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## REVISION 1

Running head: Prediction of  $\Delta H_f^\circ$  of hydrous sulfate minerals

# Prediction of enthalpies of formation of hydrous sulfates

By

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24 **Abstract-** A method for the prediction of the enthalpies of formation  $\Delta H_f^\circ$  for minerals of  
25 hydrous sulfates is proposed and is decomposed in the following two steps: 1) an evaluation  
26 of  $\Delta H_f^\circ$  for anhydrous sulfates based on the differences in the empirical electronegativity  
27 parameter  $\Delta_{\text{H}}\text{O}^- \text{M}^{Z+}(\text{c})$  characterizing the oxygen affinity of the cation  $\text{M}^{Z+}$ ; and 2) a  
28 prediction of the enthalpy of hydration based on the knowledge of the enthalpy of dissolution  
29 for anhydrous sulfates.

30 The enthalpy of formation of sulfate minerals from constituent oxides is correlated to  
31 the molar fraction of oxygen atoms bound to each cation and to the difference of the oxygen  
32 affinity  $\Delta_{\text{H}}\text{O}^- \text{M}^{Z+}(\text{c})$  between any two consecutive cations. The  $\Delta_{\text{H}}\text{O}^- \text{M}^{Z+}(\text{c})$  value, using a  
33 weighing scheme involving the electronegativity of a cation in a given anhydrous sulfate, is  
34 assumed to be constant. This value can be calculated by minimizing the difference between  
35 the experimental enthalpies and calculated enthalpies of formation of sulfate minerals from  
36 constituent oxides.

37 The enthalpy of hydration is closely related to the nature of the cation in the anhydrous  
38 salt, to the number of water molecules in the chemical formula and to the enthalpy of  
39 dissolution for the anhydrous salt.

40 The results indicate that this prediction method gives an average value within 0.55% of  
41 the experimentally measured values for anhydrous sulfates and 0.21% of the enthalpies of  
42 hydration or hydrous sulfates.

43 The relationship between  $\Delta_{\text{H}}\text{O}^- \text{M}^{Z+}(\text{sulfate})$ , which corresponds to the electronegativity  
44 of a cation in a sulfate compound, and known parameter  $\Delta_{\text{H}}\text{O}^- \text{M}^{Z+}(\text{aq})$  were determined.  
45 These determinations allowed the prediction of the electronegativity of some anhydrous  
46 transition metal double sulfate and contributed to the prediction of the enthalpy of formation  
47 for any hydrous double sulfate.

48 With a simplified prediction of the entropy of a hydrous sulfate, calculations of Gibbs

49 free energy of formation can be evaluated and contribute to the knowledge of the stability of  
50 some hydrous sulfates in different environmental conditions such as temperature or air  
51 moiety. Therefore, to check the reliability of the predictive model, stability fields for some  
52 hydrous ferric sulfates such as pentahydrate ferric sulfate, lawsonite, kornelite, coquimbite  
53 and quenstedtite versus temperature and relative humidity were studied and compared with  
54 experimental measurements.

55

56 Key words: enthalpy of formation, hydrous double sulfate, entropy, enthalpy of hydration,  
57 double sulfates, sulfate, relative humidity, hydrous ferric sulfate, kornelite, lawsonite  
58 coquimbite, quenstedtite, halotrichite, pickeringite, glauberite, picromerite, tamarugite,  
59 kalinite, syngenite, mendozite, tschermigite, krausite, goldichite, aphthitalite, bilinite,  
60 romerite, solubility product, Gibbs free energy, temperature

61

62

63 1. INTRODUCTION

64 Sulfate minerals can be of economic interest (gypsum for manufacturing wallboard,  
65 Al-sulfates in the tanning and dyeing industries, barite in petroleum industry, jarosite in  
66 metallurgical industry and in agriculture, etc.) and are of ecological interest too (sulfates are  
67 used to remove metals from polluted water), but they can also induce several environmental  
68 problems (Alpers et al. 2000). Indeed, the solubility of some sulfate minerals induces a  
69 provisional storage of metals and acidity, but when they dissolve, metals are released and  
70 water becomes very acidic, causing disastrous environmental consequences such as the death  
71 of aquatic organisms, destruction of plants, massive erosion of land and the corrosion of  
72 anthropogenic infrastructure.

