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

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16 **ABSTRACT**

17 This paper presents the results of the first experimental thermochemical investigation of two
18 natural trioctahedral chlorites - clinochlores. The study was performed with the help of a high-temperature
19 heat-flux Tian-Calvet microcalorimeter. The samples were characterized by X-ray spectroscopy analysis,
20 X-ray powder diffraction, thermal analysis, FTIR spectroscopy. The enthalpies of formation of
21 clinochlores were found using the melt solution calorimetry method to be: $-8806 \pm 16 \text{ kJ}\cdot\text{mol}^{-1}$ for
22 composition $(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})[\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{10}](\text{OH})_8$ and $-8748 \pm 24 \text{ kJ}\cdot\text{mol}^{-1}$ for composition
23 $(\text{Mg}_{4.2}\text{Fe}^{2+}_{0.6}\text{Al}_{1.2})[\text{Si}_{2.8}\text{Al}_{1.2}\text{O}_{10}](\text{OH})_8$. The experimental data for natural samples allowed calculating the
24 enthalpies of formation for end and intermediate members of the clinochlore $(\text{Mg}_5\text{Al})[\text{Si}_3\text{AlO}_{10}](\text{OH})_8$
25 - chamosite $(\text{Fe}_5\text{Al})[\text{Si}_3\text{AlO}_{10}](\text{OH})_8$ series. An important feature of the clinochlore structure is the
26 presence of two distinct hydroxyl-containing octahedral layers: the interlayer octahedral sheet and
27 octahedral 2:1 layer; enthalpies of water removal from these positions in clinochlore structure were
28 determined as: $53 \pm 20 \text{ kJ}/(\text{mol H}_2\text{O})$ and $131 \pm 10 \text{ kJ}/(\text{mol H}_2\text{O})$, respectively. The obtained first
29 thermodynamic characteristics of Mg-Fe clinochlores can be used for quantitative thermodynamic
30 modeling of geological and industrial processes including clinochlores of different composition.
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32 **Keywords:** Clinochlore, chlorite, thermochemistry, microcalorimetry, enthalpy of dehydroxylation,
33 enthalpy of formation
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INTRODUCTION

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39 Clinochlore is a widespread magnesian chlorite, which is formed during the processes of
40 hydrothermal-metasomatic and metamorphic changes of ultramafic and carbonate rocks;
41 sometimes it is formed in the hydrothermally altered zones around ore bodies. Also this mineral
42 occurs as a result of the hypergenic processes in modern sediments, in the weathering crust and in
43 soils. Several exchange equilibria involving Mg-Fe clinochlores were proposed as
44 geothermometers and geobarometers (Laird 1988). The currently used nomenclature (Bailey
45 1988; Guggenheim et al. 2006) recommends for clinochlore the following formula
46 $(R^{2+}_5Al)[Si_3AlO_{10}](OH)_8$, where R is dominant octahedral cation Mg^{2+} ; in natural samples the
47 isomorphic admixture of Fe^{2+} in this position almost always presents.

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

58 The available data on thermodynamic properties of clinochlores of different compositions are
59 summarized in Table 1. These data were obtained mainly by using evaluations or calculations
60 based on the phase equilibrium experiments. The results of calculations on the experimentally
61 studied equilibria for clinochlore are given in the reference books and the bulletins on the
62 thermodynamic characteristics of minerals (Robie and Hemingway 1995; Holland and Powell
63 1998, 2011). Several authors (Hemingway et al. 1984; Gailhanou et al. 2009) studied clinochlores
64 with the different contents of ferrous using an adiabatic calorimetry method; for these substances
65 the low-temperature heat capacities were measured and the values of standard entropies were
66 calculated. The enthalpy of formation of the Fe-rich clinochlore was determined by means of acid
67 solution calorimetry in the work of Gailhanou et al. (2007). Kittrick (1982) calculated the values
68 of Gibbs energy of formation of two samples of the Mg-Fe clinochlores using the solubility data.

69 The values of the enthalpies of formation for clinochlore with theoretical composition differ
70 significantly from each other. The data for iron-containing species of clinochlore relate to the
71 different mineral compositions and therefore it is difficult to use them for modeling *P-T* equilibria
72 involving clinochlores and for building geothermometers and geobarometers. Thus, additional
73 studies to clarify these data are necessary.

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

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SAMPLES AND METHODS

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

84 The chemical analysis of the minerals was carried out on a “Camebax SX-50” (Cameca,
85 France) electron probe microanalyzer (EPMA) using the $K\alpha$ analytical line and the following
86 reference substances: sodalite for Na, hornblende for Mg and Al, tremolite for Ca and Si,
87 hedenbergite for Fe, nickel oxide (Cameca) for Ni, and spinel for Cr. All these substances were
88 provided by A.E. Fersman Mineralogical Museum and were tested using standards provided by
89 company “Cameca” (albite for Al, Na, Si; orthoclase for Al, K, Si; wollastonite for Ca; Cr_2O_3 and
90 Fe_2O_3 for Fe) using the “Camebax SX-50” and a Jeol JSM-6480LV scanning electron microscope
91 equipped with an INCA-Wave 500 wavelength dispersive spectrometer (Jeol, Japan). The
92 calculated compositions of used reference substances corresponded to stoichiometric formulas.
93 The mode of operation was as follows: accelerating voltage 15 kV; probe current 30 nA.

