

SHORT
COMMUNICATIONS

Thermochemical Study of Natural Phengite

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INTRODUCTION

Phengite, $K(Mg,Fe)_{0.5}Al_{1.5}[Si_{3.5}Al_{0.5}O_{10}](OH)_2$, is a dioctahedral mica intermediate between muscovite and aluminoceladonite in the nomenclature of [1]. Divalent cations, mainly Mg^{2+} and Fe^{2+} , substitute for Al in the octahedral sites of phengite. Since the total number of octahedral cations in the mineral remains two per formula unit, the content of tetrahedrally coordinated aluminum also decreases. Therefore, compared with normal muscovite, phengite is enriched both in Mg and Fe^{2+} (no more than 0.5 atoms per formula unit) and Si. Phengite occurs as a major rock-forming mineral mainly in metamorphic and hydrothermal metasomatic rocks. It was speculated that its composition can be used as an indicator of the P – T conditions of metamorphism.

The thermochemical properties of this mineral were previously never investigated, and there is no thermodynamic data in the literature.

This paper reports the first experimental determination of the enthalpy of formation of natural phengite by high-temperature melt solution calorimetry, measurements of high-temperature enthalpy increment, and an equation for the temperature dependence of heat capacity.

SAMPLE CHARACTERISTICS

A sample of natural phengite from the Southern Urals, Russia was used for investigations. Its chemical analysis (Table 1) was carried out on a Camebax SX 50 electron microprobe at the mineralogy Department of the Division of Geology, Moscow State University. Since this method yields only total iron, the contents of ferric and ferrous iron were determined by the microchemical method at the Fedorovskii All-Russia Institute of Mineral Resources. Water content was measured by thermal analysis on a Derivatograph Q-1500D thermogravimeter and from the results of sample annealing at $T = 950$ – 1000°C .

The crystal chemical formula calculated for a charge of 22 is $(K_{0.78}Na_{0.07})(Mg_{0.41}Fe_{0.09}^{2+})(Al_{1.53}Ti_{0.02}Fe_{0.02}^{3+})[Si_{3.39}Al_{0.61}O_{10}]F_{0.03}(OH)_{1.97}$ (molecular weight 396.194). All the thermodynamic parameters obtained in this study were calculated to this phengite formula.

EXPERIMENTAL PROCEDURE

The thermochemical investigation of the phengite was carried out on a Setaram high-temperature Tian–Calvet microcalorimeter [2]. The enthalpy of formation was determined by melt solution calorimetry. A sample with a weight of 3–10 ($\pm 2 \times 10^{-3}$) mg was thermostated at room temperature and dropped into $2PbO \cdot B_2O_3$

Table 1. Chemical composition of the phengite

Component	wt %
SiO ₂	51.49
TiO ₂	0.48
Al ₂ O ₃	27.59
Cr ₂ O ₃	0.02
Fe ₂ O ₃	0.39
FeO	1.58
MnO	0.02
MgO	4.20
CaO	0.01
Na ₂ O	0.53
K ₂ O	9.29
H ₂ O ⁺	4.50
H ₂ O [–]	0.90
F	0.14
Σ	101.14
–O=F ₂	0.06
Σ	101.08

Table 2. Experimental data on the enthalpy increment $H^0(T) - H^0(298.15 \text{ K})$ of natural phengite (molecular weight of 396.184 g/mol) obtained in this study

T, K	J/g	kJ/mol
444	127.7 ± 2.6 (6)*	50.6 ± 1.1
508	186.7 ± 7.32 (6)	74.0 ± 2.9
565	239.0 ± 9.3 (8)	94.7 ± 3.7
733	424.3 ± 14.7 (7)	168.1 ± 5.8
833	548.5 ± 7.6 (6)	217.3 ± 3.0
920	648.4 ± 15.4 (6)	256.9 ± 6.1
973	740.4 ± 10.2 (5)	293.4 ± 4.1

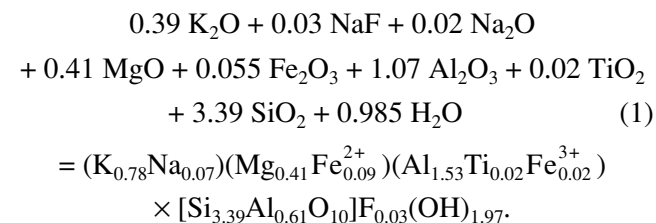
* Errors correspond to a confidence level of 95%, and numerals in parentheses show the number of measurements.

melt-solvent occurring in the calorimeter at $T = 973 \text{ K}$. The sum of the enthalpy increment of the sample and the heat of its solution, $H^0(973 \text{ K}) - H^0(298.15 \text{ K}) + \Delta_{\text{soln}}H^0(973 \text{ K})$, was measured. The experimental measurement of the enthalpy increment of phengite, $H^0(973 \text{ K}) - H^0(298.15 \text{ K})$, at $T = 444, 508, 565, 733, 833, 920$, and 972 K was conducted by dropping samples with weights of 3–10 mg into the calorimeter without melt. In order to eliminate a small amount of adsorbed water, the samples were heated before the experiments at a temperature of 150°C . The calorimeter was calibrated by dropping standard substances: platinum (in dissolution experiments) and corundum α - Al_2O_3 (for measurement of enthalpy increment), and the necessary thermochemical data for them were adopted from [3].

