Natural Mg-Fe clinochlores: Enthalpies of formation and dehydroxylation derived from calorimetric study

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ABSTRACT

This paper presents the results of the first experimental thermochemical investigation of two natural trioctahedral chlorites - clinochlores. The study was performed with the help of a high-temperature heat-flux Tian-Calvet microcalorimeter. The samples were characterized by X-ray spectroscopy analysis, X-ray powder diffraction, thermal analysis, FTIR spectroscopy. The enthalpies of formation of clinochlores were found using the melt solution calorimetry method to be: -8806 ± 16 kJ·mol⁻¹ for composition (Mg₄.⁹Fe²⁺₀.₃Al₀.₈)[Si₃.²Al₀.⁸O₁₀](OH)₈ and -8748 ± 24 kJ·mol⁻¹ for composition (Mg₄.⁴Fe²⁺₀.₆Al₁.₂)[Si₂.₈Al₁.₂O₁₀](OH)₈. The experimental data for natural samples allowed calculating the enthalpies of formation for end and intermediate members of the clinochlore (Mg₅Al)[Si₃AlO₁₀](OH)₈ - chamosite (Fe₅Al)[Si₃AlO₁₀](OH)₈ series. An important feature of the clinochlore structure is the presence of two distinct hydroxyl-containing octahedral layers: the interlayer octahedral sheet and octahedral 2:1 layer; enthalpies of water removal from these positions in clinochlore structure were determined as: 53 ± 20 kJ/(mol H₂O) and 131 ± 10 kJ/(mol H₂O), respectively. The obtained first thermodynamic characteristics of Mg-Fe clinochlores can be used for quantitative thermodynamic modeling of geological and industrial processes including clinochlores of different composition.

Keywords: Clinochlore, chlorite, thermochemistry, microcalorimetry, enthalpy of dehydroxylation, enthalpy of formation
INTRODUCTION

Clinochlore is a widespread magnesian chlorite, which is formed during the processes of hydrothermal-metasomatic and metamorphic changes of ultramafic and carbonate rocks; sometimes it is formed in the hydrothermally altered zones around ore bodies. Also this mineral occurs as a result of the hypergenic processes in modern sediments, in the weathering crust and in soils. Several exchange equilibria involving Mg-Fe clinochlores were proposed as geothermometers and geobarometers (Laird 1988). The currently used nomenclature (Bailey 1988; Guggenheim et al. 2006) recommends for clinochlore the following formula (R$^{2+}$,Al)$[Si_3AlO_{10}](OH)_8$, where R is dominant octahedral cation Mg$^{2+}$; in natural samples the isomorphic admixture of Fe$^{2+}$ in this position almost always presents.

The chlorite structure consists of three-layer packages of 2:1 type, which alternate with the octahedral interlayer hydroxide sheets. The minerals of this group have numerous polytypic modifications with different arrangements of the layers in the structure. An important feature of the chlorites structure is the presence of two distinct hydroxyl-containing octahedral layers (inside the 2:1 packages and between them) that distinguishes chlorites from other layered minerals. Villiéras et al. (1993, 1994) indicated that the first step of water removal through heating of a magnesian chlorite (dehydroxylation of interlayer octahedral sheet) leads to the formation of a microporous “modified chlorite structure”. Although this dehydroxylation process was explored with the help of various physicochemical methods in the works mentioned above, quantitative thermal characteristics of this process were not determined.

The available data on thermodynamic properties of clinochlores of different compositions are summarized in Table 1. These data were obtained mainly by using evaluations or calculations based on the phase equilibrium experiments. The results of calculations on the experimentally studied equilibria for clinochlore are given in the reference books and the bulletins on the thermodynamic characteristics of minerals (Robie and Hemingway 1995; Holland and Powell 1998, 2011). Several authors (Hemingway et al. 1984; Gailhanou et al. 2009) studied clinochlores with the different contents of ferrous using an adiabatic calorimetry method; for these substances the low-temperature heat capacities were measured and the values of standard entropies were calculated. The enthalpy of formation of the Fe-rich clinochlore was determined by means of acid solution calorimetry in the work of Gailhanou et al. (2007). Kittrick (1982) calculated the values of Gibbs energy of formation of two samples of the Mg-Fe clinochlores using the solubility data.
The values of the enthalpies of formation for clinochlore with theoretical composition differ significantly from each other. The data for iron-containing species of clinochlore relate to the different mineral compositions and therefore it is difficult to use them for modeling $P$-$T$ equilibria involving clinochlores and for building geothermometers and geobarometers. Thus, additional studies to clarify these data are necessary.

The purposes of this work were the experimental calorimetric determination of the enthalpies of formation for the natural Mg-Fe clinochlores, the thermochemical study of the dehydroxylation processes, and the measurement of the enthalpies of the removal of water from 2:1 layer and from the interlayer hydroxide sheet.

**SAMPLES AND METHODS**

We examined two samples of the clinochlores: from the Nicolae-Maximilian Mine (Southern Urals, Russia) (sample I) and from the Tarlashkinskii massiv (East Tuva, Russia) (sample II). The samples were presented as light green plates with the size up to 1-2 centimeters.

The chemical analysis of the minerals was carried out on a “Camebax SX-50” (Cameca, France) electron probe microanalyzer (EPMA) using the $K\alpha$ analytical line and the following reference substances: sodalite for Na, hornblende for Mg and Al, tremolite for Ca and Si, hedenbergite for Fe, nickel oxide (Cameca) for Ni, and spinel for Cr. All these substances were provided by A.E. Fersman Mineralogical Museum and were tested using standards provided by company “Cameca” (albite for Al, Na, Si; orthoclase for Al, K, Si; wollastonite for Ca; $\text{Cr}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ for Fe) using the “Camebax SX-50” and a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength dispersive spectrometer (Jeol, Japan). The calculated compositions of used reference substances corresponded to stoichiometric formulas. The mode of operation was as follows: accelerating voltage 15 kV; probe current 30 nA.