94 X-ray diffraction study was performed using a powder diffractometer Ultima-IV (Rigaku,
95 Japan). The diffractometer was equipped with a $CuK\alpha$ ($\lambda=1,54183\text{\AA}$) 3 kV radiation source and
96 semiconductor detector of a new generation - DTex / Ultra, due to its use a high quality of
97 experimental measurements was achieved in the range of 3.6° to $65^\circ 2\theta$ with a step on the scan
98 corner $0.02^\circ 2\theta$ and with a rotation speed of $5^\circ 2\theta/\text{min}$. Mineral identification was performed by
99 comparing the experimental spectra with the reference diffraction pattern of the database ICCD
100 PDF-2 software package Jade 6.5 of company MDI. The unit cell parameters were refined by the
101 Rietveld method (Post and Bish 1989) using BGMN program (www.bgm.de).

102 IR spectroscopic examination was carried out using a Fourier-spectrometer “FSM 1201”
103 (LOMO, Russia) with a resolution of 4 cm^{-1} in the spectral range of $400\text{-}4000\text{ cm}^{-1}$. The study was

104 carried out at an ambient air and room temperature. FTIR-spectra were recorded with the
105 suspension of clinoclors powders in vaseline oil (Nujol) to avoid the adsorption of atmospheric
106 water on the KBr pellets. The accuracy of the frequencies of the absorption bands was $\pm 2 \text{ cm}^{-1}$.

107 The thermal analysis of clinoclors was performed using a derivatograph "Q-1500 D"
108 (MOM, Hungary) with $20^\circ/\text{min}$ heating rate in the range from room temperature to 1000°C , the
109 sample weights were 270-350 mg.

110 The thermochemical investigation of clinoclors was done using a high temperature heat-flux
111 Tian-Calvet microcalorimeter (Setaram, France) by means of two experimental techniques. The
112 enthalpies of formation were determined by melt solution calorimetry method using a
113 thermochemical cycle, including the dissolution of the minerals and their constituent components
114 (magnesium, iron, aluminum and silicon oxides, and magnesium hydroxide). The pieces of the
115 minerals weighing 3-15 ($\pm 2 \times 10^{-3}$) mg were dropped from room temperature into solvent-melt
116 with composition: $2\text{PbO} \cdot \text{B}_2\text{O}_3$, located in a platinum crucible in the calorimeter at $T = 973 \text{ K}$. The
117 total effect including the heat absorption of the sample and its dissolution heat [$H^0(973 \text{ K}) -$
118 $H^0(298.15 \text{ K}) + \Delta_{\text{sol}}H^0(973 \text{ K})$] was measured. We used 30-35 grams of the solvent for 6-8
119 experiments; in this case the ratio of dissolved substance to solvent may be classified as an
120 infinitely dilute solution for which the mixing enthalpy close to zero.

121 The determination of the enthalpy of the OH-groups removal was carried out by the "double
122 drop" method. Initially the pieces of samples weighing 5-20 ($\pm 2 \times 10^{-3}$) mg were dropped from
123 room temperature (25°C) into an empty platinum crucible in the calorimeter at the temperature T
124 $= 973 \text{ K}$ (700°C); the heat effect measured was a sum of the heat absorption of the sample and its
125 dehydroxylation heat [$H^0(T) - H^0(298.15 \text{ K}) + \Delta_{\text{dehydr}}H^0(T)$]. Then the dehydroxylated sample was
126 taken out from the calorimeter and was dropped again in the calorimeter at the same temperature;
127 wherein the value of its heat absorption [$H^0(T) - H^0(298.15 \text{ K})$] was measured. The water content
128 in the substances was tested by weighing before and after the calorimetric experiments. The
129 calibration of the calorimeter was performed by dropping pieces of the reference substances,
130 platinum wire (in solution experiments) and corundum $\alpha\text{-Al}_2\text{O}_3$ (in the dehydroxylation
131 experiments), and using their reference heat content data (Robie and Hemingway 1995).

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

134 RESULTS AND DISCUSSION

135

136 Samples characterization

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

139 $(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})[\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{10}](\text{OH})_8$ (I) and $(\text{Mg}_{4.2}\text{Fe}^{2+}_{0.6}\text{Al}_{1.2})[\text{Si}_{2.8}\text{Al}_{1.2}\text{O}_{10}](\text{OH})_8$ (II). In
140 accordance with the currently used nomenclature (Guggenheim et al. 2006) both minerals may be
141 classified according to their composition as clinochlores.

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

147 **FTIR spectroscopic research.** IR spectroscopic results for the studied samples (Fig. 2) are
148 similar to the clinochlore spectrum № Si195 (Chukanov 2014). The assignment of the absorption
149 bands was made in accordance with Prieto et al. (1991). The absorption bands at $3678\text{-}3675\text{ cm}^{-1}$
150 are assigned to the stretching vibrations of OH-groups in the interlayer octahedral sheet, and the
151 bands at $3590\text{-}3574$ and at $3440\text{-}3417\text{ cm}^{-1}$ are assigned to the stretching vibrations of OH-groups
152 in the 2:1 layer (in the coordinations (Si,Al)O-OH and (Si,Al)O-OH, respectively). The increase
153 of the aluminum content in the tetrahedral layers and the total iron content causes a shift of these
154 absorption bands to low-frequency region. The weak “shoulders” near $1083\text{-}1081\text{ cm}^{-1}$ and 1061-
155 1055 cm^{-1} together with two very intense bands at $998\text{-}986$ and 959 cm^{-1} are related to the
156 stretching vibrations of the (Si,Al) O_4 -tetrahedra. The bands at $823\text{-}820$, $775\text{-}766$, $656\text{-}651\text{ cm}^{-1}$
157 and $463\text{-}460\text{ cm}^{-1}$ are assigned to the librations of OH-groups.