73 Sulfate minerals occur in various natural environments (points 1, 2, 3, 5 and 6 below)  
74 and are sometimes modified later by human activities (point 2 below) or are only the result of  
75 human activities (point 4 below). Some examples of sulfate occurrences are presented below,  
76 and the usefulness of thermodynamic data of sulfate minerals are demonstrated in a few  
77 examples.

78 1) Evaporite deposits: the evaporation of sea water or continental water leads to sequences of  
79 mineral formation, including especially sulfate minerals. Spencer (2000) predicted various  
80 sequences of sulfate formation from modern marine or non-marine water using the  
81 thermochemical model of Harvie et al. (1984). Concurrently, Spencer (2000) performed  
82 careful petrographic studies (mineral texture and fabric, replacement features...) on evaporite  
83 rock, formed from the evaporation of modern sea water. His ultimate goal is to calibrate the  
84 model to perform the reverse modelling, i.e., find the chemical compositions of ancient sea  
85 waters from the mineralogy of evaporite deposits. Note that, in the mineralogical sequences  
86 predicted by Spencer (2000), few double sulfates occur and thermodynamic data of them are  
87 rarely available in literature. Do not take into account the multitude of potential intermediate

88 phases which can form, can lead to errors in the prediction of sulfates formation.

89 2) Weathering (oxidation) of sulfide minerals in coal deposits or pyritiferous rocks (pyrite,  
90 marcasite) and in metallic sulfides ore deposits (galena, sphalerite, chalcocite, bornite,  
91 covellite, etc.) induces the formation of sulfate efflorescence. Many sulfide deposits  
92 are exploited, while other mine sites have been abandoned (500,000 inactive sites in the US  
93 (Lyon et al. 1993)). Efflorescences are found in open pits, on waste rock and on tailing piles.  
94 Numerous and various sulfates can precipitate, for example, at the Comstock Lode (Nevada),  
95 the following were found: epsomite, pickeringite, gypsum, melanterite, goslarite,  
96 pentahydrate, copiapite, voltaite and rhomboclase (Milton and Johnston 1938). Problems  
97 occurred when rainfall events induced the dissolution of sulfate efflorescence; the water is  
98 enriched with metals and acidifies. This is the case at Richmond Mine at Iron Mountain  
99 (California), where approximately 600,000 m<sup>3</sup> of underground water have very low pH (<1  
100 and sometime negative (Nordstrom and Alpers 1999) and contain many g/l of heavy metals. It  
101 is necessary to plan for the remediation of such a mining site during exploitation, not when  
102 problems occur, by simulating the water composition as a function of the sulfate precipitation  
103 sequence and sulfate dissolution after a rainfall, which requires knowledge of the  
104 thermodynamic properties of all possible sulfate minerals.

105 3) Sulfates can occur in acidic soil developed from sulfide deposits accumulated under  
106 mangroves and reed swamps in tidal areas (Bigham and Nordstrom 2000).

107 4) Sulfates are produced by mineral processing in ore deposits. For example, to extract  
108 uranium from ore, sulfuric acid is used to attack U-bearing minerals and release uranium,  
109 which will complex with the SO<sub>4</sub><sup>2-</sup> anion to form UO<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub><sup>4-</sup>. However, not only uranium  
110 bearing minerals are dissolved, others ore minerals can dissolved to, releasing elements in  
111 solution. These elements can complex them with sulfates anions to form sulfate minerals. The  
112 tailing piles are often stored in mine sites, and the same problems describe above can occur

113 during rainfall.

114 5) Volcanic environments (around crater lakes, fumaroles and acid hot springs) where

115 magmatic gases ( $\text{H}_2\text{S}$  and  $\text{SO}_2$ ) are oxidized by microbial activity to form  $\text{H}_2\text{SO}_4$ , which

116 reacts with volcanic rock to form sulfate minerals (Jambor et al. 2000).

117 6) Sulfate minerals have been found in abundance and on extensive areas on the surface of

118 Mars, which requires the ancient presence of an acid-sulfate brine. Simulations of the

119 evaporation of hypothetical Martian water were processed using the FREZCHEM model

120 (Marion et al. 2008). Many sulfate minerals were predicted to form ( $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$ ,

121  $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ ,  $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ , sulfates of the jarosite family and mixed  $\text{Fe}^{2+}$ -

122  $\text{Fe}^{3+}$  sulfate such as romerite or bilinite). However, the thermodynamic data used for some of

123 these sulfates come from debatable estimations (Hemingway et al. 2002).

