

SHORT COMMUNICATIONS

Thermochemical Study Mg–Fe Amphiboles

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Abstract—The paper presents data on the thermochemical study (high-temperature melt calorimetry in a Tian–Calvet microcalorimeter) of two natural Mg–Fe amphiboles: anthophyllite $\text{Mg}_{2.0}(\text{Mg}_{4.8}\text{Fe}_{0.2}^{2+})[\text{Si}_{8.0}\text{O}_{22}](\text{OH})_2$ from Kukh-i-Lal, southwestern Pamirs, Tajikistan, and gedrite $\text{Na}_{0.4}\text{Mg}_{2.0}(\text{Mg}_{1.7}\text{Fe}_{0.2}^{2+}\text{Al}_{1.3})[\text{Si}_{6.3}\text{Al}_{1.7}\text{O}_{22}](\text{OH})_2$ from the Kola Peninsula, Russia. The enthalpy of formation from elements is obtained as -12021 ± 20 kJ/mol for anthophyllite and as -11545 ± 12 kJ/mol for gedrite. The standard entropy, enthalpy, and Gibbs energy of formation are evaluated for Mg–Fe amphiboles of theoretical composition.

Keywords: Tian–Calvet microcalorimeter, enthalpy of formation, amphibole, anthophyllite, gedrite

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INTRODUCTION

Fe–Mg amphiboles are found as rock-forming minerals in metamorphic rocks of diverse composition that were formed within broad ranges of P – T parameters. Mg–Fe amphiboles are orthorhombic and monoclinic minerals, with the former more often found in natural rocks. Amphiboles of anthophyllite–ferroanthophyllite and gedrite–ferrogedrite isomorphic series crystallize in the orthorhombic system; amphiboles of gedrite series are formed in rocks high in alumina.

The only currently available experimental determination of the enthalpy of formation of natural anthophyllite was made by the acid (HF) calorimetry technique (Weeks, 1956). This value was later recalculated using newly obtained data on the dissolution heat of the composing oxides (Hemingway, 1991) and is reported in the widely known reference book (Robie and Hemingway, 1995). Other available data on the enthalpy and Gibbs energy of formation of anthophyllite were calculated from equilibria involving this amphibole (Zen, 1976; Chernosky, 1979) and were obtained using various simulation techniques (Day et al., 1985; Valero et al., 2012). Thermodynamic data on anthophyllite and ferroanthophyllite published in (Holland and Powell, 1998, 2011) were also calculated from mineral equilibria. Only rough estimates are currently available for the enthalpy and Gibbs energy of formation of gedrite (Valero et al., 2012).

Our study was aimed at experimental determination of the enthalpy of formation of natural Fe–Mg

amphibole (anthophyllite and gedrite) by high-temperature melt solution calorimetry.

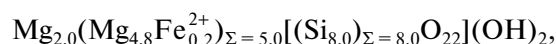
EXPERIMENTAL

Samples. The samples used in this study were natural Fe–Mg amphiboles: anthophyllite from Kukh-i-Lal in the southwestern Pamirs, Tajikistan, and gedrite from the Kola Peninsula, Russia. The anthophyllite sample consisted of colorless long-prismatic crystals up to 3–5 cm long, and the gedrite composed large (3–4 cm) long-prismatic dark green crystals. The samples were analyzed on a Camebax SX-50 (Cameca, France) microprobe using the $K\alpha$ lines of elements and the following standards: sodalite for Na, KTiPO_5 for K, hornblende for Mg and Al, tremolite for Ca and Si, and hedenbergite for Fe. The accelerating voltage was 15 kV, and the beam current was 30 nA. The composition of the amphiboles is reported in Table 1, and their formulas, which were calculated by normalizing to 46 charges, are as follows:

anthophyllite



i.e., approximately



gedrite

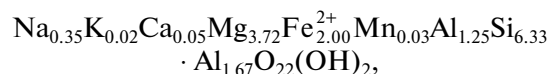
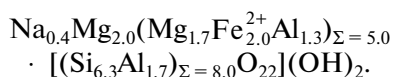


Table 1. Chemical composition (wt %) of the amphiboles

Oxide	Anthophyllite	Gedrite
SiO ₂	61.72	44.42
TiO ₂	n.d.	0.04
Al ₂ O ₃	0.63	17.33
FeO	1.30	16.82
MgO	34.98	17.50
MnO	n.d.	0.22
CaO	0.30	0.32
Na ₂ O	0.17	1.26
K ₂ O	0.01	0.09

i.e., approximately



The compositions of the minerals comply with those of anthophyllite and gedrite in the modern systematics (Hawthorne et al., 2012).