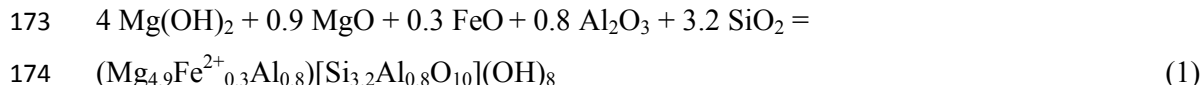
158 **Thermal and thermogravimetric analyses.** The DTA and TG parameters (Table 4) for
159 studied minerals are typical of clinochlore and are in a good agreement with the literature data for
160 this mineral (Villieras et al. 1993; Foldvari 2011). DTA curves showed two endothermic effects
161 which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

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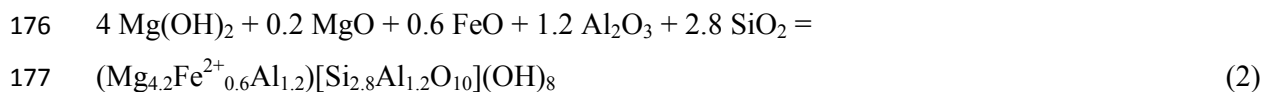
168 **Calorimetric measurements**

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

172 For the sample I



175 for the sample II



178

179 $\Delta_{r(1,2,3)}H^0(298.15 \text{ K}) = \sum v_i \Delta H_{\text{component}_i} - \Delta H_{\text{clinochlore}}$ (3)

180 $\Delta H_f^0(298.15 \text{ K})_{\text{clinochlore}} = \Delta_{r(1,2,3)}H^0(298.15 \text{ K}) + \sum v_i \Delta H_f^0(298.15 \text{ K})_{\text{component}_i}$ (4)

181

182 where v_i is the stoichiometric coefficients in the reactions 1 and 2; $\Delta H = [H^0(973 \text{ K}) - H^0(298.15$
183 $\text{ K}) + \Delta_{\text{sol}}H^0(973 \text{ K})]$ is the calorimetric dissolution data for the clinoclhlores (Table 5) and for the
184 corresponding components of the reactions (Table 6); the values of $\Delta H_f^0(298.15 \text{ K})$ of the
185 components of these reactions needed for the calculations are also shown in the Table 6.
186 Determination of the enthalpy of dissolution of iron oxide is impossible under the conditions of
187 the calorimetric experiments due to its partial oxidation during the dissolution. We accepted that
188 all minor amount of iron contained in the minerals was in the trivalent form; the calculation was
189 made using thermochemical data for iron trioxide (Table 6). The calculated values of the
190 enthalpies of formation of studied clinoclhlores are listed in the Table 7.

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

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

201



203

204 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;
205 $(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{11.7}(\text{OH})_{4.6}$ is the partly dehydroxylated clinochlore after the
206 dehydroxylation of the interlayer octahedral sheet at $T=973$ K.

207

208 The calculation was made according to Equation 6

$$\begin{aligned} 209 \quad \Delta_{(\text{step A})}H^0(298.15 \text{ K}) &= [H^0(973 \text{ K}) - H^0(298.15 \text{ K}) + \Delta_{(\text{step A})}H^0(973\text{K})]\text{clinocllore} - \\ 210 \quad [H^0(973 \text{ K}) - H^0(298.15 \text{ K})]\text{partly dehydrohlyated clinocllore} - \\ 211 \quad 1.7 [H^0(600 \text{ K}) - H^0(298.15 \text{ K})]\text{H}_2\text{O}(\text{l}) \end{aligned} \quad (6)$$

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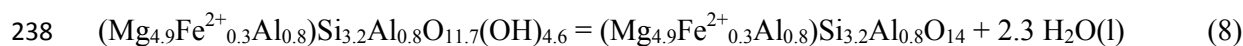
213 where $[H^0(973 \text{ K}) - H^0(298.15 \text{ K}) + \Delta_{(\text{step A})}H^0(973 \text{ K})]\text{clinocllore}$ and $[H^0(973 \text{ K}) - H^0(298.15$
214 $\text{K})]\text{partly dehydrohlyated clinocllore}$ are the experimental data obtained in the present work;
215 $[H^0(973 \text{ K}) - H^0(298.15 \text{ K})]\text{H}_2\text{O}(\text{l})$ is the reference data (Robie and Hemingway, 1995) for liquid
216 water.

