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SHORT COMMUNICATIONS

Low-Temperature Thermodynamic Properties of Natural Biotite

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INTRODUCTION

Biotite is a phyllosilicate widespread in various geologic environments, which indicates its origin within a wide range of temperatures, pressures, and acidity–alkalinity of mineral-forming media. In terms of composition, biotites are complex trioctahedral micas with extensive isovalent and heterovalent isomorphic substitutions. The former are mainly represented by the substitution of Fe^{2+} and Mn^{2+} for Mg and Fe^{3+} for Al, and heterovalent substitutions occur mainly via the schemes $(Mg, Fe)^{2+} + Si \longrightarrow 2Al$ and $2(Fe, Mg)^{2+} \longrightarrow Si$ (with aluminum redistribution between the tetrahedral and octahedral positions). Biotites occupy an intermediate position between the end members of the phlogopite–siderophyllite–annite solid solution series.

The composition of biotite from igneous and metamorphic rocks reflects the chemical characteristics of the rocks and the P-T-fO_2 conditions of their formation. Among the most important parameters of biotites are their total iron content, degree of oxidation, aluminum content, and alkali/aluminum ratio. Many authors showed that these parameters can be used for the characterization of the conditions of mica formation. Knowledge of the thermodynamic data for iron-bearing biotites of a certain composition with the known ratios of Fe^{2+}/Fe^{3+} and Fe/Al together with experimental phase equilibrium data may help determine the conditions of formation of metamorphic and igneous rocks enriched in ferriferous biotite.

Experimental data on the low-temperature thermodynamic properties of biotites are very limited. Hemingway and Robie [1] calorimetrically investigated the heat capacity of Al–Fe biotite between 7 and 650 K and presented its thermodynamic properties up to 1000 K. The composition of biotite was determined by these authors using an electron microprobe; therefore, the Fe^{2+}/Fe^{3+} ratio was not constrained and only the total iron content was reported (22.40%). The lithium content was also not measured. The biotite sample used in [1] showed a very high alumina content (about 20%), and, according to the modern mica classification [2, 3], it is siderophyllite, an aluminous iron-rich mica with a trioctahedral structure. Previously [4], we studied the thermodynamic properties of natural iron-rich biotite–annite within the temperature range 5.6–303 K and calculated its thermodynamic functions under standard conditions and within 0–300 K. In our opinion, it is interesting to perform a similar investigation of low-temperature thermodynamic properties for Mg–Fe biotite, compare the obtained results with the data for iron-rich biotite–annite, and consider the influence of the composition on the thermodynamic properties of biotites.

SAMPLE CHARACTERISTICS

A fine-grained scaly biotite sample from a porphyroblastic amphibole–biotite rock of the Katuginskoe rare-metal deposit (Northern Transbaikalia, Russia) was used in our study. The complete chemical analysis of the sample was performed by G.P. Sinyugina (chemical laboratory of the Fedorovskii All-Russia Institute of Mineral Resources), and trace components (Li, Pb, and Cs) were determined by flame photometry at the spectral laboratory of the same institute. The biotite contains 21.90% FeO and 8.96% MgO (Table 1) and is compositionally an intermediate member of the annite–phlogopite series, i.e., magnesium–iron biotite. The crystal chemical formula of the biotite calculated for a cation charge of 22 is $(K_{0.90}Na_{0.03}Rb_{0.01})(Li_{0.19}Fe^{2+}_{1.38}Mg_{1.01}Mn_{0.03}Al_{0.03}Fe^{3+}_{0.08}Ti_{0.17})[Si_{3.01}Al_{0.99}O_{10}][F_{0.96}(OH_{0.84})O_{0.10}]$, and its molecular mass is 460.101 g/mol. A characteristic feature of the biotite is the presence of lithium in the octahedral layer and a rather high fluorine content. Its structure was investigated by the X-ray diffraction (Fedorovskii All-Russia Institute of Mineral Resources) and electron diffraction methods (Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences). It was found that the