124 Most sulfates formed in the environments described briefly above are hydrated in specific

125 humidity conditions, and thermodynamic data for hydrated sulfates are useful to explain

126 different mineral paragenesis. However, few values are available in the literature for hydrated

127 sulfates and even fewer for hydrated double sulfates. The aim of this study is to provide a way

128 to evaluate the thermodynamic properties of hydrous double sulfates from existing

129 thermodynamic values in the literature.

130 Tardy and Gartner (1977) were the first to propose a method of evaluating the Gibbs

131 free energy of anhydrous simple sulfates using a method developed by Tardy and Garrels

132 (1976, 1977) and Tardy and Vieillard (1977) to predict the Gibbs free energy of formation of

133 hydroxides, silicates and phosphates. Tardy and Gartner (1977)'s method involves a linear

134 correlation between the Gibbs free energy from the constituent oxides of the sulfate and a

135 parameter noted as  $\Delta_G O^\ominus$  (difference in electronegativities) for the specific cation in sulfate

136 compounds. At the same time, Gartner (1979) adapted the method of Tardy and Gartner

137 (1977) to evaluate the enthalpy of formation of anhydrous simple sulfates.

138 Mercury et al. (2001) provided a way of evaluating the enthalpy of formation of  
139 hydrated sulfates by an additive model in which the enthalpy of formation of ice-like water in  
140 sulfates is assumed to be constant. However, these two combined methods (anhydrous and  
141 hydrous sulfates) have a rather large gap: Gartner (1977)'s model is not appropriate for  
142 double hydrous sulfates and enthalpy of formation of hydrous sulfates is not linearly  
143 correlated with number of H<sub>2</sub>O molecules as described by Mercury et al. (2001).

144 An improved method of prediction of  $\Delta H^{\circ}_f$  of hydrous sulfates is proposed through the  
145 following two methods of evaluation: first based on the difference in electronegativities (or  
146  $\Delta_{\text{H}}\text{O}^-$  cation parameter) similar to Vieillard and Tardy (1988a) and Vieillard (1994a, 1994b)  
147 but with a better integration of double sulfates and second based on the enthalpy of hydration  
148 and the enthalpy of dissolution of the anhydrous phase (Vieillard and Jenkins 1986a, 1986b,  
149 1986c; Vieillard 2012).

150

## 151 2. METHODOLOGY

### 152 2.1. Enthalpy of formation of anhydrous sulfates

153 The details concerning the prediction method of enthalpies of formation of minerals  
154 have been explained by Vieillard and Tardy (1988a) and are based on the parameters  $\Delta_{\text{H}}\text{O}^-$   
155  $\text{M}^{Z+}(\text{aq})$  and the enthalpies of formation from constituent oxides,  $\Delta H^{\circ}_{f,\text{ox}}$ . The model of  
156 prediction was initially developed within different families of compounds such as phosphates  
157 (Tardy and Vieillard 1977; Vieillard 1978), hydroxides (Tardy and Garrels 1976), silicates  
158 (Tardy and Garrels 1977), nitrates, and sulfates carbonates (Tardy and Gartner 1977; Gartner  
159 1979).

#### 160 2.1.1. Definitions of parameters $\Delta_{\text{H}}\text{O}^- \text{M}^{Z+}(\text{aq})$ and $\Delta H^{\circ}_{f,\text{ox}}$

161 The parameter  $\Delta_{\text{H}}\text{O}^- \text{M}^{Z+}(\text{aq})$  characterizes a given cation  $\text{M}^{Z+}$  and is defined as the  
162 difference between the enthalpy of formation of the corresponding oxide  $\Delta H^{\circ}_f \text{MO}_x(\text{c})$  and the



163 enthalpy of formation of the corresponding aqueous cation  $\Delta H_f^\circ M^{z+}(\text{aq})$  as follows:

164 
$$\Delta_{\text{H}}\text{O}^\ominus\text{M}^{\text{Z}^+}(\text{aq}) = \frac{1}{x} [\Delta H_f^\circ \text{MO}_x(\text{c}) - \Delta H_f^\circ \text{M}^{\text{Z}^+}(\text{aq})] \quad (1)$$