The experimental calorimetric data are given in Tables 2 and 3. Table 4 presents the enthalpies of solution and enthalpies of constituent oxides and sodium fluoride necessary for the calculation of the enthalpy of formation of phengite as well as the enthalpies of their formation from the elements.

RESULTS

Using the experimental results (Table 3) and necessary thermochemical data for oxides and sodium fluoride (Table 4), the standard enthalpies of formation of phengite from the corresponding oxides and fluoride [reaction (1)] and from the elements were calculated.



The calculations were performed using the equation

$$\Delta_f H_{\text{el}}^0(298.15 \text{ K}) \text{ phengite} = \sum v_i [H^0(973 \text{ K})$$

Table 3. Experimental data on the $[H^0(973 \text{ K}) - H^0(298.15 \text{ K}) + \Delta_{\text{soln}}H^0(973 \text{ K})]$ of natural phengite (molecular weight of 396.184 g/mol) obtained in this study

Sample weight, mg	J/g	kJ/mol
12.611	1249.65	495.10
6.419	1213.69	480.86
14.380	1205.77	477.72
11.074	1254.99	497.22
5.287	1201.01	475.83
3.485	1204.95	477.39
		Average: 484.0 ± 10.1

Table 4. Thermochemical data used for the calculation of the enthalpy of formation of phengite, kJ/mol

Substance	$[H^0(973 \text{ K}) - H^0(298.15 \text{ K}) + \Delta_{\text{soln}}H^0(973 \text{ K})]$	$-\Delta_f H_{\text{el}}^0(298.15 \text{ K})$
$\text{Na}_2\text{O}(\text{cr})$	-111.8 ± 0.8^a	414.8 ± 0.3^b
$\text{K}_2\text{O}(\text{cr})$	-193.7 ± 1.1^a	363.2 ± 2.1^b
$\text{MgO}(\text{cr})$	36.38 ± 0.59^c	601.6 ± 0.3^b
$\text{Fe}_2\text{O}_3(\text{cr})$	171.6 ± 1.9^d	826.2 ± 1.3^b
$\text{Al}_2\text{O}_3(\text{corundum})$	107.38 ± 0.59^e	1675.7 ± 1.3^b
$\text{SiO}_2(\text{quartz})$	39.43 ± 0.21^f	910.7 ± 1.0^b
$\text{TiO}_2(\text{rutile})$	54.4 ± 1.5^g	944.0 ± 0.8^b
$\text{NaF}(\text{cr})$	92.72 ± 0.79^h	573.6 ± 0.7^b
$\text{H}_2\text{O}(\text{liq})$	40.9 ± 2.5^i	285.8 ± 0.1^b

^a After [4]; ^b after [3]; ^{c-f} calculated using published reference data on $[H^0(973 \text{ K}) - H^0(298.15 \text{ K})]$ [3] and experimental values of $\Delta_{\text{soln}}H^0(973 \text{ K})$ after ^c [5], ^d [6], ^e [7], ^f [2], ^g [8], ^h [9], and ⁱ estimate of [10].

$$\begin{aligned}
 & - H^0(298.15 \text{ K}) + \Delta_{\text{soln}}H^0(973 \text{ K})] \text{ component} \\
 & - [H^0(973 \text{ K}) - H^0(298.15 \text{ K}) \quad (2) \\
 & + \Delta_{\text{soln}}H^0(973 \text{ K})] \text{ phengite} \\
 & + \sum v_i \Delta_f H_{\text{el}}^0(298.15 \text{ K}) \text{ component,}
 \end{aligned}$$

where v_i are the stoichiometric coefficients in Eq. (1). It was assumed that all the iron in the phengite is ferric. The obtained value for the enthalpy of formation of the natural phengite from the elements is $-5885 \pm 11 \text{ kJ/mol}$.

Using the experimental enthalpy increment data, the following equations were obtained for the temperature dependencies of the heat capacity and enthalpy increment of the phengite:

$$C_p^0 = 79.04 + 497.26 \times 10^{-3}T$$

$$+ 109.86 \times 10^5 T^{-2} \text{ J/K mol} \quad (3)$$

(maximum approximation error of $\pm 0.9\%$)

$$H^0(973 \text{ K}) - H^0(298.15 \text{ K}) \\ = 79.04T + 248.63 \times 10^{-3} T^2 \quad (4)$$

$$- 109.86 \times 10^5 T^{-1} - 8820 \text{ J/mol.}$$

The first thermodynamic data obtained for natural phengite in our study can be used for the estimation of the physicochemical parameters of mineral formation processes with the participation of phengite.

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