Table 1. Chemical composition of the biotite sample, wt %

Component	Biotite
SiO_2	39.87
TiO_2	2.95
Al_2O_3	11.44
Fe_2O_3	1.47
FeO	21.90
MnO	0.41
MgO	8.96
CaO	–
Na_2O	0.20
K_2O	9.33
Rb_2O	0.24
Cs_2O	0.003
Li_2O	0.63
F	4.00
H_2O^+	1.66
H_2O^-	–
Total	103.06
$–O=F_2$	1.68
Total	101.38

biotite belongs to the 1 M polytype. Its unit-cell parameters are typical of biotite: a = 5.31 Å, b = 9.20 Å, c = 10.1 Å, β = 100°.

The preliminary treatment and preparation of samples included crushing, quartering, and purification by elutriation, which proved to be rather efficient owing to the good flotation capacity of micas. The obtained mica concentrate was examined and additionally purified by hand-picking under a binocular microscope.

EXPERIMENTAL RESULTS AND DISCUSSION

The heat capacity of biotite was measured on the same automated calorimetric set-up that was used for the measurement of annite [5] within the temperature range 5.7–300.4 K. The mass of the sample loaded into a calorimetric ampoule was 3.4094 g. The experimental data on the heat capacity of biotite are given in Table 2. The smoothed values of the heat capacity and thermodynamic functions at selected temperatures calculated on the basis of the $C_p^\circ(T)$ dependency are listed in Table 3. The reported uncertainties in the thermodynamic functions at standard temperature were estimated taking into account the results of control measurements of the heat capacity of a standard substance and the chemical analysis of the sample.

Table 2. Experimental $C_p^\circ(T)$ values of biotite, J/K mol

T, K	$C_p^\circ(T)$	T, K	$C_p^\circ(T)$	T, K	$C_p^\circ(T)$	T, K	$C_p^\circ(T)$
5.71	2.424	15.44	8.909	64.87	75.64	172.70	235.4
6.64	2.991	16.38	9.765	69.88	83.72	180.65	244.7
6.78	3.085	17.03	10.32	74.85	91.65	188.62	253.6
6.87	3.137	17.79	10.98	79.83	99.95	196.54	261.9
7.72	3.650	18.61	11.83	82.22	103.6	204.42	270.0
7.83	3.730	19.53	12.73	87.22	112.2	212.34	277.9
8.00	3.819	20.18	13.51	92.28	120.4	220.31	285.1
8.80	4.307	21.30	14.68	97.35	128.8	228.26	292.8
8.92	4.385	23.25	16.91	102.35	136.9	236.19	299.7
9.89	5.064	25.33	19.32	107.39	145.0	244.11	306.3
9.99	5.032	27.40	21.79	112.47	152.9	252.02	312.6
10.92	5.611	29.48	24.49	117.50	160.8	260.14	319.8
11.07	5.676	31.57	27.30	122.52	168.4	268.32	325.3
11.97	6.281	34.18	30.78	127.47	175.6	276.31	331.0
12.18	6.439	37.34	35.02	132.39	182.8	284.34	336.6
13.03	7.062	40.46	39.16	137.35	189.8	292.40	342.2
13.25	7.301	44.06	44.34	142.35	196.8	297.04	344.9
14.08	7.848	50.16	53.07	148.86	205.5	300.01	346.9
14.30	7.952	54.71	59.71	156.82	215.9	300.39	347.4
15.34	8.797	59.78	67.53	164.76	225.8	–	–

Table 3. Heat capacity and thermodynamic functions of biotite. $C_p^\circ(T)$, $S^\circ(T)$, and $\Phi^\circ(T)$ are in J/K mol; and the $H^v(T) - H^v(0)$ values are in J/mol