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

222 *The enthalpy of dehydroxylation of the 2:1 layer (step B).* To determine the enthalpy of
223 dehydroxylation of octahedral layer in the 2:1 package (*step B*), the additional dissolution
224 experiments were performed using the samples which were calcinated at 973 K (700°C) for about
225 1 h and at 1223 K (950°C) for about 30 min. The IR absorption spectrum of the sample, which
226 was heated at 973 K (Fig. 2 a), shows a decrease of the intensity of the absorption bands in the
227 region of 3590-3416 cm^{-1} ; it corresponds to the removal of OH-groups from the interlayer
228 octahedral sheet. The spectrum of the sample, which was warmed at 1223 K (Fig. 2 b),
229 demonstrates the absence of the absorption bands in the range of 3300-3700 cm^{-1} ; it confirms the
230 full dehydroxylation of the sample. The sample weight was controlled before and after heating.
231 The sample weight loss during heating to 973 K was 5.5 % that corresponded to the removal of
232 1.7 moles of water. The weight loss during calcinations at 1223 K was equal to 13.1 % that
233 corresponded to the removal of 4 moles of water (the fully dehydroxylation of clinochlore).

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

236



239

240 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;
241 $(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{11.7}(\text{OH})_{4.6}$ is the partly dehydroxylated clinochlore after
242 dehydroxylation of the interlayer octahedral sheet at $T=973$ K (according to the reaction 5);
243 $(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{14}$ is the fully dehydroxylated clinochlore.

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

245

246 $\Delta_{(\text{step } A + \text{step } B)}H^0(298.15 \text{ K}) = \Delta H_f^0(298.15 \text{ K}) (\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{14} +$

247 $4 \Delta H_f^0(298.15 \text{ K}) \text{H}_2\text{O}(\text{l}) - \Delta H_f^0(298.15 \text{ K}) (\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})[\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{10}](\text{OH})_8 \quad (9)$

248 $\Delta_{(\text{step } B)}H^0(298.15 \text{ K}) = \Delta H_f^0(298.15 \text{ K}) (\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{14} +$

249 $2.7 \Delta H_f^0(298.15 \text{ K}) \text{H}_2\text{O}(\text{l}) - \Delta H_f^0(298.15 \text{ K}) (\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{11.7}(\text{OH})_{4.6}. \quad (10)$

250

251 The enthalpies of formation $\Delta H_f^0(298.15 \text{ K})$ for the fully dehydroxylated clinochlore
252 $(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{14}$ and for the partly dehydroxylated clinochlore (after *step A*)
253 $(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{11.7}(\text{OH})_{4.6}$ were calculated using the equations similar to Equation 4,
254 they were found equal to -7282 ± 18 and -8245.2 ± 8.1 kJ/mol, respectively. The latter value
255 relates to the partially dehydroxylated clinochlore, which according to Villi eras et al. (1993, 1994)
256 has a microporous “modified chlorite structure” and a broad perspective of industrial application.

257 On the basis of these data and the value of $\Delta H_f^0(298.15 \text{ K})$ for clinochlore of initial composition
258 (Table 7), and the reference data for $\Delta H_f^0(298.15 \text{ K}) \text{H}_2\text{O}(\text{l})$ (Robie and Hemingway 1995) the
259 enthalpies of the reaction 7 (*step A + step B*) and of the reaction 8 (*step B*) were found to be $383 \pm$
260 24 and 307 ± 20 kJ, respectively. The values of $\Delta_{(\text{step } B)}H^0(298.15 \text{ K})$ calculated per one mole of
261 H_2O at 298.15 K were obtained to be equal: 127 ± 18 kJ (using the reaction 5 for *step A* and
262 reaction 7 for *step A + step B*) and 133.5 ± 8.6 kJ (using the reaction 8 for *step B*). The obtained
263 data are in good agreement within the error limits and are significantly exceed the given above (in
264 the previous section) enthalpy of dehydroxylation of the interlayer octahedral sheet (*for step A*); it
265 confirms the different bond energies of the hydroxyl groups in the structure of clinochlore. The
266 average value turned out to equal: 131 ± 10 kJ/(mol H_2O).

267 The obtained value is close to the determined previously values of the enthalpy of
268 dehydroxylation for the montmorillonite (166 ± 10 kJ/(mol H_2O)) (Ogorodova et al. 2013) and for
269 the sepiolite (145 ± 14 kJ/(mol H_2O)) (Ogorodova et al. 2014). The crystal structures of all these
270 minerals have a similar structural element (three-layer packages of 2:1 type), which is composed

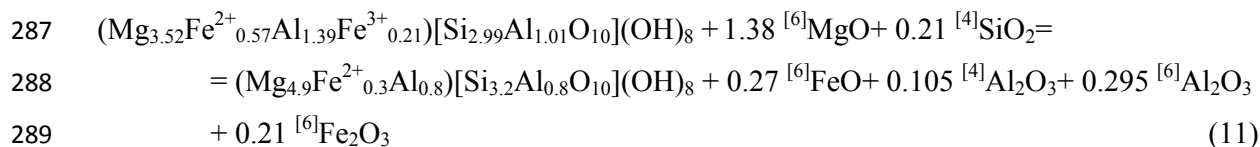
271 of two tetrahedral layers with the octahedral layer between them; each cation of this octahedral
 272 layer is surrounded by four apical oxygens and by two hydroxyl groups. The difference between
 273 the crystal structures of these minerals lies in the different filling of the space between the 2: 1
 274 packages. In montmorillonites this interlayer sheet contains the exchange cations and the water
 275 molecules; in sepiolite it contains only water molecules; in chlorites it contains Al and Mg cations
 276 associated with the hydroxyl groups.