165 where  $z$  is the charge of the cation  $M^{z+}$ , and  $x$  is the number of oxygen atoms combined with  
166 one atom of  $M$  in the oxide ( $x = z/2$ ), so the difference in Equation 1 refers to one oxygen  
167 atom. A set of values of  $\Delta_{\text{H}}\text{O}^\ominus\text{M}^{\text{Z}^+}(\text{aq})$  is proposed here (Table 1) and comes from Wagman et  
168 al. (1982), Robie and Hemingway (1995) and Cox et al. (1989). Vieillard (2000) showed the  
169 influence of a cation on its oxygen affinity by a relationship between the parameter  $\Delta_{\text{H}}\text{O}^\ominus$   
170  $M^{z+}(\text{aq})$  and the electronegativity difference between the cation and oxygen. The concept of  
171 the electronegativity  $\chi$  was defined by Pauling (1960) as the power of an atom in a molecule  
172 to attract electrons from another atom. The larger the difference in electronegativity between  
173 atoms and the oxygen, the higher the energy of formation of the compound will be.

174 Considering a binary oxide  $\text{ABO}_N$  (where  $A$  and  $B$  are different cations), it may be  
175 decomposed in a sum of two oxides  $\text{AO}_{n1}$  and  $\text{BO}_{n2}$ . The energy of formation of  $\text{ABO}_N$  can be  
176 written as:

177 
$$E(\text{ABO}_N) = E(\text{AO}_{n1}) + E(\text{BO}_{n2}) + kX_A X_B (\chi_A - \chi_B)^2 \quad (2)$$

178 The last term, representing the energy of formation of the compound from  $\text{AO}_{n1}$  and  $\text{BO}_{n2}$ , is  
179 proportional to the molar fraction of oxygen atoms related to the cations  $A$  ( $X_A$ ) and  $B$  ( $X_B$ )  
180 and to the electronegativity difference between the cations  $A$  and  $B$  bounded to the same  
181 oxygen atom. The fundamental basis of relationships between the parameter  $\Delta_{\text{H}}\text{O}^\ominus\text{M}^{\text{Z}^+}$  and  
182 the electronegativity are developed by Vieillard & Tardy, (1988b, 1989)

183

184 By considering an anhydrous sulfate  $(M_i)_{n_i} (\text{SO}_4)_{n_j}$  where the subscript  $n_i$  can be  
185 equal to 1 (simple sulfates) or 2 (double sulfates), the second parameter  $\Delta H_{f,\text{ox}}^\circ$ , designating  
186 the enthalpy of formation of a anhydrous sulfate from constituent oxides, is the difference

187 between  $\Delta H^\circ_f (M_i)_{n_i} (SO_4)_{n_j}$  and the sum of the enthalpies of formation of the different  
188 constituent oxides in the anhydrous sulfates. The formula is given by Equation 3:

$$189 \quad \Delta H^\circ_{f,ox} = \Delta H^\circ_f (M_i)_{n_i} (SO_4)_{n_j} - \sum_{i=1}^{i=n_s} (n_i) \Delta H^\circ_f (M_i O_{x_i}) \quad (3)$$

190 where  $n_i$  is the number of moles of oxides. The enthalpies of formation of oxides are given in  
191 Table 1.

192 A compilation of  $\Delta H^\circ_f$  of simple and double anhydrous sulfates is given in column I of  
193 Appendix A. The enthalpies of formation from constituent oxides are calculated and given in  
194 Column II, Appendix A. For double sulfates, an average value is generated (Equation 7) for  
195 the two cations  $M_1$  and  $M_2$  as shown for  $K_2Mg(SO_4)_2$ .

$$196 \quad \Delta H^\circ_{f,ox}[K_2Mg(SO_4)_2] = \Delta H^\circ_f [K_2Mg(SO_4)_2] - \Delta H^\circ_f [K_2O] - \Delta H^\circ_f [MgO] - 2 * \Delta H^\circ_f [SO_3] \quad (4)$$