The **X-ray powder diffraction (XRD) identification** of the minerals was carried out in a STOE-STADI MP (Germany) diffractometer equipped with a focusing Ge(111) monochromator to ensure strictly monochromatic $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$). The data were acquired by successively covering scanning regions using a position-sensitive linear detector with $2\theta = 5^\circ$ and a channel width of 0.02° . Based on the XRD data and according to the ICDD (2013) database of X-ray powder diffraction patterns, the minerals were identified as anthophyllite and gedrite. Their unit cell parameters (Table 2) were calculated with the WinXPow (2002) STOE & Cie GmbH (<https://www.stoe.com>) program package, using two algorithms: Verner's (Treor) and Louër's (Picvol). The results are consistent with data in RRUFF (R070245.9 and R050339.1) (<http://rruff.info>) and MINCRYST (nos. 258 and 1708) (<http://database.iem.ac.ru/mincryst/rus/>).

The **IR spectroscopy study** of the amphiboles was performed on FSM-1201 (LOMO, Russia) Fourier spectrometer in the region of 400 to 4000 cm^{-1} , with frequencies determined accurate to $\pm 1 \text{ cm}^{-1}$ in transmission mode at room temperature in air. The samples were prepared as suspension in paraffin oil. The IR absorption spectra of the samples can be subdivided

into four regions: $400\text{--}625 \text{ cm}^{-1}$ (region I), $625\text{--}820 \text{ cm}^{-1}$ (region II), $820\text{--}1300 \text{ cm}^{-1}$ (region III), and $3500\text{--}3800 \text{ cm}^{-1}$ (region IV). Region I comprises the absorption bands of translation vibrations of octahedrally coordinated cations (Mg^{2+} , Fe^{2+} , and Al^{3+}). Bands in region II correspond to O–Si(Al)–O and Si(Al)–O–Si(Al) deformation vibrations and librational vibrations of the OH group. The widening of the bands and the poorer resolution of the gedrite spectrum in this region is explained by accommodation of the Al cation on the tetrahedrally coordinated sites (figure). Region III is covered by a broad absorption band of six overlapping bands corresponding to symmetric and asymmetric valence vibrations of Si(Al)–O bonds in chained tetrahedrons. Spectral region IV encompasses bands corresponding to the valence vibrations of the OH group coordinated by various combinations of octahedrally coordinated cations (Mg^{2+} , Fe^{2+} , and Al^{3+}). According to their IR absorption spectra, the amphiboles were identified as anthophyllite and gedrite according to data in (Stănescu-Dumitru, 2008; Chukanov, 2014).

The **thermochemical study** of the amphiboles was carried out by melt solution calorimetry in a high-temperature Tian–Calvet microcalorimeter (Setaram, France), using a thermochemical cycle involving dissolution of the mineral and its components (oxides and hydroxides). In our experiments, samples $3\text{--}11 (\pm 2 \times 10^{-3}) \text{ mg}$ were dropped from room temperature into solvent melt of the composition $2\text{PbO} \times \text{B}_2\text{O}_3$ in the calorimeter at a temperature $T = 973 \text{ K}$, and the increase in the enthalpy of the mineral and its dissolution enthalpy [$H^0(973 \text{ K}) - H^0(298.15 \text{ K}) + \Delta_{\text{diss}}H^0(973 \text{ K})$] were measured together. If $30\text{--}35 \text{ g}$ of solvent was used and $6\text{--}8$ dissolution experiments were conducted, the ratio of the dissolved mineral to melt can be regarded as that of infinitely dilute solution, whose mixing enthalpy is zero. The calibration was conducted using the increase in the enthalpy of a standard reference material (Pt), with required thermochemical data on it compiled from (Robie and Hemingway, 1995). Our experimental data on the dissolution enthalpy of the amphiboles are summarized in Table 3.