277

278 **The Gibbs energies of formation**

279

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



$$\begin{aligned}
 290 \quad & S^\circ(298.15 \text{ K})_{\text{studied clinochlore}} = S^\circ(298.15 \text{ K})_{\text{Mg-Fe clinochlore}} + 1.38 (S-V)^{[6]}\text{MgO} \\
 291 \quad & + 0.21 \text{ }^{[4]}(S-V)\text{SiO}_2 - 0.27 (S-V)^{[6]}\text{FeO} - 0.105 (S-V)^{[4]}\text{Al}_2\text{O}_3 - 0.295 (S-V)^{[6]}\text{Al}_2\text{O}_3 \\
 292 \quad & - 0.21 (S-V)^{[6]}\text{Fe}_2\text{O}_3 \qquad \qquad \qquad (12)
 \end{aligned}$$

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

$$\begin{aligned}
 298 \quad & \Delta S_f^\circ (298.15 \text{ K})_{\text{Mg-Fe clinochlore}} = S^\circ(298.15 \text{ K})_{\text{Mg-Fe clinochlore}} - 4.9 S^\circ(298.15 \text{ K})_{\text{Mg}} \\
 299 \quad & - 0.3 S^\circ(298.15 \text{ K})_{\text{Fe}} - 1.6 S^\circ(298.15 \text{ K})_{\text{Al}} - 3.2 S^\circ(298.15 \text{ K})_{\text{Si}} - 9 S^\circ(298.15 \text{ K})_{\text{O}_2} \\
 300 \quad & - 4 S^\circ(298.15 \text{ K})_{\text{H}_2}. \qquad \qquad \qquad (13)
 \end{aligned}$$

301 The calculation for sample II was performed in a similar manner as for sample I. The obtained
 302 values of $\Delta S_f^\circ (298.15 \text{ K})$ of clinochlores and our data on the enthalpies of its formation from the
 303 elements were then used to calculate the values of $\Delta G_f^\circ (298.15 \text{ K})$ for these minerals (Table 7).

304

305 **Thermodynamic properties of clinochlores of the theoretical composition**

306 The enthalpies of formation of clinochlores of the theoretical compositions of end and
307 intermediate members of the clinochlore $(\text{Mg}_5\text{Al})[\text{Si}_3\text{AlO}_{10}](\text{OH})_8$ - chamosite
308 $(\text{Fe}_5\text{Al})[\text{Si}_3\text{AlO}_{10}](\text{OH})_8$ series (Table 8) were calculated on the basis of the dissolution
309 calorimetric data for the natural minerals. For this purpose, the results of the calorimetric
310 measurements for the studied clinochlores were corrected on the deviations of their composition
311 from the ideal formula; the amendments were estimated using the thermochemical data for the
312 corresponding oxides (Table 6). Values of the standard entropies and Gibbs energies were
313 estimated by the same way as for the natural minerals and are given in the Table 7.

314 The obtained value of the Gibbs energy of formation for clinochlore of composition
315 $(\text{Mg}_5\text{Al})[\text{Si}_3\text{AlO}_{10}](\text{OH})_8$ (Table 7) agrees with the results of the calculation from P-T equilibria
316 (Jenkins and Chernosky 1986; Berman 1988; Robie and Hemingway 1995; Holland and Powell
317 2011) (Table 1). Comparison of our data for the iron-rich minerals with literature data was
318 hampered because of a considerable difference in their composition.

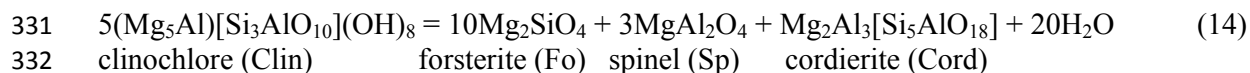
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IMPLICATIONS

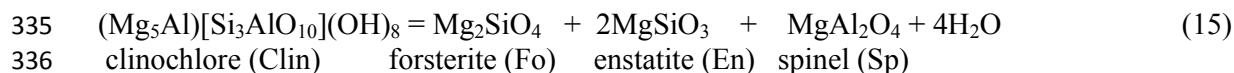
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322 Our new experimental determinations of the enthalpies of formation of clinochlores as well as
323 the enthalpies of dehydroxylation of the interlayer octahedral sheet and 2:1 layers in clinochlores
324 are significant addition for understanding of physicochemical conditions of formation of chlorites
325 in different geochemical environments. Obtained data (enthalpies and the Gibbs energies of
326 formation) allow to carry out a quantitative thermodynamic modeling of the stability of chlorites
327 in the system $(\text{Mg},\text{Fe})\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. The upper thermal stability of clinochlore
328 $(\text{Mg}_5\text{Al})[\text{Si}_3\text{AlO}_{10}](\text{OH})_8$ in the system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ with using new thermodynamic
329 data was calculated according to the reactions 14 and 15 by means of HCh software (Shvarov
330 2015).