197

$$198 \quad \Delta_{H^0}O=K^+(aq) = [\Delta H^\circ_f [K_2O] (c) - 2 * \Delta H^\circ_f [K^+ ](aq)] \quad (5)$$

$$199 \quad \Delta_{H^0}O=Mg^{2+}(aq) = [\Delta H^\circ_f [MgO](c) - \Delta H^\circ_f [Mg^{2+} ](aq)] \quad (6)$$

$$200 \quad \Delta_{H^0}O=[K_2Mg(SO_4)_2](aq) = \frac{1}{2} * [ [\Delta_{H^0}O=K^+(aq)] + [ \Delta_{H^0}O=Mg^{2+}(aq)] ] \quad (7)$$

### 201 2.1.2. Relationships between $\Delta H^\circ_{f,ox}$ and $\Delta_{H^0}O^- M^{z+}(aq)$

202 By plotting the calculated enthalpies of formation from oxides,  $\Delta H^\circ_{f,ox}$  (for 1  $SO_4$  or  
203  $\Delta H^\circ_{f,ox}/n_j$ ) versus  $\Delta_{H^0}O^- M^{z+}(aq)$  for simple sulfates or versus the average  $\Delta_{H^0}O^- M^{z+}(aq)$  of  
204 the cations for double sulfates (Figure 1), several relationships are observed among 14 simple  
205 and 37 double sulfates (corresponding to a total of 83 data). The linear relationship is  
206 (Equation 8):

$$207 \quad \Delta H^\circ_{f,ox} \text{ (per 1 } SO_4) = -1.238 * \Delta_{H^0}O^- M^{z+}(aq) - 445.29 \quad (8)$$

208 The Equation 8 is very similar to Equation 9 obtained by Gartner (1979) for 107 data  
209 points (35 simple sulfates):

$$210 \quad \Delta H^\circ_{f,ox} \text{ (per 1 } SO_4) = -1.259 * \Delta_{H^0}O^- M^{z+}(aq) - 440.88 \quad (9)$$

211 The difference between the Equations 8 and 9 can be explained by the number of

212 points and the introduction of double sulfates in this work. By considering anhydrous  
213 phosphates, sulfates, and silicates as compounds having two different cations, Vieillard and  
214 Tardy (1988a) showed an empirical relationships between  $\Delta H_{f,ox}^{\circ}$  and  $\Delta_H O^{\ominus} M^{z+}(aq)$  which  
215 can be applied to sulfate minerals by the following Equation 10:

$$216 \quad \Delta H_{f,ox}^{\circ}(M_i)_{n_i}(SO_4)_{n_j} = -\alpha * N * (X_i * X_j) * [\Delta_H O^{\ominus} M_i^{z_i+}(aq) - \Delta_H O^{\ominus} S^{6+}(aq)] \quad (10)$$

217 where N- is the total number of oxygen atoms in the compound and is equal to the sum of the  
218 number of oxygens  $X_i$  and  $X_j$ , related to the cations  $M_i$  and  $S^{6+}$ , respectively, in each oxide (  
219  $M_i O_{x_i}$  and  $SO_3$ ), *i.e.*:

$$220 \quad N = n_i * x_i + 3 * n_j \quad (11)$$

221  $X_i$  and  $X_j$  are the molar fractions of oxygen atoms related to cations  $M_i^{z_i+}$  and  $S^{6+}$ ,  
222 respectively, in the individual oxides  $M_i O_{x_i}$  and  $SO_3$ .  $\Delta_H O^{\ominus} M_i^{z_i+}(aq)$  and  $\Delta_H O^{\ominus} S^{6+}(aq)$  are  
223 calculated according to Equation 1.  $\alpha$  is an empirical coefficient characterizing a given family  
224 of compounds.

225 Rewriting Equation 8 under form of empirical Equation 10,  $\Delta_H O^{\ominus} M_i^{z_i+}(aq)$  and  $\alpha$  are  
226 evaluated to  $\Delta_H O^{\ominus} S^{6+}(aq) = -359.77 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\alpha_{\text{sulfate}} = -1.65$  for sulfates. As the enthalpy  
227 of formation of the aqueous cation  $S^{6+}(aq)$  is unknown, the value reported in table 1 is an  
228 indirect value of electronegativity of the cation  $S^{6+}$ .