X-ray diffraction study was performed using a powder diffractometer Ultima-IV (Rigaku, Japan). The diffractometer was equipped with a CuK$_\alpha$ ($\lambda=1.54183$ Å) 3 kV radiation source and semiconductor detector of a new generation - DTex / Ultra, due to its use a high quality of experimental measurements was achieved in the range of 3.6° to 65°2θ with a step on the scan corner 0.02°2θ and with a rotation speed of 5°2θ/min. Mineral identification was performed by comparing the experimental spectra with the reference diffraction pattern of the database ICCD PDF-2 software package Jade 6.5 of company MDI. The unit cell parameters were refined by the Rietveld method (Post and Bish 1989) using BGMN program (www.bgmn.de).

IR spectroscopic examination was carried out using a Fourier-spectrometer “FSM 1201” (LOMO, Russia) with a resolution of 4 cm$^{-1}$ in the spectral range of 400-4000 cm$^{-1}$. The study was
carried out at an ambient air and room temperature. FTIR-spectra were recorded with the suspension of clinoclore powders in vaseline oil (Nujol) to avoid the adsorption of atmospheric water on the KBr pellets. The accuracy of the frequencies of the absorption bands was ± 2 cm⁻¹.

The thermal analysis of clinochlores was performed using a derivatograph “Q-1500 D” (MOM, Hungary) with 20°/min heating rate in the range from room temperature to 1000°C, the sample weights were 270-350 mg.

The thermochemical investigation of clinochlores was done using a high temperature heat-flux Tian-Calvet microcalorimeter (Setaram, France) by means of two experimental techniques. The enthalpies of formation were determined by melt solution calorimetry method using a thermochemical cycle, including the dissolution of the minerals and their constituent components (magnesium, iron, aluminum and silicon oxides, and magnesium hydroxide). The pieces of the minerals weighing 3-15 (±2×10⁻³) mg were dropped from room temperature into solvent-melt with composition: 2PbO.B₂O₃, located in a platinum crucible in the calorimeter at T = 973 K. The total effect including the heat absorption of the sample and its dissolution heat \([H^0(973 \text{ K}) - H^0(298.15 \text{ K}) + \Delta_{\text{sol}}H^0(973 \text{ K})]\) was measured. We used 30-35 grams of the solvent for 6-8 experiments; in this case the ratio of dissolved substance to solvent may be classified as an infinitely dilute solution for which the mixing enthalpy close to zero.

The determination of the enthalpy of the OH-groups removal was carried out by the "double drop" method. Initially the pieces of samples weighing 5-20 (±2×10⁻³) mg were dropped from room temperature (25°C) into an empty platinum crucible in the calorimeter at the temperature T = 973 K (700°C); the heat effect measured was a sum of the heat absorption of the sample and its dehydroxylation heat \([H^0(T) - H^0(298.15 \text{ K}) + \Delta_{\text{dehyd}}H^0(T)]\). Then the dehydroxylated sample was taken out from the calorimeter and was dropped again in the calorimeter at the same temperature; wherein the value of its heat absorption \([H^0(T) - H^0(298.15 \text{ K})]\) was measured. The water content in the substances was tested by weighing before and after the calorimetric experiments. The calibration of the calorimeter was performed by dropping pieces of the reference substances, platinum wire (in solution experiments) and corundum \(\alpha\)-Al₂O₃ (in the dehydroxylation experiments), and using their reference heat content data (Robie and Hemingway 1995).

All used equipment is located on the Geological Faculty of M.V. Lomonosov Moscow State University.

RESULTS AND DISCUSSION

Samples characterization
Chemical analysis. EPMA data for the investigated samples are given in the Table 2. The chemical formulas calculated for 28 charges have the forms: 

\[(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})[\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{10}(\text{OH})_8](\text{I})\text{ and } (\text{Mg}_{4.2}\text{Fe}^{2+}_{0.6}\text{Al}_{1.2})[\text{Si}_{2.8}\text{Al}_{1.2}\text{O}_{10}(\text{OH})_8](\text{II}).\] 

In accordance with the currently used nomenclature (Guggenheim et al. 2006) both minerals may be classified according to their composition as clinochlores.

X-ray diffraction study. XRD investigation of studied samples showed the diffraction patterns (Fig. 1) similar to the PDF № 07-0078. Positions of the non-basal reflexes and the ratio of their intensities showed that studied clinochlores belong to the IIb-polytype according to Drits and Kossovskaya (1991). The obtained values of the unit-cell parameters and the calculated values of the unit-cell volume and the molar volume of clinochlores are listed in Table 3.

FTIR spectroscopic research. IR spectroscopic results for the studied samples (Fig. 2) are similar to the clinochlore spectrum № Sil95 (Chukanov 2014). The assignment of the absorption bands was made in accordance with Prieto et al. (1991). The absorption bands at 3678-3675 cm\(^{-1}\) are assigned to the stretching vibrations of OH-groups in the interlayer octahedral sheet, and the bands at 3590-3574 and at 3440-3417 cm\(^{-1}\) are assigned to the stretching vibrations of OH-groups in the 2:1 layer (in the coordinations (Si,Al)O-OH and (Si,Al)O-OH, respectively). The increase of the aluminum content in the tetrahedral layers and the total iron content causes a shift of these absorption bands to low-frequency region. The weak “shoulders” near 1083-1081 cm\(^{-1}\) and 1061-1055 cm\(^{-1}\) together with two very intense bands at 998-986 and 959 cm\(^{-1}\) are related to the stretching vibrations of the (Si,Al)O\(_4\)-tetrahedra. The bands at 823-820, 775-766, 656-651 cm\(^{-1}\) and 463-460 cm\(^{-1}\) are assigned to the librations of OH-groups.

Thermal and thermogravimetric analyses. The DTA and TG parameters (Table 4) for studied minerals are typical of clinochlore and are in a good agreement with the literature data for this mineral (Villiéras et al. 1993; Foldvari 2011). DTA curves showed two endothermic effects which corresponded to two stages of the removal of constitutional water (the dehydroxylation process). In the first stage the removal of OH-groups occurred from the octahedral interlayer hydroxide sheets (hereinafter referred to as “step A”), in the second stage the removal of the remaining OH-groups took place from 2:1 layer (hereinafter referred to as “step B”). The temperature of the beginning of the dehydroxylation process decreased with increase of the iron content in the composition of clinochlores.