T, K	$C_p^\circ(T)$	$S^\circ(T)$	$H^\circ(T) - H^\circ(0)$	$\Phi^\circ(T)$*	T, K	$C_p^\circ(T)$	$S^\circ(T)$	$H^\circ(T) - H^0(0)$	$\Phi^\circ(T)$*
5.71	2.426	0.8053	3.449	0.2013	100	133.0	96.08	5685	39.22
10	5.050	2.830	19.47	0.8825	120	164.5	123.1	8664	50.94
15	8.560	5.507	53.08	1.968	140	193.5	150.7	12250	63.22
20	13.26	8.584	107.1	3.228	160	219.9	178.3	16390	75.88
25	18.92	12.14	187.3	4.647	180	243.9	205.6	21030	88.79
30	25.17	16.13	297.3	6.223	200	265.5	232.4	26130	101.8
35	31.79	20.51	439.6	7.947	220	285.1	258.7	31640	114.9
40	38.60	25.20	615.6	9.807	240	302.9	284.3	37520	127.9
45	45.61	30.15	826.0	11.79	260	319.0	309.2	43740	140.9
50	52.83	35.32	1072	13.88	280	333.6	333.3	50270	153.8
60	67.93	46.28	1675	18.36	300	347.3	356.8	57080	166.6
70	83.82	57.93	2433	23.17	300.39	347.6	357.3	57210	166.8
80	100.1	70.19	3353	28.28	298.15	346.1 ± 0.5	354.7 ± 0.5	56440 ± 80	165.4 ± 0.4
90	116.6	82.93	4437	33.64					

* $\Phi^0(T) = S^0(T) - S^0(0) - [H^0(T) - H^0(0)]/T$.

The heat capacity, calorimetric entropy, enthalpy difference, and reduced Gibbs potential of the Fe–Mg biotite at 298.15 K are 346 ± 0.5 J/K mol, 354.7 ± 0.5 J/K mol, 56440 ± 80 J/mol, and 165.4 ± 0.4 J/K mol, respectively.

The $C_p^\circ(T)$ dependency of biotite (Fig. 1) is a smooth S-shaped curve without any apparent anomalies. Figure 1 also shows published data [1] for Al–Fe biotite and our previous measurements of the $C_p^\circ(T)$ dependency of iron-rich annite [4] within the range 5–30 K. A comparison of the obtained experimental data with the results of [1] showed good agreement between the two $C_p^\circ(T)$ dependencies. They intersect at 100 K; our curve passes below that of [1] above this temperature, and the difference increases gradually up to 3.5% at 290 K. Below 100 K, the maximum discrepancy is 5% at 25 K. The curves are practically identical at 10–15 K but diverge abruptly below 10 K owing to an anomaly on the $C_p^\circ(T)$ curve detected by Hemingway and Robie [1]. It can be seen from Fig. 1 that the annite studied in [1] has to be in fact considered as biotite, because the data of [1] are in good agreement with our data for biotite (above 10 K) and significantly different from our $C_p^\circ(T)$ dependency for annite. It should be noted that practically identical values of the calorimetric entropy of biotite at 298.15 K were obtained in this study and in [1] (354.7 and 354.9 J/K mol, respectively). However, this coincidence has to be considered

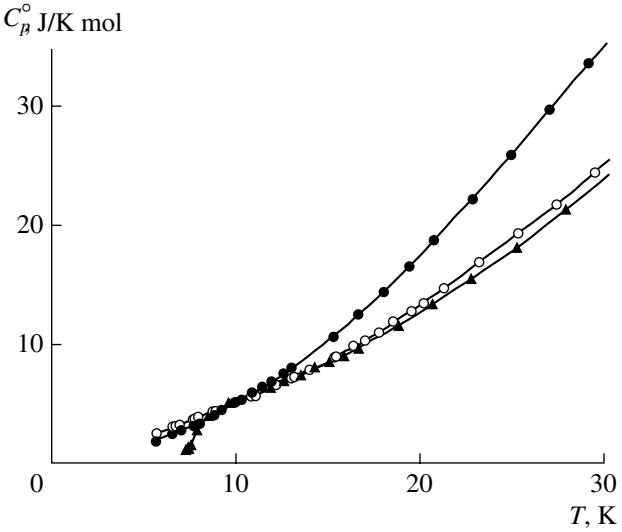

Fig. 1. The $C_p^\circ(T)$ dependency of biotite and annite at low temperatures. The filled circles show annite; the open circles, biotite; and the triangles, data of [1].