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334 and



337

338 The Gibbs energies of formation for cordierite, enstatite, spinel and forsterite were computed with
339 parameters from Unitherm database (Shvarov 2015). Water properties were calculated from Gibbs
340 code using Haar-Gallagher-Kell (HGK) model (Kestin et al. 1984). The results of calculation

341 (Fig. 3) demonstrate a good agreement with experimental data on clinochlore *P-T* stability
342 (Fawcett and Yoder 1966; Chernovsky 1974; Staudigel and Schreyer 1977; Jenkins 1981; Jenkins
343 and Chernovsky 1986). The obtained thermodynamic parameters of Mg-Fe clinochlores can be
344 useful also for defining optimal technological conditions for the industrial processing of ores
345 containing clinochlores. It may be iron ores from skarn deposits in which the clinochlores present
346 as a part of the main ore body; as well as it may be the various polymetallic ores from
347 hydrothermal deposits, where the host rocks near the ore bodies were subjected to the strong
348 chloritization as a result of weathering. The first results concerning the enthalpy of the
349 dehydroxylation of Mg-chlorite and the enthalpy of formation of the new microporous phase with
350 modified chlorite structure formed during dehydroxylation of the interlayer hydroxide sheet can
351 be used to optimize conditions of obtaining this new promising microporous adsorbent on the
352 basis of chlorite deposits for industrial applications.

353

354

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355

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TABLE 2. Chemical composition (wt%) of the studied clinochlores^a

| Oxides | Sample I ^b (Nicolae- Maximilianovskaya mine) | Sample II ^c (Tarlashkinsky massif) |
|--------------------------------|---|---|
| SiO ₂ | 33.59 ± 0.31 | 29.97 ± 0.54 |
| TiO ₂ | - | - |
| Al ₂ O ₃ | 16.09 ± 0.27 | 20.34 ± 0.38 |
| Cr ₂ O ₃ | 0.01 ± 0.00 | - |
| MgO | 33.91 ± 0.48 | 29.07 ± 0.51 |
| FeO | 3.31 ± 0.08 | 7.92 ± 0.42 |
| NiO | - | 0.03 ± 0.01 |
| MnO | 0.01 ± 0.00 | - |
| CaO | 0.01 ± 0.00 | 0.01 ± 0.00 |
| Na ₂ O | - | 0.15 ± 0.01 |
| K ₂ O | - | 0.01 ± 0.01 |
| H ₂ O ^d | 13.1 | 12.5 |

^aUncertainties are calculated using Student's *t*-distribution with a 95% confidence interval.

^bUncertainties are calculated on the basis of 7 determinations.

^cUncertainties are calculated on the basis of 5 determinations.

^dThe water content was determined by thermogravimetric method.

TABLE 6. Thermochemical data used in calculation of the enthalpies of formation of studied clinochlores (kJ/mol)

| Component | $[H^0(973\text{ K})-H^0(298.15\text{ K})+\Delta_{sol}H^0(973\text{ K})]$ | $\Delta H_f^0(298.15\text{ K})^a$ |
|---|--|-----------------------------------|
| Mg(OH) ₂ (brucite) | 111.5 ± 1.6^b | -924.5 ± 0.4 |
| SiO ₂ (quartz) | 39.43 ± 0.2^c | -910.7 ± 1.0 |
| Al ₂ O ₃ (corundum) | 107.38 ± 0.59^d | -1675.7 ± 1.3 |
| Fe ₂ O ₃ (hematite) | 130.71 ± 0.54^e | -826.2 ± 1.3 |
| MgO(periclase) | 36.38 ± 0.59^f | -601.6 ± 0.3 |

^a Reference data (Robie and Hemingway 1995).

^b According to Kiseleva and Ogorodova (1984).

^c Calculated using the reference data on $[H^0(973\text{ K})-H^0(298.15\text{ K})]$ (Robie and Hemingway 1995) and experimental data on $\Delta_{sol}H^0(973\text{ K})$ according to Kiseleva et al. (1979).

^d Calculated using the reference data on $[H^0(973\text{ K})-H^0(298.15\text{ K})]$ (Robie and Hemingway 1995) and experimental data on $\Delta_{sol}H^0(973\text{ K})$ according to Ogorodova et al. (2003).

^e Calculated using the reference data on $[H^0(973\text{ K})-H^0(298.15\text{ K})]$ (Robie and Hemingway 1995) and experimental data on $\Delta_{sol}H^0(973\text{ K})$ according to Kiseleva (1976).

^f Calculated using the reference data on $[H^0(973\text{ K})-H^0(298.15\text{ K})]$ (Robie and Hemingway 1995) and experimental data on $\Delta_{sol}H^0(973\text{ K})$ according to Navrotsky and Coons (1976).

TABLE 1. Summary of thermodynamic properties of clinochlores at $T=298.15$ K

| ΔH_f^0 (kJ/mol) | S^0 [J/(K·mol)] | ΔG_f^0 (kJ/mol) | Reference | Method of determination |
|---|---------------------|-------------------------|--------------------------------|---------------------------------|
| (Mg₅Al)[Si₃AlO₁₀](OH)₈ | | | | |
| | | - 8259.2 | (Zen 1972) | Estimation |
| | | - 8195.2 | (Tardy and Garrels 1974) | -»- |
| | | - 8181.4 5 | (Nriagu 1975) | -»- |
| - 8856.2 | 465.3 | - 8207.8 | (Helgeson et al. 1978) | Calculation from P-T equilibria |
| | | - 8232.3 ± 3.8 | (Dorogokupetz and Karpov 1984) | -«- |
| - 8872 ± 27 | 459 ± 33 | - 8220 ± 27 | (Jenkins and Chernosky 1986) | -«- |
| - 8909.59 | 435.15 | - 8250.55 | (Berman 1988) | -«- |
| - 8919 ± 20 | 421.0 ± 15 | - 8255.8 ± 20 | (Robie and Hemingway 1995) | -«- |
| - 8929.86 ± 1.65 | 410.50 | - 8263.35 | (Holland and Powell 1998) | |
| | | - 8190.83 | (Vicillard 2002) | Estimation |
| | 425.6 ± 0.4 | | (Bertoldi et al. 2007) | Heat-pulse calorimetry |
| - 8909.23 ± 1.55 | 437.00 ^a | - 8250.62 ^b | (Holland and Powell 2011) | Calculation from P-T equilibria |