Calorimetric measurements

The standard enthalpies of formation. The values of standard enthalpies of formation from the elements for the studied clinochlores were calculated according to the reactions 1, 2 and Equations 3, 4 using the dissolution calorimetric data (Table 5).
For the sample I

\[ 4 \text{Mg(OH)}_2 + 0.9 \text{MgO} + 0.3 \text{FeO} + 0.8 \text{Al}_2\text{O}_3 + 3.2 \text{SiO}_2 = \]

\[(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})[\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{10}](\text{OH})_8\] \hspace{1cm} (1)

for the sample II

\[ 4 \text{Mg(OH)}_2 + 0.2 \text{MgO} + 0.6 \text{FeO} + 1.2 \text{Al}_2\text{O}_3 + 2.8 \text{SiO}_2 = \]

\[(\text{Mg}_{4.2}\text{Fe}^{2+}_{0.6}\text{Al}_{1.2})[\text{Si}_{2.8}\text{Al}_{1.2}\text{O}_{10}](\text{OH})_8\] \hspace{1cm} (2)

\[\Delta_{r(1,2,3)} H_0^{0}(298.15 \text{K}) = \sum \nu_i \Delta H_{\text{component}_i} - \Delta H_{\text{clinochlore}} \] \hspace{1cm} (3)

\[\Delta H_f^{0}(298.15 \text{K}) \text{ clinochlore} = \Delta_{r(1,2,3)} H_f^{0}(298.15 \text{K}) + \sum \nu_i \Delta H_f^{0}(298.15 \text{K}) \text{ component}_i \] \hspace{1cm} (4)

where \(\nu_i\) is the stoichiometric coefficients in the reactions 1 and 2; \(\Delta H = [H_f^{0}(973 \text{K}) - H_f^{0}(298.15 \text{K}) + \Delta_{\text{sol}} H_f^{0}(973 \text{K})]\) is the calorimetric dissolution data for the clinochores (Table 5) and for the corresponding components of the reactions (Table 6); the values of \(\Delta H_f^{0}(298.15 \text{K})\) of the components of these reactions needed for the calculations are also shown in the Table 6.

Determination of the enthalpy of dissolution of iron oxide is impossible under the conditions of the calorimetric experiments due to its partial oxidation during the dissolution. We accepted that all minor amount of iron contained in the minerals was in the trivalent form; the calculation was made using thermochemical data for iron trioxide (Table 6). The calculated values of the enthalpies of formation of studied clinochores are listed in the Table 7.

**The enthalpies of dehydroxylation.** As noted above, the distinctive feature of the clinochores is the presence of two types of constitutional water in the form of hydroxyl groups: in the interlayer hydroxide sheet and in the 2:1 layer. To obtain quantitative thermal characteristics of the processes of the removal of OH-groups from these positions in the clinochlore structure, the calorimetric study of the sample I was performed.

*The enthalpy of dehydroxylation of the interlayer octahedral sheet (step A).* The measurement of the enthalpy of dehydroxylation of the interlayer sheet was carried out at \(T = 973 \text{ K} \) \(700^\circ\text{C}\). The "double drop" method was used for this purpose. On the basis of the calorimetric data (Table 5), the enthalpy of dehydroxylation \((\Delta_{\text{step A}} H_f^{0}(298.15 \text{K}))\) was calculated according to the reaction

\[(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})[\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{10}](\text{OH})_8 = (\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{11.7}(\text{OH})_{4.6} + 1.7 \text{H}_2\text{O} \] \hspace{1cm} (5)
where \((\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})[\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{10}]\text{(OH)}_{8}\) is clinochlore of the initial composition; 
\((\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{11.7}\text{(OH)}_{4.6}\) is the partly dehydroxylated clinochlore after the dehydroxylation of the interlayer octahedral sheet at \(T=973\ K\).

The calculation was made according to Equation 6

\[
\Delta_{\text{step A}} H^0(298.15\ K) = [H^0(973\ K) - H^0(298.15\ K) + \Delta_{\text{step A}} H^0(973\ K)]\text{clinochlore} - \\
[H^0(973\ K) - H^0(298.15\ K)]\text{partly dehydroxylated clinochlore} - \\
1.7 [H^0(600\ K) - H^0(298.15\ K)]\text{H}_2\text{O(l)} \\
(6)
\]

where \([H^0(973\ K) - H^0(298.15\ K) + \Delta_{\text{step A}} H^0(973\ K)]\text{clinochlore}\) and \([H^0(973\ K) - H^0(298.15\ K)]\text{partly dehydroxylated clinochlore}\) are the experimental data obtained in the present work; 
\([H^0(973\ K) - H^0(298.15\ K)]\text{H}_2\text{O(l)}\) is the reference data (Robie and Hemingway, 1995) for liquid water.

The obtained value of the enthalpy of dehydroxylation process at the \textit{step A} for clinochlore was found as 90 \(\pm\) 34 kJ. The calculated enthalpy of the removal of 1 mole of constitutional water (in the form of OH-groups) from the interlayer sheet in the studied magnesian clinochlore was equal to 53 \(\pm\) 20 kJ. It is the first experimental determination of this thermodynamic characteristic of clinochlore.

The \textit{enthalpy of dehydroxylation of the 2:1 layer (step B)}.

To determine the enthalpy of dehydroxylation of the octahedral layer in the 2:1 package (\textit{step B}), the additional dissolution experiments were performed using the samples which were calcinated at 973 K (700°C) for about 1 h and at 1223 K (950°C) for about 30 min. The IR absorption spectrum of the sample, which was heated at 973 K (Fig. 2 a), shows a decrease of the intensity of the absorption bands in the region of 3590-3416 cm\(^{-1}\); it corresponds to the removal of OH-groups from the interlayer octahedral sheet. The spectrum of the sample, which was warmed at 1223 K (Fig. 2 b), demonstrates the absence of the absorption bands in the range of 3300-3700 cm\(^{-1}\); it confirms the full dehydroxylation of the sample. The sample weight was controlled before and after heating. The sample weight loss during heating to 973 K was 5.5 % that corresponded to the removal of 1.7 moles of water. The weight loss during calcinations at 1223 K was equal to 13.1 % that corresponded to the removal of 4 moles of water (the fully dehydroxylation of clinochlore).

