

SHORT  
COMMUNICATIONS

## Low-Temperature Heat Capacity and Thermodynamic Properties of Natural Annite

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### INTRODUCTION

Annite is an iron-rich trioctahedral mica close in composition to the hypothetical end-member  $\text{KFe}_3^{2+}[\text{Si}_3\text{AlO}_{10}](\text{OH})_2$ . Annite with an ideal composition is known only as a synthetic compound. Natural annites may approach the theoretical composition. Their  $\text{Fe}^{2+}$  content is about 2.0–2.5 per formula unit (28–36 wt % FeO), and  $\text{Fe}^{3+}$  is up to 0.5 per formula unit. The synthesis experiments of Eugster [1] showed that the stability of annite is a function of temperature, total pressure, and, especially, oxygen fugacity. The knowledge of the thermodynamic properties of annite and other ferriferous biotites with known  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and Fe/Al ratios together with phase equilibrium experimental data may help elucidate the conditions for the formation of metamorphic and magmatic rocks containing abundant ferriferous biotites.

There is little experimental evidence for the thermodynamics of annite. The only available data were reported by Hemingway and Robie [2], who measured the heat capacity of natural annite (Al–Fe biotite) from 7 to 650 K by the methods of adiabatic and differential scanning calorimetry, calculated its calorimetric entropy at 298.15 K ( $354.9 \pm 0.7$  J/K mol), and provided its thermodynamic properties up to 1000 K. Since the biotite sample was analyzed by these authors with an electron microprobe, its  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio was not determined and only the total iron content (22.40%) was reported; the concentration of lithium is also unknown. According to the modern nomenclature of micas [3, 4], the sample studied by Hemingway and Robie [2] is too poor in ferrous iron to match the annite composition (natural annite usually contains 32–38% FeO), and the high alumina content of this sample (about 20%) allows its classification as siderophyllite, a trioctahedral high-alumina ferrous mica, rather than annite.

This paper presents the results of measurements of the low-temperature heat capacity of natural annite

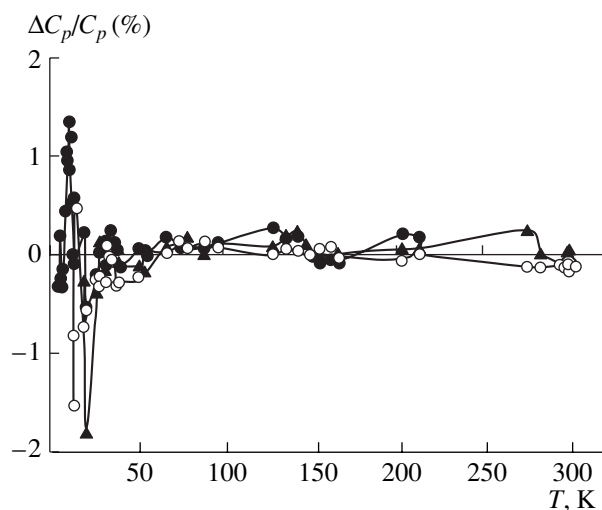
obtained by adiabatic calorimetry in the temperature range 5–300 K; these results were used to calculate the calorimetric entropy of annite at 298.15 K and its thermodynamic functions at 5–300 K.

### SAMPLE CHARACTERISTICS

The investigation was carried out using samples of fine-scaled annite from a riebeckite–annite alkaline metasomatic rock from the Katuginskoe rare-metal deposit (northern Transbaikalia, Russia). Its chemical composition (Table 1) was analyzed by

**Table 1.** Chemical composition of the annite sample (wt %)

| Component               | Annite |
|-------------------------|--------|
| $\text{SiO}_2$          | 36.00  |
| $\text{TiO}_2$          | 2.10   |
| $\text{Al}_2\text{O}_3$ | 10.08  |
| $\text{Fe}_2\text{O}_3$ | 4.92   |
| FeO                     | 32.69  |
| MnO                     | 0.82   |
| MgO                     | 0.12   |
| CaO                     | –      |
| $\text{Na}_2\text{O}$   | 0.16   |
| $\text{K}_2\text{O}$    | 8.30   |
| $\text{Rb}_2\text{O}$   | 0.47   |
| $\text{Cs}_2\text{O}$   | <0.001 |
| $\text{Li}_2\text{O}$   | 0.53   |
| F                       | 3.40   |
| $\text{H}_2\text{O}^+$  | 2.30   |
| $\text{H}_2\text{O}^-$  | –      |
| Total                   | 101.89 |
| –O=F <sub>2</sub>       | 1.43   |
| Total                   | 100.46 |



**Fig. 1.** Deviation of the results of heat capacity measurements for benzoic acid from the smoothed values obtained in previous studies [6–8]. Filled circles—[6], unfilled circles—[7], and triangles—[8].

