966) Geology of the northwest quarter of the Anaconda quadrangle, Deer Lodge County, Montana. In Contributions to Economic Geology 1965. U.S. Geological Survey Bulletin 1222, B18–B20.

Wones, D.R., and Eugster, H.P. (1965) Stability of biotite: Experiment, theory and application. American Mineralogist, 50, 1228–1272.

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