The enthalpy of the OH-groups removal from the 2:1 layer can be obtained in accordance with the law of Hess using the reactions \(7\) (\textit{step A + step B}) and \(8\) (\textit{step B})

\[
(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})[\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{10}]\text{(OH)}_{8} = (\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{14} + 4 \text{H}_2\text{O(l)} \\
(7)
\]

\[
(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{11.7}\text{(OH)}_{4.6} = (\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{14} + 2.3 \text{H}_2\text{O(l)} \\
(8)
\]
where \((\text{Mg}_{4.9}\text{Fe}^{2+0.3}\text{Al}_{0.8})[\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{10}](\text{OH})_8\) is the clinochlore of initial composition; 
\((\text{Mg}_{4.9}\text{Fe}^{2+0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{11.7}(\text{OH})_{4.6}\) is the partly dehydroxylated clinochlore after dehydroxylation of the interlayer octahedral sheet at \(T=973\ \text{K}\) (according to the reaction 5); 
\((\text{Mg}_{4.9}\text{Fe}^{2+0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{14}\) is the fully dehydroxylated clinochlore.

The enthalpies of these reactions were calculated using Equations 9 and 10.

\[
\Delta_{(\text{step A}+\text{step B})}H^0(298.15\ \text{K}) = \Delta H^0_f(298.15\ \text{K}) (\text{Mg}_{4.9}\text{Fe}^{2+0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{14} + 4 \Delta H^0_f(298.15\ \text{K}) \text{H}_2\text{O}(l) - \Delta H^0_f(298.15\ \text{K}) (\text{Mg}_{4.9}\text{Fe}^{2+0.3}\text{Al}_{0.8})[\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{10}](\text{OH})_8 \quad (9)
\]

\[
\Delta_{(\text{step B})}H^0(298.15\ \text{K}) = \Delta H^0_f(298.15\ \text{K}) (\text{Mg}_{4.9}\text{Fe}^{2+0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{14} + 2.7 \Delta H^0_f(298.15\ \text{K}) \text{H}_2\text{O}(l) - \Delta H^0_f(298.15\ \text{K}) (\text{Mg}_{4.9}\text{Fe}^{2+0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{11.7}(\text{OH})_{4.6}. \quad (10)
\]

The enthalpies of formation \(\Delta H^0_f(298.15\ \text{K})\) for the fully dehydroxylated clinochlore 
\((\text{Mg}_{4.9}\text{Fe}^{2+0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{14}\) and for the partly dehydroxylated clinochlore (after \(\text{step A}\)) 
\((\text{Mg}_{4.9}\text{Fe}^{2+0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{11.7}(\text{OH})_{4.6}\) were calculated using the equations similar to Equation 4, 
they were found equal to \(-7282 \pm 18\) and \(-8245.2 \pm 8.1\ \text{kJ/mol}\), respectively. The latter value 
relates to the partially dehydroxylated clinochlore, which according to Villiéras et al. (1993, 1994) 
has a microporous “modified chlorite structure” and a broad perspective of industrial application.

On the basis of these data and the value of \(\Delta H^0_f(298.15\ \text{K})\) for clinochlore of initial composition 
(Table 7), and the reference data for \(\Delta H^0_f(298.15\ \text{K})\) \text{H}_2\text{O}(l) (Robie and Hemingway 1995) the 
enthalpies of the reaction 7 (\(\text{step A + step B}\)) and of the reaction 8 (\(\text{step B}\)) were found to be \(383 \pm 24\) and \(307 \pm 20\ \text{kJ}\), respectively. The values of \(\Delta_{(\text{step B})}H^0(298.15\ \text{K})\) calculated per one mole of 
\text{H}_2\text{O} at 298.15 K were obtained to be equal: \(127 \pm 18\ \text{kJ}\) (using the reaction 5 for \(\text{step A}\) and 
reaction 7 for \(\text{step A + step B}\)) and \(133.5 \pm 8.6\ \text{kJ}\) (using the reaction 8 for \(\text{step B}\)). The obtained 
data are in good agreement within the error limits and are significantly exceed the given above (in 
the previous section) enthalpy of dehydroxylation of the interlayer octahedral sheet (for \(\text{step A}\)); it 
confirms the different bond energies of the hydroxyl groups in the structure of clinochlore. The 
average value turned out to equal: \(131 \pm 10\ \text{kJ/(mol H}_2\text{O)}\).

The obtained value is close to the determined previously values of the enthalpy of 
dehydroxylation for the montmorillonite \((166 \pm 10\ \text{kJ/(mol H}_2\text{O)}\) (Ogorodova et al. 2013) and for 
the sepiolite \((145 \pm 14\ \text{kJ/(mol H}_2\text{O)}\) (Ogorodova et al. 2014). The crystal structures of all these 
minerals have a similar structural element (three-layer packages of 2:1 type), which is composed
of two tetrahedral layers with the octahedral layer between them; each cation of this octahedral layer is surrounded by four apical oxygens and by two hydroxyl groups. The difference between the crystal structures of these minerals lies in the different filling of the space between the 2:1 packages. In montmorillonites this interlayer sheet contains the exchange cations and the water molecules; in sepiolite it contains only water molecules; in chlorites it contains Al and Mg cations associated with the hydroxyl groups.

The Gibbs energies of formation

To calculate the Gibbs energies of formation of the studied minerals, we estimated the values of their standard entropies (Table 7), which cannot be found in the literature. The evaluation was performed by means of an additive scheme (reaction 11 for sample I) using the value of 3rd law entropy $S^0(298.15 \text{ K})$ (Table 1) for natural Mg-Fe clinochlore (Hemingway et al. 1984). The differences in composition of minerals were taken into account using the contributions from the entropy-volume ($S-V$) method (Holland 1989) for appropriate oxides (Table 8). The calculation was made using Equation 12.

$$
\begin{align*}
(Mg_{3.52}Fe^{2+}_{0.57}Al_{1.39}Fe^{3+}_{0.21})[Si_{2.99}Al_{1.01}O_{10}](OH)_8 + 1.38 \left[6\right]&MgO + 0.21 \left[4\right]SiO_2 = \\
= (Mg_{4.9}Fe^{2+}_{0.3}Al_{0.8})[Si_{3.2}Al_{0.8}O_{10}](OH)_8 + 0.27 \left[6\right]FeO + 0.105 \left[4\right]Al_2O_3 + 0.295 \left[6\right]Al_2O_3 + 0.21 \left[6\right]Fe_2O_3 \\
S^0(298.15 \text{ K})_{\text{studied clinochlore}} = S^0(298.15 \text{ K})_{\text{Mg-Fe clinochlore}} + 1.38 (S-V)_{\left[6\right]MgO} \\
+ 0.21 (S-V)_{\left[4\right]SiO_2} - 0.27 (S-V)_{\left[6\right]FeO} - 0.105 (S-V)_{\left[4\right]Al_2O_3} - 0.295 (S-V)_{\left[6\right]Al_2O_3} - 0.21(S-V)_{\left[6\right]Fe_2O_3} \\
(11)
\end{align*}
$$