G.P. Sinyugina (Fedorovskii All-Russia Institute of Mineral Resources), and trace elements (Li, Rb, and Cs) were determined by flame photometry at the Fedorovskii All-Russia Institute of Mineral Resources. The following crystal chemical formula was calculated on the basis of a cation charge of 22:  $(K_{0.87}Na_{0.03}Rb_{0.02})(Li_{0.18}Fe_{2.25}^{2+}Mg_{0.02}Mn_{0.06}Fe_{0.26}^{3+}Ti_{0.13})[Si_{2.97}Al_{0.98}Fe_{0.05}^{3+}O_{10}](F_{0.89}(OH)_{1.11})$ , and its molecular

mass is 496.279 g/mol. This ferroan biotite contains 32.69% FeO and corresponds to the composition of typical natural annite; characteristic features of its composition are the presence of lithium in the octahedral layer and a minor ferric iron substitution for aluminum in the tetrahedral position. The structure was studied by X-ray (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 shown that the annite is the 1*M* polytype. Its unit-cell parameters are typical for annite:  $a = 5.34 \text{ \AA}$ ,  $b = 9.24 \text{ \AA}$ ,  $c = 10.2 \text{ \AA}$ , and  $\beta = 100^\circ$ . The preliminary treatment and preparation of the sample included crushing, quartering, and refinement by elutriation. The separated mica concentrate was examined and additionally purified by hand-picking under a binocular microscope.

## METHODS OF MEASUREMENTS

The heat capacity of annite was determined using an automated vacuum adiabatic calorimeter. The calorimetric set-up and measurement techniques are described in detail elsewhere [5]. A sample was loaded into a silver-coated copper capsule with a volume of 6 cm<sup>3</sup> and a mass of 20.4 g, similar to that described in [5]. Heat capacity was automatically measured within the temperature range 6–300 K. In order to improve heat exchange between the sample and the capsule, it was filled with helium gas at a pressure of 30 mm Hg ( $1.3 \times 10^3 \text{ Pa}$ ). The heat capacity of the empty calorimetric capsule was measured in 69 points within a temperature range of 5.7–304.3 K. The accuracy of the measure-

**Table 2.** Experimental values of the  $C_p$  of annite, J/(K mol)

| $T, K$ | $C_p$ | $T, K$ | $C_p$ | $T, K$ | $C_p$ | $T, K$ | $C_p$ |
|--------|-------|--------|-------|--------|-------|--------|-------|
| 5.65   | 1.826 | 19.38  | 16.27 | 79.10  | 114.9 | 193.79 | 272.4 |
| 6.60   | 2.386 | 20.73  | 18.46 | 85.04  | 124.6 | 203.61 | 282.5 |
| 7.01   | 2.650 | 22.82  | 21.94 | 85.61  | 125.5 | 213.48 | 292.3 |
| 7.73   | 3.142 | 24.90  | 25.61 | 90.57  | 133.6 | 223.42 | 301.8 |
| 8.05   | 3.370 | 27.01  | 29.31 | 95.54  | 141.6 | 233.41 | 310.7 |
| 8.79   | 3.946 | 29.15  | 33.23 | 100.49 | 149.5 | 243.40 | 319.3 |
| 9.24   | 4.298 | 31.27  | 37.10 | 105.45 | 157.3 | 253.24 | 327.4 |
| 9.87   | 4.855 | 33.85  | 41.92 | 110.42 | 164.9 | 263.09 | 335.1 |
| 10.27  | 5.177 | 36.93  | 47.33 | 116.59 | 174.2 | 272.96 | 342.6 |
| 10.92  | 5.744 | 40.14  | 52.76 | 123.95 | 185.1 | 282.79 | 349.7 |
| 11.47  | 6.265 | 43.84  | 58.84 | 131.35 | 195.7 | 292.64 | 356.6 |
| 11.97  | 6.715 | 47.90  | 65.33 | 138.80 | 206.1 | 299.70 | 361.7 |
| 12.62  | 7.395 | 51.93  | 71.73 | 148.09 | 218.5 | 302.53 | 363.3 |
| 13.02  | 7.839 | 55.98  | 78.06 | 155.50 | 228.1 | 302.64 | 363.7 |
| 15.32  | 10.51 | 61.10  | 86.08 | 164.20 | 238.8 | –      | –     |
| 16.67  | 12.24 | 67.18  | 95.79 | 174.06 | 250.6 | –      | –     |
| 18.02  | 14.17 | 73.16  | 105.3 | 183.91 | 261.7 | –      | –     |