DISCUSSION

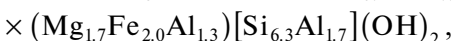
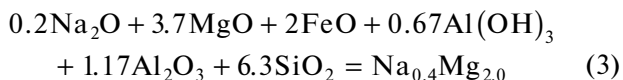
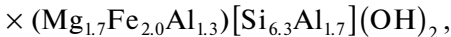
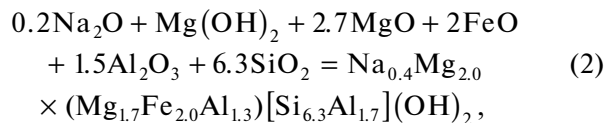
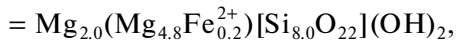
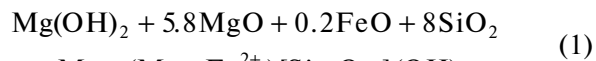
Enthalpy of formation of natural Fe–Mg amphiboles. The standard enthalpy of formation of the

Table 2. Unit cell parameters, molar volume, and density of the Mg–Fe amphiboles

Amphibole	$a, \text{ \AA}$	$b, \text{ \AA}$	$c, \text{ \AA}$	$\alpha = \beta = \gamma, ^\circ$	$V, \text{ \AA}^3$	$V_m^0(298.15 \text{ K}), \text{ cm}^3/\text{mol}^*$	$\rho, \text{ g/cm}^3$
Anthophyllite	18.558	17.931	5.046	90.0	1679.1	252.8	3.11
Gedrite	18.544	17.946	5.283	90.0	1758.1	264.7	3.23

* Calculated by the formula $V_m^0(298.15 \text{ K}) = abcN_A/Z$, where $Z = 4$ and N_A is the Avogadro number.

amphiboles from elements were calculated from our experimental calorimetric data on the dissolution of the minerals (Table 2) according to reactions (1), (2), and (3) and Eqs. (4) and (5)



$$\Delta_{\text{reactions (1)–(3)}} H^0(298.15 \text{ K}) \\ = \sum v_i \Delta H_{\text{component}_i} - \Delta H_{\text{amphibole}}, \quad (4)$$

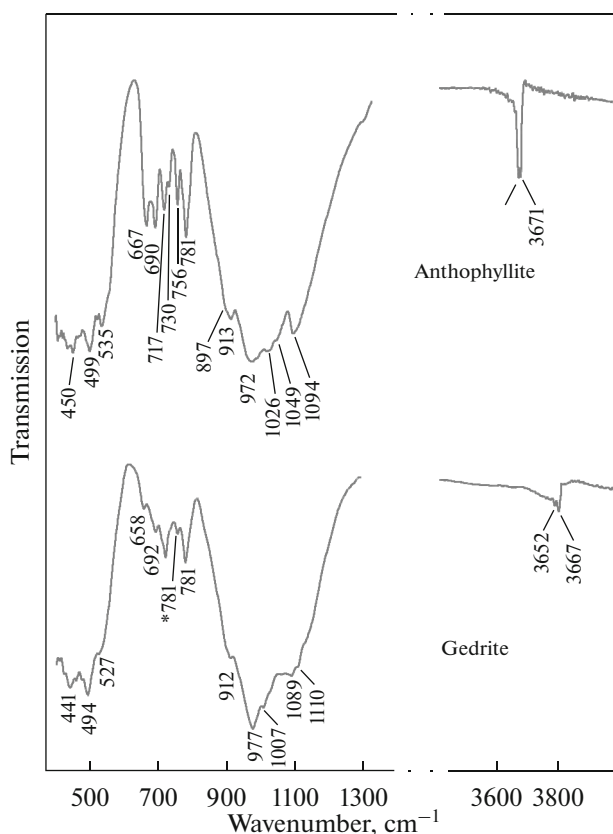
$$\Delta_f H^0(298.15 \text{ K})_{\text{amphibole}} \\ = \Delta_{\text{reactions (1)–(3)}} H^0(298.15 \text{ K}) \quad (5)$$

$$+ \sum v_i \Delta_f H^0(298.15 \text{ K})_{\text{component}_i},$$

where v_i are stoichiometric coefficients in Eqs. (1), (2), and (3); $\Delta H = H^0(973 \text{ K}) - H^0(298.15 \text{ K}) + \Delta_{\text{diss}} H^0(973 \text{ K})$ is thermochemical data on the minerals (Table 3), pertinent oxides, Al and Mg hydroxides (Table 4); the enthalpies of formation $\Delta_f H^0(298.15 \text{ K})$ of components of the reactions required for the calculations are also reported in Table 4. The enthalpy of mixing for infinitely diluted solution is close to zero. We assumed that all Fe occurs in the minerals in the form of Fe^{3+} (the calculations were carried out with data on hematite in Table 4). The enthalpies of formation calculated from the foregoing reactions are reported in Table 5.