The calculated value of $S^0(298.15 \text{ K})$ was found to be 433.8±5.1 J/(K·mol). The entropy of Si-Al disorder on tetrahedral sites in clinochlores (11.5 J/(K·mol)) was added to this 3rd law entropy according to Holland and Powell (2011). The value of the entropy of formation of studied clinochlore was obtained on the basis of reference data on $S^0(298.15 \text{ K})$ for constituent elements (Table 8) using the Equation 13.

$$
\begin{align*}
\Delta S^0_f (298.15 \text{ K})_{\text{Mg-Fe clinochlore}} = S^0(298.15 \text{ K})_{\text{Mg-Fe clinochlore}} - 4.9 S^0(298.15 \text{ K})_{\text{Mg}} \\
- 0.3 S^0(298.15 \text{ K})_{\text{Fe}} - 1.6 S^0(298.15 \text{ K})_{\text{Al}} - 3.2 S^0(298.15 \text{ K})_{\text{Si}} - 9 S^0(298.15 \text{ K})_{\text{O}_2} \\
- 4 S^0(298.15 \text{ K})_{\text{H}_2}. \\
(13)
\end{align*}
$$

The calculation for sample II was performed in a similar manner as for sample I. The obtained values of $\Delta S^0_f (298.15 \text{ K})$ of clinochlores and our data on the enthalpies of its formation from the elements were then used to calculate the values of $\Delta G^0_f (298.15 \text{ K})$ for these minerals (Table 7).
Thermodynamic properties of clinochlores of the theoretical composition

The enthalpies of formation of clinochlores of the theoretical compositions of end and intermediate members of the clinochlore \((\text{Mg}_5\text{Al})[\text{Si}_3\text{AlO}_{10}](\text{OH})_8\) - chamosite \((\text{Fe}_5\text{Al})[\text{Si}_3\text{AlO}_{10}](\text{OH})_8\) series (Table 8) were calculated on the basis of the dissolution calorimetric data for the natural minerals. For this purpose, the results of the calorimetric measurements for the studied clinochlores were corrected on the deviations of their composition from the ideal formula; the amendments were estimated using the thermochemical data for the corresponding oxides (Table 6). Values of the standard entropies and Gibbs energies were estimated by the same way as for the natural minerals and are given in the Table 7.

The obtained value of the Gibbs energy of formation for clinochlore of composition \((\text{Mg}_5\text{Al})[\text{Si}_3\text{AlO}_{10}](\text{OH})_8\) (Table 7) agrees with the results of the calculation from P-T equilibria (Jenkins and Chernosky 1986; Berman 1988; Robie and Hemingway 1995; Holland and Powell 2011) (Table 1). Comparison of our data for the iron-rich minerals with literature data was hampered because of a considerable difference in their composition.

**IMPLICATIONS**

Our new experimental determinations of the enthalpies of formation of clinochlores as well as the enthalpies of dehydroxylation of the interlayer octahedral sheet and 2:1 layers in clinochlores are significant addition for understanding of physicochemical conditions of formation of chlorites in different geochemical environments. Obtained data (enthalpies and the Gibbs energies of formation) allow to carry out a quantitative thermodynamic modeling of the stability of chlorites in the system \((\text{Mg,Fe})\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}\). The upper thermal stability of clinochlore \((\text{Mg}_5\text{Al})[\text{Si}_3\text{AlO}_{10}](\text{OH})_8\) in the system \(\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}\) with using new thermodynamic data was calculated according to the reactions 14 and 15 by means of HCh software (Shvarov 2015).

\[
5(\text{Mg}_5\text{Al})[\text{Si}_3\text{AlO}_{10}](\text{OH})_8 = 10\text{Mg}_2\text{SiO}_4 + 3\text{MgAl}_2\text{O}_4 + \text{Mg}_2\text{Al}_3[\text{Si}_5\text{AlO}_{18}] + 20\text{H}_2\text{O} \quad (14)
\]

\[
\text{clinochlore (Clin)} \quad \text{forsterite (Fo)} \quad \text{spinel (Sp)} \quad \text{cordierite (Cord)}
\]

and

\[
(\text{Mg}_5\text{Al})[\text{Si}_3\text{AlO}_{10}](\text{OH})_8 = \text{Mg}_5\text{SiO}_4 + 2\text{MgSiO}_3 + \text{MgAl}_2\text{O}_4 + 4\text{H}_2\text{O} \quad (15)
\]

\[
\text{clinochlore (Clin)} \quad \text{forsterite (Fo)} \quad \text{enstatite (En)} \quad \text{spinel (Sp)}
\]

The Gibbs energies of formation for cordierite, enstatite, spinel and forsterite were computed with parameters from Unitherm database (Shvarov 2015). Water properties were calculated from Gibbs code using Haar-Gallagher-Kell (HGK) model (Kestin et al. 1984). The results of calculation
Fig. 3) demonstrate a good agreement with experimental data on clinoclere $P$-$T$ stability (Fawcett and Yoder 1966; Chernovsky 1974; Staudigel and Schreyer 1977; Jenkins 1981; Jenkins and Chernovsky 1986). The obtained thermodynamic parameters of Mg-Fe clinochlores can be useful also for defining optimal technological conditions for the industrial processing of ores containing clinochlores. It may be iron ores from skarn deposits in which the clinochlores present as a part of the main ore body; as well as it may be the various polymetallic ores from hydrothermal deposits, where the host rocks near the ore bodies were subjected to the strong chloritization as a result of weathering. The first results concerning the enthalpy of the dehydroxylation of Mg-chlorite and the enthalpy of formation of the new microporous phase with modified chlorite structure formed during dehydroxylation of the interlayer hydroxide sheet can be used to optimize conditions of obtaining this new promising microporous adsorbent on the basis of chlorite deposits for industrial applications.