ment was checked by determining the heat capacity of the benzoic acid standard in 53 point within the temperature range 5.8–308 K. High-purity benzoic acid (K-1 grade, heat of combustion of 26 432.5 J/g) was obtained for these measurements from the Mendeleev Research Institute of Metrology, St. Petersburg. The mass of the benzoic acid sample was 4.063 g. The obtained results were compared with the accurate data of [6], accepted as a standard of the USSR and the more recent measurements by Moriya et al. [7] and Sorai et al. [8]. Figure 1 shows deviations of the obtained experimental values for the heat capacity of benzoic acid from the smoothed  $C_p(T)$  values reported by these authors. The average difference was 0.6% with a maximum of 1.5% within the range 5–15 K, 0.3 and 1.8% between 15 and 40 K, and 0.1 and 0.3% between 40 and 300 K. Taking into account that the mass of our benzoic acid sample was much smaller than that used in the above-cited studies, it can be concluded that our results are in good agreement with reliable data from the literature.

### EXPERIMENT AND DISCUSSION

The heat capacity of annite was measured in the temperature range 5.6–302.6 K. The mass of the sample loaded into the calorimetric capsule was 6.0103 g. The experimental data for the heat capacity of annite are given in Table 2. The smoothed values of heat capacity and thermodynamic functions at selected temperature values, calculated on the basis of the  $C_p(T)$  dependency, are shown in Table 3. The reported errors of thermodynamic functions at standard temperature were estimated taking into account the results of control measurements of the heat capacity of the standard substance and the chemical analysis of the sample.

The  $C_p(T)$  dependency of annite is a smooth S-shaped curve. Figure 2 shows our results together with the data of Hemingway [2]. The maximum difference is ~40% at 50 K, decreasing to ~1% at room temperature.

Since the structure of annite is a network of three layers (2 : 1) consisting of interconnected Si–Al tetrahedra linked by cations lying in a common plane and having an octahedral coordination, it could be expected that these structural features would be manifested at the lowest temperatures. According to the Debye theory of the isotropic continuum, heat capacity decreases at very low temperatures following the cubic law  $C_p(T) \sim T^3$ . In the case of strong anisotropy, when interaction within a layer is much higher than interaction between layers, the heat capacity must be proportional to the square of temperature,  $C_p(T) \sim T^2$ , which was theoretically demonstrated by Tarasov [9] and Lifshitz [10]. Figure 3 shows  $C_p$  against the square of temperature. It can be seen that the quadratic dependency is maintained at  $T < 12$  K.

The  $C_p(T)$  curve of annite (Fig. 2) displays a slight upward concavity at temperatures of 20–40 K, which is

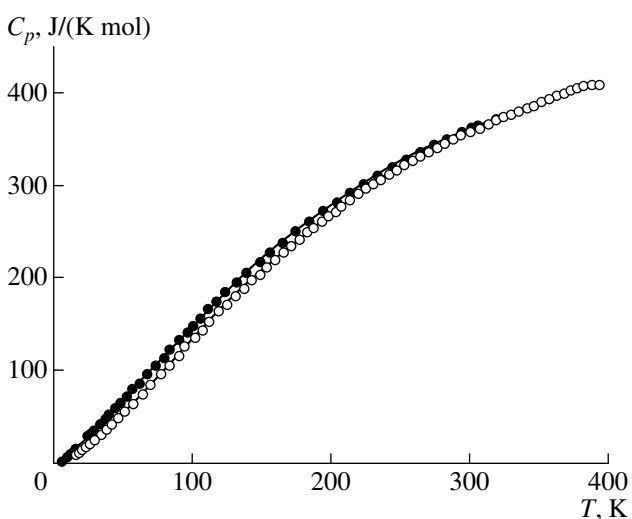


Fig. 2. Heat capacity of annite as a function of temperature according to our results (filled circles) and data of [2] (unfilled circles).