TABLE 1 continued

| | | | | | |
|-------------------|---------------|-------------------|---|--|--|
| | | | $(\text{Mg}_{3.52}\text{Fe}^{2+}_{0.57}\text{Al}_{1.39}\text{Fe}^{3+}_{0.21})[\text{Si}_{2.99}\text{Al}_{1.01}\text{O}_{10}](\text{OH})_8$ | | |
| | | - 7869 ± 3 | (Kittrick 1982) | | Study of solubility |
| | | | $(\text{Mg}_{3.24}\text{Fe}^{2+}_{0.99}\text{Al}_{1.44}\text{Fe}^{3+}_{0.07})[\text{Si}_{2.97}\text{Al}_{1.03}\text{O}_{10}](\text{OH})_8$ | | |
| | | - 7793 ± 3 | (Kittrick 1982) | | --<< |
| | | | $(\text{Mg}_{3.52}\text{Fe}^{2+}_{0.57}\text{Al}_{1.39}\text{Fe}^{3+}_{0.21})[\text{Si}_{2.99}\text{Al}_{1.01}\text{O}_{10}](\text{OH})_8$ | | |
| | 431.7 ± 5.0 | | (Hemingway et al. 1984) | | Measurement of low-temperature heat capacity |
| | | | $(\text{Mg}_{4.2}\text{Fe}^{2+}_{0.5}\text{Al}_{1.65}\text{Fe}^{3+}_{0.07}\text{Mn}_{0.005}\text{Ca}_{0.01}\text{Ni}_{0.01}\text{Cr}_{0.005}\square_{0.035})[\text{Si}_{2.83}\text{Al}_{1.17}\text{O}_{10}](\text{OH})_8$ | | |
| - 8770.64 ± 35.24 | 430 | - 8120.54 ± 32.63 | (Aja 2002) | | Calculation from P-T equilibria |
| | | | $(\text{Mg}_{2.952}\text{Fe}^{2+}_{1.712}\text{Al}_{1.116}\text{Fe}^{3+}_{0.215}\text{Mn}_{0.012}\text{Ca}_{0.011})[\text{Si}_{2.633}\text{Al}_{1.367}\text{O}_{10}](\text{OH})_8$ | | |
| - 8253.70 ± 22.75 | 468.40 ± 0.31 | - 7607.1 ± 23.4 | (Gailhanou et al. 2007) | | Acide solution calorimetry |
| | 469.4 ± 2.9 | | (Gailhanou et al. 2009) | | Measurement of low-temperature heat capacity |
| | | | $(\text{Mg}_{3.75}\text{Fe}_{1.25}\text{Al})[\text{Si}_3\text{AlO}_{10}](\text{OH})_8$ | | |
| - 8435.5 | | - 7796.6 | (Valero et al. 2012) | | Estimation |

^a 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.

^b Calculated in this work.

TABLE 3. Unit-cell dimensions and molar volumes for studied clinochlores

| Sample | a (Å) | b (Å) | c (Å) | β (°) | V (Å ³) | V_m^0 (298.15 K) (cm ³ /mol)* |
|--------|-----------|-----------|-------------|-------------|-----------------------|---|
| I | 5.3335(3) | 9.2377(5) | 14.3980(9) | 97.138(4) | 703.88 | 211.94 |
| II | 5.3374(4) | 9.2400(5) | 14.3308(10) | 97.222(7) | 701.15 | 211.12 |

* The molar volume was calculated using formula: $V_m^0(298.15\text{ K}) = a b c \sin(\beta) N_A/Z$, where $Z = 2$, N_A – the Avogadro constant.

TABLE 4. The results of thermal analysis of studied clinochlores

| Sample | Dehydroxylation | | | | | |
|--------|---------------------------|----------------|------------------------|---------------------------|----------------|------------------------|
| | step A | | | step B | | |
| | Temperature interval (°C) | t_{max} (°C) | The loss of mass (wt%) | Temperature interval (°C) | t_{max} (°C) | The loss of mass (wt%) |
| I | 550-800 | 695 | 6.3 | 800-950 | 900 | 6.8 |
| II | 550-750 | 665 | 2.9 | 750-950 | 890 | 9.6 |