**ACKNOWLEDGMENTS**

We are very grateful to Prof. Andrey Yu. Bychkov (M.V. Lomonosov Moscow State University, Geological Faculty) for his fruitful discussion of the results of our thermochemical studies and for his calculation of clinoclere thermal stability. Financial support from the Russian Foundation for Basic Research (projects № 12-05-00211) is gratefully acknowledged.
REFERENCES CITED


Jenkins D.M. (1981) Experimental phase relations of hydrous peridotites modelled in the system

H2O-CaO-MgO-Al2O3-SiO2. Contributions to Mineralogy and Petrology 77, 166-176.


TABLE 2. Chemical composition (wt%) of the studied clinochlores\textsuperscript{a}

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Sample I \textsuperscript{b} (Nicolae-Maximilianovskaya mine)</th>
<th>Sample II \textsuperscript{c} (Tarlashkinsky massif)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}</td>
<td>33.59 ± 0.31</td>
<td>29.97 ± 0.54</td>
</tr>
<tr>
<td>TiO\textsubscript{2}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>16.09 ± 0.27</td>
<td>20.34 ± 0.38</td>
</tr>
<tr>
<td>Cr\textsubscript{2}O\textsubscript{3}</td>
<td>0.01 ± 0.00</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>33.91 ± 0.48</td>
<td>29.07 ± 0.51</td>
</tr>
<tr>
<td>FeO</td>
<td>3.31 ± 0.08</td>
<td>7.92 ± 0.42</td>
</tr>
<tr>
<td>NiO</td>
<td>-</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>MnO</td>
<td>0.01 ± 0.00</td>
<td>-</td>
</tr>
<tr>
<td>CaO</td>
<td>0.01 ± 0.00</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td>Na\textsubscript{2}O</td>
<td>-</td>
<td>0.15 ± 0.01</td>
</tr>
<tr>
<td>K\textsubscript{2}O</td>
<td>-</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>H\textsubscript{2}O\textsuperscript{d}</td>
<td>13.1</td>
<td>12.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Uncertainties are calculated using Student’s \textit{t}-distribution with a 95% confidence interval.
\textsuperscript{b} Uncertainties are calculated on the basis of 7 determinations.
\textsuperscript{c} Uncertainties are calculated on the basis of 5 determinations.
\textsuperscript{d} The water content was determined by thermogravimetric method.
TABLE 6. Thermochemical data used in calculation of the enthalpies of formation of studied clinochlores (kJ/mol)

<table>
<thead>
<tr>
<th>Component</th>
<th>([H_f^0(973 \text{ K})-H_f^0(298.15 \text{ K})+\Delta_{\text{sol}}H_f^0(973 \text{ K})])</th>
<th>(\Delta H_f^0(298.15 \text{ K})^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(OH)(_2) (brucite)</td>
<td>111.5 (\pm) 1.6(^b)</td>
<td>- 924.5 (\pm) 0.4</td>
</tr>
<tr>
<td>SiO(_2) (quartz)</td>
<td>39.43 (\pm) 0.2(^c)</td>
<td>- 910.7 (\pm) 1.0</td>
</tr>
<tr>
<td>Al(_2)O(_3) (corundum)</td>
<td>107.38 (\pm) 0.59(^d)</td>
<td>- 1675.7 (\pm) 1.3</td>
</tr>
<tr>
<td>Fe(_2)O(_3) (hematite)</td>
<td>130.71 (\pm) 0.54(^e)</td>
<td>- 826.2 (\pm) 1.3</td>
</tr>
<tr>
<td>MgO (periclase)</td>
<td>36.38 (\pm) 0.59(^f)</td>
<td>- 601.6 (\pm) 0.3</td>
</tr>
</tbody>
</table>