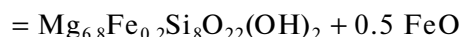
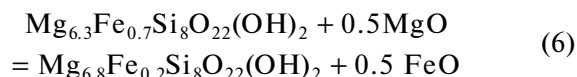
Gibbs free energies of natural Fe–Mg amphiboles.

The values of the standard entropy $S^0(298.15 \text{ K})$ needed to calculate the Gibbs free energies were evaluated from reactions (6) and (7) and the entropy of Fe-bearing anthophyllite of the composition $\text{Mg}_{6.3}\text{Fe}_{0.7}\text{Si}_8\text{O}_{22}(\text{OH})_2$ ($S^0(298.15 \text{ K}) = 554.2 \pm 3.0 \text{ J/K mol}$) (Hemingway, 1991) derived from the low-temperature heat capacity values.

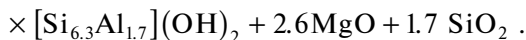
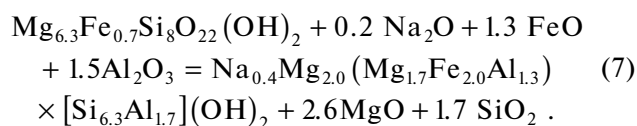


IR absorption spectra of the amphiboles. *Absorption band of paraffin oil.

For the anthophyllite,



and for the gedrite



The contribution to the entropy due to the differences in the amphibole compositions was calculated using a technique suggested in (Holland, 1989) to estimate the entropies of silicates. The quoted estimates of the ($S-V$) terms of oxides with regard for the coordina-

Table 3. Our calorimetric data on the dissolution of the amphiboles*

Sample	M , g/mol	$H^0(973 \text{ K}) - H^0(298.15 \text{ K}) + \Delta_{\text{diss}} H^0(973 \text{ K})$	
		J/g	kJ/mol
Anthophyllite	787.14	1135.9 ± 22.2 (6)	894.1 ± 17.5
Gedrite	854.71	715.3 ± 17.1 (7)	611.4 ± 14.6

* The errors were determined with 95% probability, the numeral in parentheses is the number of the measurements.

Table 4. Thermochemical data used to calculate the enthalpy of formation of the amphiboles (kJ/mol)

Component	ΔH^a	$-\Delta_f H^0(298.15 \text{ K})^b$
Al(OH) ₃ (gibbsite)	172.6 ± 1.9 ^c	1293.1 ± 1.2
Mg(OH) ₂ (brucite)	111.5 ± 1.6 ^d	924.5 ± 0.4
SiO ₂ (quartz)	39.43 ± 0.21 ^e	910.7 ± 1.0
Al ₂ O ₃ (corundum)	107.38 ± 0.59 ^f	1675.7 ± 1.3
Fe ₂ O ₃ (hematite)	171.6 ± 1.9 ^g	826.2 ± 1.3
MgO(periclase)	36.38 ± 0.59 ^h	601.6 ± 0.3
Na ₂ O(c.)	-111.8 ± 0.8 ⁱ	414.8 ± 0.3

^a The value of $\Delta H = [H^0(973 \text{ K}) - H^0(298.15 \text{ K}) + \Delta_{\text{diss}} H^0(973 \text{ K})]$. ^b Tabulated data from (Robie and Hemingway, 1995). ^c According to (Ogorodova et al., 2011). ^d According to (Kiseleva and Ogorodova, 1983). ^{e-h} Calculated using tabulated data on $[H^0(973 \text{ K}) - H^0(298.15 \text{ K})]$ (Robie and Hemingway, 1995) and experimental dissolution data $\Delta_{\text{diss}} H^0(973 \text{ K})$: ^e (Kiseleva et al., 1979), ^f Ogorodova et al., 2003), ^g (Kiseleva, 1976), ^h (Navrotsky and Coons, 1976). ⁱ According to (Kiseleva et al., 2001).