Table 4. Heat capacity and entropy at 298.15 K of biotites of various compositions*

Biotite	ΣFe, wt %	FeO, wt %	C_p°, J/K mol	S°, J/K mol	Reference
Mg–Fe biotite	23.37	21.90	346.1 ± 0.5	354.7 ± 0.5	This study
Annite (Fe-biotite)	37.61	32.69	360.5 ± 0.5	391.2 ± 0.5	[2]
Al–Fe biotite	22.40	–	357.8 ± 0.7	354.9 ± 0.7	[1]

* The complete chemical analyses of biotites are given in [1] and [2].

accidental. It is related to the fact that the $C_p^\circ(T)$ dependencies obtained in the two studies intersect at 100 K.

Similar to annite, biotite has a layer structure. Therefore it could be expected that the $C_p^\circ(T^2)$ dependency would be linear at the lowest temperatures in agreement with the theoretical studies of Tarasov [6] and Lifshitz [7]. However, this is not the case. Figure 2 shows $C_p^\circ(T^2)$ curves for biotite and annite studied by us previously [4]. It can be seen that the dependency for biotite shows an inflection below 10 K. This inflection can also be detected in the $C_p^\circ(T)$ dependency by analyzing the first derivative of the heat capacity with respect to temperature. A possible reason for such a behavior of the $C_p^\circ(T^2)$ of biotite is that the compositions of annite and biotite are significantly different in magnesium and ferrous iron contents. This, in principle, can lead to a certain distortion of the structure of the double silicate layer and, as a consequence, a change in the behavior of $C_p^\circ(T^2)$ at the lowest temperatures.

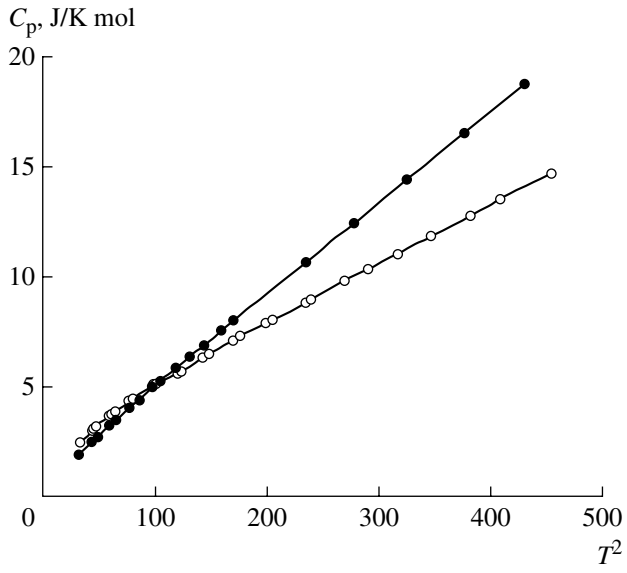

Fig. 2. The $C_p(T^2)$ dependency of biotite (open circles) and annite (filled circles).

A comparison of the obtained experimental data on the heat capacity and entropy at 298.15 K of Fe–Mg biotite with our previous results for ferroan biotite–annite and available data on Al–Fe biotite from the literature is shown in Table 4. As can be seen from Table 4 and Fig. 1, an increase in the ferrous iron content in the octahedral layer of biotite results in an increase in the heat capacity and thermodynamic functions. The data of Table 4 can be used to estimate the heat capacity and entropy of biotites with varying iron content, which is important for the thermodynamic modeling of mineral-forming processes occurring in the presence of iron-bearing micas.

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