\(^a\) Reference data (Robie and Hemingway 1995).
\(^b\) According to Kiseleva and Ogorodova (1984).
\(^c\) Calculated using the reference data on \([H_f^0(973 \text{ K})-H_f^0(298.15 \text{ K})]\) (Robie and Hemingway 1995) and experimental data on \(\Delta_{\text{sol}}H_f^0(973 \text{ K})\) according to Kiseleva et al. (1979).
\(^d\) Calculated using the reference data on \([H_f^0(973 \text{ K})-H_f^0(298.15 \text{ K})]\) (Robie and Hemingway 1995) and experimental data on \(\Delta_{\text{sol}}H_f^0(973 \text{ K})\) according to Ogorodova et al. (2003).
\(^e\) Calculated using the reference data on \([H_f^0(973 \text{ K})-H_f^0(298.15 \text{ K})]\) (Robie and Hemingway 1995) and experimental data on \(\Delta_{\text{sol}}H_f^0(973 \text{ K})\) according to Kiseleva (1976).
\(^f\) Calculated using the reference data on \([H_f^0(973 \text{ K})-H_f^0(298.15 \text{ K})]\) (Robie and Hemingway 1995) and experimental data on \(\Delta_{\text{sol}}H_f^0(973 \text{ K})\) according to Navrotsky and Coons (1976).
<table>
<thead>
<tr>
<th>$\Delta H^0_f$ (kJ/mol)</th>
<th>$S^0[J/(K\cdot mol)]$</th>
<th>$\Delta G^0_f$ (kJ/mol)</th>
<th>Reference</th>
<th>Method of determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>8259.2</td>
<td></td>
<td>8207.8</td>
<td>(Zen 1972)</td>
<td>Estimation</td>
</tr>
<tr>
<td>8195.2</td>
<td></td>
<td></td>
<td>(Tardy and Garrels 1974)</td>
<td>- »-</td>
</tr>
<tr>
<td>8181.45</td>
<td></td>
<td></td>
<td>(Nriagu 1975)</td>
<td>- »-</td>
</tr>
<tr>
<td>- 8856.2</td>
<td>465.3</td>
<td>- 8207.8</td>
<td>(Helgeson et al. 1978)</td>
<td>Calculation from P-T equilibria</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 8232.3 ± 3.8</td>
<td>(Dorogokupetz and Karpov 1984)</td>
<td>- «-</td>
</tr>
<tr>
<td>- 8872 ± 27</td>
<td>459 ± 33</td>
<td>- 8220 ± 27</td>
<td>(Jenkins and Chernosky 1986)</td>
<td>- «-</td>
</tr>
<tr>
<td>- 8909.59</td>
<td>435.15</td>
<td>- 8250.55</td>
<td>(Berman 1988)</td>
<td>- «-</td>
</tr>
<tr>
<td>- 8919 ± 20</td>
<td>421.0 ± 15</td>
<td>- 8255.8 ± 20</td>
<td>(Robie and Hemingway 1995)</td>
<td>- «-</td>
</tr>
<tr>
<td>- 8929.86 ± 1.65</td>
<td>410.50</td>
<td>- 8263.35</td>
<td>(Holland and Powell 1998)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 8190.83</td>
<td>(Vicillard 2002)</td>
<td>Estimation</td>
</tr>
<tr>
<td>425.6 ± 0.4</td>
<td></td>
<td></td>
<td>(Bertoldi et al. 2007)</td>
<td>Heat-pulse calorimetry</td>
</tr>
<tr>
<td>- 8909.23 ± 1.55</td>
<td>437.00$^a$</td>
<td>- 8250.62$^b$</td>
<td>(Holland and Powell 2011)</td>
<td>Calculation from P-T equilibria</td>
</tr>
<tr>
<td>Formula</td>
<td>Temperature (K)</td>
<td>Notes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>-----------------</td>
<td>--------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{Mg}<em>{3.52}\text{Fe}^{2+}</em>{0.57}\text{Al}<em>{1.39}\text{Fe}^{3+}</em>{0.21})[\text{Si}<em>{2.99}\text{Al}</em>{1.01}\text{O}_{10}]\text{(OH)}_8)</td>
<td>- 7869 ± 3</td>
<td>Study of solubility</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{Mg}<em>{3.24}\text{Fe}^{2+}</em>{0.99}\text{Al}<em>{1.44}\text{Fe}^{3+}</em>{0.07})[\text{Si}<em>{2.97}\text{Al}</em>{1.03}\text{O}_{10}]\text{(OH)}_8)</td>
<td>- 7793 ± 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{Mg}<em>{3.52}\text{Fe}^{2+}</em>{0.57}\text{Al}<em>{1.39}\text{Fe}^{3+}</em>{0.21})[\text{Si}<em>{2.99}\text{Al}</em>{1.01}\text{O}_{10}]\text{(OH)}_8)</td>
<td>431.7 ± 5.0</td>
<td>Measurement of low-temperature heat capacity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{Mg}<em>{4.2}\text{Fe}^{2+}</em>{0.5}\text{Al}<em>{1.65}\text{Fe}^{3+}</em>{0.07}\text{Mn}<em>{0.005}\text{Ca}</em>{0.01}\text{Ni}<em>{0.01}\text{Cr}</em>{0.005})[\text{Si}<em>{2.83}\text{Al}</em>{1.17}\text{O}_{10}]\text{(OH)}_8)</td>
<td>- 8770.64 ± 35.24</td>
<td>Calculation from P-T equilibria</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{Mg}<em>{2.952}\text{Fe}^{2+}</em>{1.712}\text{Al}<em>{1.116}\text{Fe}^{3+}</em>{0.215}\text{Mn}<em>{0.012}\text{Ca}</em>{0.011})[\text{Si}<em>{2.633}\text{Al}</em>{1.367}\text{O}_{10}]\text{(OH)}_8)</td>
<td>- 8253.70 ± 22.75</td>
<td>Acide solution calorimetry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{Mg}<em>{3.75}\text{Fe}</em>{1.25}\text{Al})[\text{Si}_3\text{Al}<em>0\text{O}</em>{10}]\text{(OH)}_8)</td>
<td>469.4 ± 2.9</td>
<td>Measurement of low-temperature heat capacity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{Mg}<em>{3.75}\text{Fe}</em>{1.25}\text{Al})[\text{Si}_3\text{Al}<em>0\text{O}</em>{10}]\text{(OH)}_8)</td>
<td>- 8435.5</td>
<td>Estimation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Used the value of Bertoldi et al. (2007) with addition of 11.5 J/(K.mol) as entropy of Si-Al disorder on tetrahedral sites.
* Calculated in this work.
### TABLE 3. Unit-cell dimensions and molar volumes for studied clinochlores

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\beta$ (°)</th>
<th>$V$ (Å$^3$)</th>
<th>$V_0^m$ (298.15 K) (cm$^3$/mol)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>5.3353(3)</td>
<td>9.2377(5)</td>
<td>14.3980(9)</td>
<td>97.138(4)</td>
<td>703.88</td>
<td>211.94</td>
</tr>
<tr>
<td>II</td>
<td>5.3374(4)</td>
<td>9.2400(5)</td>
<td>14.3308(10)</td>
<td>97.222(7)</td>
<td>701.15</td>
<td>211.12</td>
</tr>
</tbody>
</table>

* The molar volume was calculated using formula: $V_0^m$ (298.15 K) = $a \cdot b \cdot c \cdot \sin(\beta) \cdot \frac{N_A}{Z}$, where $Z = 2$, $N_A$ – the Avogadro constant.
TABLE 4. The results of thermal analysis of studied clinochlores

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dehydroxylation</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>step A</td>
<td></td>
<td>step B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>$t_{\text{max}}$ ($^\circ$C)</td>
<td>The loss of mass (wt%)</td>
<td>Temperature</td>
<td>$t_{\text{max}}$ ($^\circ$C)</td>
<td>The loss of mass (wt%)</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>interval ($^\circ$C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>550-800</td>
<td>695</td>
<td>6.3</td>
<td>800-950</td>
<td>900</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>550-750</td>
<td>665</td>
<td>2.9</td>
<td>750-950</td>
<td>890</td>
<td>9.6</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 5. Results of calorimetric study of dehydroxylation and solution processes for studied clinochlores