Table 5. Thermodynamic properties of the Mg–Fe amphiboles

Amphibole composition	<i>M</i> , g/mol	$-\Delta_f H^0(298.15 \text{ K})$, kJ/mol	$S^0(298.15 \text{ K})^a$, J/K mol	$-\Delta_f G^0(298.15 \text{ K})$, kJ/mol
Natural amphiboles				
Mg _{2.0} (Mg _{4.8} Fe _{0.2} ²⁺)[Si _{8.0} O ₂₂](OH) ₂ anthophyllite	787.14	12021 ± 20 ^b	546.7 ± 3.0	11298 ± 20
Na _{0.4} Mg _{2.0} (Mg _{1.7} Fe _{2.0} ²⁺ Al _{1.3})[(Si _{6.3} Al _{1.7})O ₂₂](OH) ₂ gedrite	854.71	11552 ± 17 ^b 11537 ± 16 ^c average: 11545 ± 12	574.1 ± 4.1	10824 ± 12
Amphiboles of theoretical composition				
Mg _{2.0} (Mg ₅)[Si _{8.0} O ₂₂](OH) ₂ anthophyllite	780.82	12061 ± 20 ^b	543.7 ± 3.0	11337 ± 20
Mg _{2.0} (Mg ₃ Al ₂)[Si ₆ Al ₂ O ₂₂](OH) ₂ gedrite	783.97	11999 ± 15 ^b 11984 ± 15 ^c average: 11992 ± 11	528.8 ± 3.4	11261 ± 11
Mg _{2.0} (MgFe _{2.0} ²⁺ Al ₂)[Si ₆ Al ₂ O ₂₂](OH) ₂ Fe-gedrite	847.06	11568 ± 16 ^b 11554 ± 16 ^c average: 11561 ± 11	558.8 ± 4.0	10842 ± 11

^a Calculated based on data on $S^0(298.15 \text{ K})$ of natural anthophyllite (Hemingway, 1991). ^b Calculated from the reaction involving Mg hydroxide. ^c Calculated from the reaction involving Al hydroxide.

tion of the corresponding cation in the mineral were used in calculating by Eqs. (8) and (9)

$$S^0(29815 \text{ K})_{\text{anthophyllite}} = S^0(298.15 \text{ K}) \times \text{Mg}_{6.3}\text{Fe}_{0.7}\text{Si}_8\text{O}_{22}(\text{OH})_2 + 0.5(S-V)^{[6]} \text{MgO} \quad (8) \\ - 0.5(S-V)^{[6]} \text{FeO},$$

$$S^0(29815 \text{ K})_{\text{gedrite}} = S^0(298.15 \text{ K}) \times \text{Mg}_{6.3}\text{Fe}_{0.7}\text{Si}_8\text{O}_{22}(\text{OH})_2 + 0.2(S-V)\text{Na}_2\text{O} \\ + 1.3(S-V)^{[6]} \text{FeO} + 0.65(S-V)^{[6]} \text{Al}_2\text{O}_3 \quad (9) \\ + 0.85(S-V)^{[4]} \text{Al}_2\text{O}_3 - 2.6(S-V)^{[6]} \text{MgO} \\ - 1.7(S-V)^{[4]} \text{SiO}_2.$$

The obtained $S^0(29815 \text{ K})$ values of the amphiboles are reported in Table 4. Using these values, the values of $S^0(298.15 \text{ K})$ of the elements (Robie and Hemingway, 1995), and our enthalpy of formation values, we calculated $\Delta_f G^0(298.15 \text{ K})$ of the Mg–Fe amphiboles (Table 4).

Thermodynamic properties of the Mg–Fe amphiboles of theoretical composition. Based on our experimental data on the dissolution of the natural amphiboles, we have calculated the enthalpies of formation of the Mg–Fe amphiboles of theoretical composition: the end members and intermediate members of the anthophyllite–ferroanthophyllite and gedrite–ferrogedrite series. To do this, the results of our calorimetric measurements of the samples were recalculated

to the molecular weights of the minerals of theoretical composition. The values of $\Delta_f H^0(298.15 \text{ K})$ (Table 5) were calculated by Eqs. (1)–(5), and the standard entropy values of $S^0(298.15 \text{ K})$ (Table 5) of the amphiboles of theoretical composition were calculated analogously to those of the natural minerals (Eqs. (6)–(9)). The calculated enthalpy of formation of anthophyllite of theoretical composition (Table 5) is in good agreement with that presented in (Robie and Hemingway, 1995) ($-12070.0 \pm 8.0 \text{ kJ/mol}$), which was obtained in (Hemingway, 1991) by recalculating calorimetric data on anthophyllite dissolution in HF (Weeks, 1956). Our data on $\Delta_f G^0(298.15 \text{ K})$ are also in good agreement with results derived by studying anthophyllite equilibria: -11332 ± 17 (Zen and Chernosky, 1976), -11323.26 ± 5.35 (Chernosky and Autio, 1979) and -11342.22 kJ/mol (Holland and Powell, 1998).

The newly obtained thermodynamic data on the Mg–Fe amphiboles can be integrated into the database of thermodynamic properties of rock-forming minerals and can be utilized in the thermodynamic simulation of systems involving these minerals and also to refine currently used geothermometers and geobarometers.

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