TABLE 5. Results of calorimetric study of dehydroxylation and solution processes for studied clinochlores

| Composition of sample | Molar mass (g/mol) | Measured value | | |
|--|-----------------------|--|-----------------------|-----------------|
| | | | (J/g) | (kJ/mol) |
| Sample (I) | | | | |
| $(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})[\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{10}](\text{OH})_8$ | 564.95 | $H^\circ(973\text{ K})-H^\circ(298.15\text{ K})+\Delta_{\text{sol}}H^\circ(973\text{ K})$ | 1600.2 ± 25.3 (7) | 904 ± 14 |
| $(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})[\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{10}](\text{OH})_8$ | 564.95 | $H^\circ(973\text{ K})-H^\circ(298.15\text{ K})+\Delta_{\text{dehydr}}H^\circ(973\text{ K})$ | 1121.8 ± 52.8 (5) | 634 ± 30 |
| $(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{11.7}(\text{OH})_{4.6}$ | 534.32 | $H^\circ(973\text{ K})-H^\circ(298.15\text{ K})$ | 798.2 ± 28.3 (7) | 427 ± 15 |
| $(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{11.7}(\text{OH})_{4.6}$ | 534.32 | $H^\circ(973\text{ K})-H^\circ(298.15\text{ K})+\Delta_{\text{sol}}H^\circ(973\text{ K})$ | 1431.6 ± 11.3 (6) | 764.9 ± 6.1 |
| $(\text{Mg}_{4.9}\text{Fe}^{2+}_{0.3}\text{Al}_{0.8})\text{Si}_{3.2}\text{Al}_{0.8}\text{O}_{14}$ | 492.88 | $H^\circ(973\text{ K})-H^\circ(298.15\text{ K})+\Delta_{\text{sol}}H^\circ(973\text{ K})$ | 753.9 ± 36.1 (6) | 372 ± 18 |
| Sample (II) | | | | |
| $(\text{Mg}_{4.2}\text{Fe}^{2+}_{0.6}\text{Al}_{1.2})[\text{Si}_{2.8}\text{Al}_{1.2}\text{O}_{10}](\text{OH})_8$ | 575.04 | $H^\circ(973\text{ K})-H^\circ(298.15\text{ K})+\Delta_{\text{sol}}H^\circ(973\text{ K})$ | 1505.0 ± 39.3 (6) | 865 ± 23 |

* 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

| Composition of mineral | ΔH_f^0 (kJ/mol) | S^0 [J/(K mol)] | ΔG_f^0 (kJ/mol) |
|---|-------------------------|--------------------------|-------------------------|
| Natural clinochlores | | | |
| (Mg _{4.9} Fe ²⁺ _{0.3} Al _{0.8})[Si _{3.2} Al _{0.8} O ₁₀](OH) ₈ (sample I) | - 8806 ± 16 | 445.3 ± 5.1 | -8151 ± 16 |
| (Mg _{4.2} Fe ²⁺ _{0.6} Al _{1.2})[Si _{2.8} Al _{1.2} O ₁₀](OH) ₈ (sample II) | - 8748 ± 24 | 446.8 ± 5.1 | - 8093 ± 24 |
| Clinochlores of theoretical composition | | | |
| (Mg ₅ Al)[Si ₃ AlO ₁₀](OH) ₈ ^b | - 8895 ± 16 | 439.3 ± 5.1 ^c | - 8237 ± 16 |
| (Mg ₄ Fe ²⁺ Al)[Si ₃ AlO ₁₀](OH) ₈ ^d | - 8640 ± 24 | 454.4 ± 5.1 | -7990 ± 24 |
| (Mg ₃ Fe ²⁺ ₂ Al)[Si ₃ AlO ₁₀](OH) ₈ ^d | - 8452 ± 24 | 469.3 ± 5.1 | - 7811 ± 24 |

^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 $S^\circ(298.15\text{ K})$ on the elements in their reference state (Robie and Hemingway 1995) [J/(K mol)]

| ^{[6]*} MgO | ^[6] FeO | ^[6] Al ₂ O ₃ | ^[4] Al ₂ O ₃ | ^[4] SiO ₂ | Mg | Fe | Al | Si | O ₂ | H ₂ |
|---------------------|--------------------|---|---|---------------------------------|--------|--------|--------|--------|----------------|----------------|
| 15.75 | 30.78 | 22.60 | 28.89 | 17.45 | 32.67 | 27.09 | 28.30 | 18.81 | 205.15 | 130.68 |
| ±0.53 | ± 0.83 | ± 0.84 | ± 1.06 | ± 0.38 | ± 0.10 | ± 0.13 | ± 0.08 | ± 0.08 | ± 0.02 | ± 0.02 |

* The coordination number of cation.

Figure 1

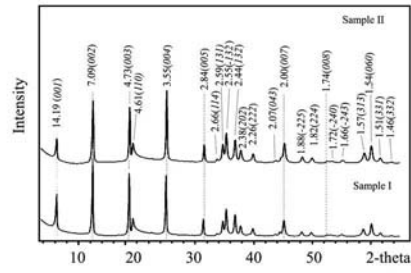


Figure 2

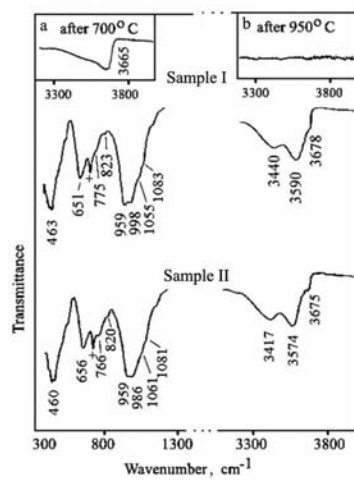


Figure 3