<table>
<thead>
<tr>
<th>Composition of sample</th>
<th>Molar mass (g/mol)</th>
<th>Measured value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><em>(J/g)</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>(kJ/mol)</em></td>
</tr>
<tr>
<td><strong>Sample (I)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{Mg}<em>{4.9}\text{Fe}^{2+}</em>{0.3}\text{Al}<em>{0.8})[\text{Si}</em>{3.2}\text{Al}<em>{0.8}\text{O}</em>{10}]\text{(OH)}_8)</td>
<td>564.95</td>
<td>(H^\circ(973\text{ K})-H^\circ(298.15\text{ K})+\Delta_{\text{sol}}H^\circ(973\text{ K}))</td>
</tr>
<tr>
<td>((\text{Mg}<em>{4.9}\text{Fe}^{2+}</em>{0.3}\text{Al}<em>{0.8})[\text{Si}</em>{3.2}\text{Al}<em>{0.8}\text{O}</em>{10}]\text{(OH)}_8)</td>
<td>564.95</td>
<td>(H^\circ(973\text{ K})-H^\circ(298.15\text{ K})+\Delta_{\text{dehydr}}H^\circ(973\text{ K}))</td>
</tr>
<tr>
<td>((\text{Mg}<em>{4.9}\text{Fe}^{2+}</em>{0.3}\text{Al}<em>{0.8})\text{Si}</em>{3.2}\text{Al}<em>{0.8}\text{O}</em>{11.7}\text{(OH)}_{4.6})</td>
<td>534.32</td>
<td>(H^\circ(973\text{ K})-H^\circ(298.15\text{ K}))</td>
</tr>
<tr>
<td>((\text{Mg}<em>{4.9}\text{Fe}^{2+}</em>{0.3}\text{Al}<em>{0.8})\text{Si}</em>{3.2}\text{Al}<em>{0.8}\text{O}</em>{11.7}\text{(OH)}_{4.6})</td>
<td>534.32</td>
<td>(H^\circ(973\text{ K})-H^\circ(298.15\text{ K})+\Delta_{\text{sol}}H^\circ(973\text{ K}))</td>
</tr>
<tr>
<td>((\text{Mg}<em>{4.9}\text{Fe}^{2+}</em>{0.3}\text{Al}<em>{0.8})\text{Si}</em>{3.2}\text{Al}<em>{0.8}\text{O}</em>{14})</td>
<td>492.88</td>
<td>(H^\circ(973\text{ K})-H^\circ(298.15\text{ K})+\Delta_{\text{sol}}H^\circ(973\text{ K}))</td>
</tr>
<tr>
<td><strong>Sample (II)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{Mg}<em>{4.2}\text{Fe}^{2+}</em>{0.6}\text{Al}<em>{1.2})[\text{Si}</em>{2.8}\text{Al}<em>{1.2}\text{O}</em>{10}]\text{(OH)}_8)</td>
<td>575.04</td>
<td>(H^\circ(973\text{ K})-H^\circ(298.15\text{ K})+\Delta_{\text{sol}}H^\circ(973\text{ K}))</td>
</tr>
</tbody>
</table>

* Uncertainties are calculated using Student’s *t*-distribution with a 95% confidence interval, in brackets the number of determination is given.

---

TABLE 7. Thermodynamic properties at \(T = (298.15\text{ K})\) for Mg-Fe clinochlores obtained in present work \(^a\)
<table>
<thead>
<tr>
<th>Composition of mineral</th>
<th>$\Delta H_f^\circ$ (kJ/mol)</th>
<th>$S^\circ$ [J/(K mol)]</th>
<th>$\Delta G_f^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Natural clinochlores</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mg$<em>{4.9}$Fe$</em>{2+0.3}$Al$_{0.8}$)<a href="OH">Si$<em>{3.2}$Al$</em>{0.8}$O$_{10}$</a>$_8$ (sample I)</td>
<td>-8806 ± 16</td>
<td>445.3 ± 5.1</td>
<td>-8151 ± 16</td>
</tr>
<tr>
<td>(Mg$<em>{4.2}$Fe$</em>{2+0.6}$Al$_{1.2}$)<a href="OH">Si$<em>{2.8}$Al$</em>{1.2}$O$_{10}$</a>$_8$ (sample II)</td>
<td>-8748 ± 24</td>
<td>446.8 ± 5.1</td>
<td>-8093 ± 24</td>
</tr>
<tr>
<td><strong>Clinochlores of theoretical composition</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mg$_5$Al)<a href="OH">Si$<em>3$AlO$</em>{10}$</a>$_8$</td>
<td>-8895 ± 16</td>
<td>439.3 ± 5.1$^c$</td>
<td>-8237 ± 16</td>
</tr>
<tr>
<td>(Mg$<em>4$Fe$</em>{2-}$Al)<a href="OH">Si$<em>3$AlO$</em>{10}$</a>$_8$</td>
<td>-8640 ± 24</td>
<td>454.4 ± 5.1</td>
<td>-7990 ± 24</td>
</tr>
<tr>
<td>(Mg$<em>3$Fe$</em>{2-2}$Al)<a href="OH">Si$<em>3$AlO$</em>{10}$</a>$_8$</td>
<td>-8452 ± 24</td>
<td>469.3 ± 5.1</td>
<td>-7811 ± 24</td>
</tr>
</tbody>
</table>

$^a$ The uncertainties are calculated on the basis of the law of propagation of uncertainty
$^b$ Calculated using calorimetric data on dissolution for sample (I).
$^c$ Calculated in a similar manner as for sample I on the basis of data of Hemingway et al. (1984).
$^d$ Calculated using calorimetric data on dissolution for sample (II).
**TABLE 8.** Values used in calculations of the standard entropies and the entropies of formation of clinochlores: the regression $S(V)$ data on oxides (Holland 1989); the entropies data $S_o(298.15 \text{ K})$ on the elements in their reference state (Robie and Hemingway 1995) [J/(K mol)]

<table>
<thead>
<tr>
<th>$[^6]\text{MgO}$</th>
<th>$[^6]\text{FeO}$</th>
<th>$[^6]\text{Al}_2\text{O}_3$</th>
<th>$[^4]\text{Al}_2\text{O}_3$</th>
<th>$[^4]\text{SiO}_2$</th>
<th>Mg</th>
<th>Fe</th>
<th>Al</th>
<th>Si</th>
<th>O$_2$</th>
<th>H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.75 ± 0.53</td>
<td>30.78 ± 0.83</td>
<td>22.60 ± 1.06</td>
<td>28.89 ± 0.38</td>
<td>17.45 ± 0.10</td>
<td>32.67 ± 0.13</td>
<td>27.09 ± 0.08</td>
<td>28.30 ± 0.08</td>
<td>18.81 ± 0.08</td>
<td>205.15 ± 0.02</td>
<td>130.68 ± 0.02</td>
</tr>
</tbody>
</table>

* The coordination number of cation.