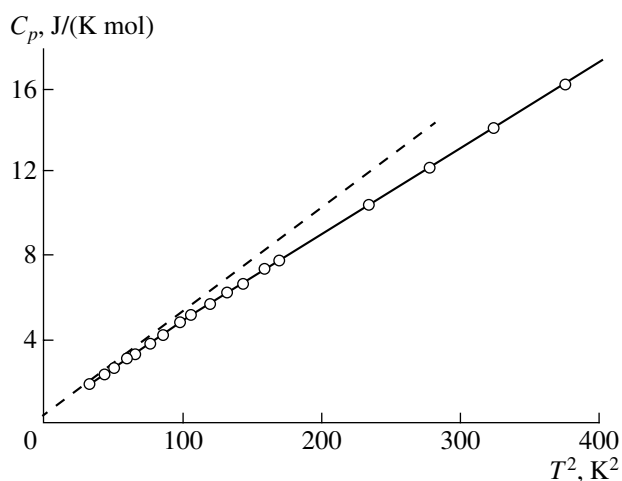


Fig. 3. Heat capacity of annite as a function of  $T^2$ .

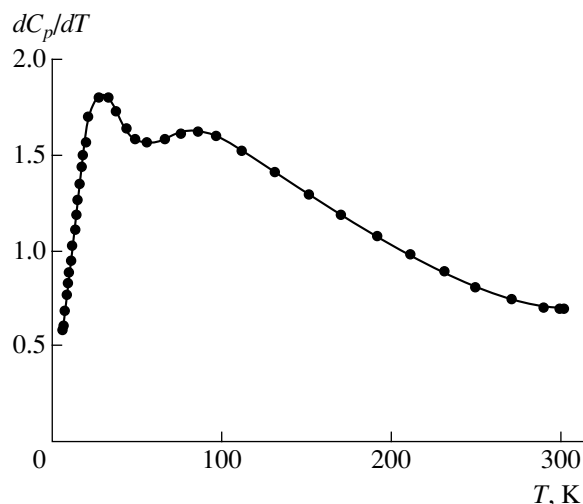


Fig. 4. Derivative of the heat capacity of annite as a function of temperature.

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

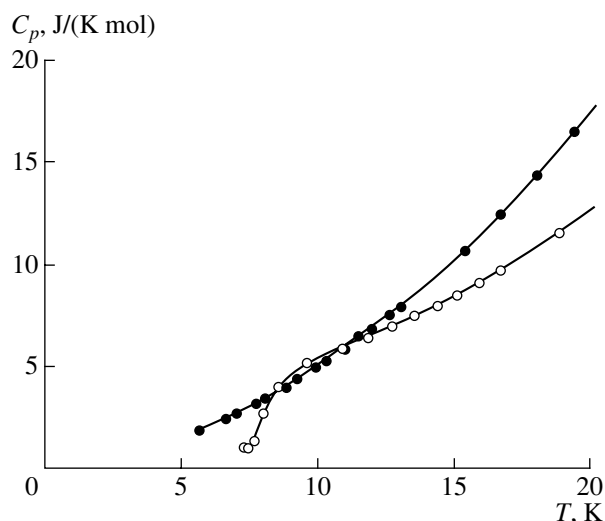
| $T, K$ | $C_p^\circ(T)$ | $S^\circ(T)$ | $H^\circ(T)-H^\circ(0)$ | $\Phi^\circ(T)$ |
|--------|----------------|--------------|-------------------------|-----------------|
| 5.655  | 1.819          | 0.572        | 2.42                    | 0.144           |
| 10     | 4.942          | 2.354        | 16.64                   | 0.690           |
| 15     | 10.11          | 5.270        | 53.45                   | 1.706           |
| 20     | 17.24          | 9.110        | 121.1                   | 3.057           |
| 25     | 25.74          | 13.85        | 228.2                   | 4.728           |
| 30     | 34.78          | 19.34        | 379.3                   | 6.698           |
| 35     | 43.82          | 25.39        | 575.9                   | 8.930           |
| 40     | 52.47          | 31.81        | 816.8                   | 11.39           |
| 45     | 60.72          | 38.47        | 1100                    | 14.02           |
| 50     | 68.71          | 45.28        | 1424                    | 16.81           |
| 60     | 84.43          | 59.20        | 2189                    | 22.71           |
| 70     | 100.3          | 73.40        | 3113                    | 28.93           |
| 80     | 116.4          | 87.84        | 4196                    | 35.39           |
| 90     | 132.6          | 102.5        | 5441                    | 42.03           |
| 100    | 148.6          | 117.3        | 6848                    | 48.82           |
| 120    | 179.3          | 147.1        | 10130                   | 62.71           |
| 140    | 207.7          | 176.9        | 14000                   | 76.91           |
| 160    | 233.7          | 206.4        | 18420                   | 91.26           |
| 180    | 257.3          | 235.3        | 23340                   | 105.7           |
| 200    | 278.9          | 263.6        | 28700                   | 120.0           |
| 220    | 298.5          | 291.1        | 34480                   | 134.3           |
| 240    | 316.4          | 317.8        | 40630                   | 148.5           |
| 260    | 332.7          | 343.8        | 47120                   | 162.6           |
| 280    | 347.6          | 369.0        | 53930                   | 176.4           |
| 300    | 361.8          | 393.5        | 61030                   | 190.1           |
| 302.64 | 363.7          | 396.7        | 61980                   | 191.9           |
| 298.15 | 360.5 ± 0.5    | 391.2 ± 0.5  | 60360 ± 80              | 188.8 ± 0.5     |

supported by the temperature dependence of the derivative of heat capacity. In the case of an ordinary regular  $C_p(T)$  curve, the initial increase of  $dC_p/dT$  is followed by a decrease after the inflection point of the heat capacity curve. Thus, the  $dC_p/dT(T)$  curve must display one broad maximum.

Figure 4 shows the derivative of heat capacity as a function of temperature,  $dC_p/dT(T)$ , obtained from the experimental data for the  $C_p(T)$  of annite. The additional maximum of the derivative indicates an anomaly in heat capacity superimposed upon its regular variations. Hemingway [2] studied annite (ferroan aluminous biotite) of a somewhat different composition and observed a slight heat capacity anomaly near 10 K, which can be considered as a Schottky anomaly related to the splitting of the spin states of transition elements in the crystal field and/or antiferromagnetic ordering. Beausoleil et al. [11] studied the magnetic properties of biotites of various compositions and detected a consid-

erable anomaly in magnetic susceptibility related to an antiferromagnetic transition at 7 K in a biotite containing 27.6% of iron, which is similar to the composition of our sample. In our study a smooth and monotonous  $C_p(T)$  dependency was obtained at these temperatures (Fig. 5).

It is conceivable that variations in the thermodynamic and magnetic properties of annites can be related not only to different contents of paramagnetic ions, such as iron and manganese, but also to the presence of titanium and, especially, lithium, which strongly affects the optic, thermal, and other properties of micas. The peculiar properties of lithium-bearing micas are related to the small charge and size of the lithium cation, which is coupled mainly with ferrous iron and occupies octahedra of the 2 : 1 layers following a near trioctahedral law. The proportions of the fractions of various octahedral cations control the unit-cell parameters, other structural and chemical characteristics, and polytypic



**Fig. 5.** Low-temperature  $C_p(T)$  of annite according to our results (filled circles) and data of [2] (unfilled circles).

features of lithium-bearing micas [12]. It is known that the magnetic characteristics of minerals depend also on the presence of various volume and surface imperfections and dislocations in the crystal lattice. Additional investigations of the low-temperature magnetic properties of annite are required to clarify the nature of the anomalies detected at very low temperatures by Hemingway and Robie [2] and in our study.

#### ACKNOWLEDGMENTS

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