229 The enthalpy of formation of minerals, derived from their constituent oxides, appears to  
230 be proportional to the following three parameters: (1) coefficient  $\alpha$ , which relates to the  
231 nature of the family, (2) the stoichiometric coefficient  $N * (X_i * X_j)$ , and (3) the difference  
232  $[\Delta_H O^{\ominus} M_i^{z_i+}(aq) - \Delta_H O^{\ominus} S^{6+}(aq)]$ . When two cations have the same oxygen affinity, the  
233 enthalpy of formation of a compound from the two oxides must be equal or close to zero. On  
234 the contrary, the lowest enthalpies of formation from oxides are obtained for electropositive

235 cations, which show a  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}_i^{\text{Z}_i^+}(\text{aq})$  value very different from  $\Delta_{\text{H}}\text{O}^{\ominus} \text{S}^{6+}(\text{aq})$ .

236 For double sulfates, the average value of  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}_i^{\text{Z}_i^+}(\text{aq})$  proposed by Gartner (1979)

237 hides the effective energetic cost between the two cations in the double sulfate. To take the

238 interaction among three any cations of a double sulfate into account, a new equation of the

239 enthalpy of formation from the oxides,  $\Delta\text{H}_{\text{f,ox}}^{\circ}$ , is proposed by Equation 12:

$$240 \quad \Delta\text{H}_{\text{f,ox}}^{\circ} = -\alpha * N * \left[ \sum_{i=1}^{i=2} \sum_{j=i+1}^{j=3} X_i * X_j * \left( \Delta_{\text{H}}\text{O}^{\ominus} \text{M}_i^{\text{Z}_i^+}(\text{aq}) - \Delta_{\text{H}}\text{O}^{\ominus} \text{M}_j^{\text{Z}_j^+}(\text{aq}) \right) \right] \quad (12)$$

241 where  $X_i$  and  $X_j$  are the molar fractions of oxygen bound to the cations  $\text{M}_i^{\text{Z}_i^+}$  and  $\text{M}_j^{\text{Z}_j^+}$  in

242 the individual oxides  $\text{M}_i\text{O}_{x_i}$  and  $\text{M}_j\text{O}_{x_j}$ , respectively, in the mineral formula:

$$243 \quad X_i = \frac{1}{N} (n_i x_i) \quad (13)$$

$$244 \quad X_j = \frac{1}{N} (n_j x_j) \quad (14)$$

245 The total number of oxygen atoms of the compound must be equal to N:

$$246 \quad \sum_{i=1}^{i=n_s} n_i x_i = N \quad (15)$$

247 The parameters  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}_i^{\text{Z}_i^+}(\text{aq})$  and  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}_j^{\text{Z}_j^+}(\text{aq})$  are the same parameters defined

248 previously. By using the new formalism, the enthalpy of formation of simple and double

249 sulfates are calculated with values of  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}^{\text{Z}^+}(\text{aq})$  (Table 1) and displayed in column III of

250 Appendix A. The errors exhibit a large range of uncertainties (-5.61% to 7.98%, column IV of

251 Appendix A) with an average of 2.23%, i.e., an uncertainty of approximately 6 logarithm

252 units for solubility products (horizontal axis of Figure 2). For sulfate minerals with 3 or more

253 cations, this formalism (Equation 11) cannot be applied because of high probability of no-

254 sharing oxygen atom between cations.

255 These high discrepancies are due to the fact that the parameter  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}^{\text{Z}^+}(\text{aq})$  is

256 representative of the electronegativity of a cation in an aqueous state but not in a sulfate.

257 To generalize the technique and increase its accuracy, a new set of parameters  $\Delta_{\text{H}}\text{O}^{\ominus}$   
258  $\text{M}^{\text{z}+}(\text{c})$  for different cations in any simple and double sulfate is proposed. The concept of the  
259 parameter  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}^{\text{z}+}(\text{c})$  was initially proposed to predict the enthalpies of formation of  
260 different compounds (Vieillard 1982; Vieillard and Tardy 1988a) and has been extended to a  
261 wide families of silicates (Vieillard 1994a, 1994b), clay minerals (Vieillard 2000, 2002),  
262 alunite supergroup (Gaboreau and Vieillard 2004), and zeolites (Mathieu and Vieillard 2010).  
263 All these models of prediction are based on a new electronegativity scale for different ions  
264 located in different structural sites related to the crystallochemistry of silicates,  
265 phyllosilicates, alunite minerals and zeolites, respectively. In the case of sulfate compounds,  
266 one assumes one type of site such that the parameter  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}^{\text{z}+}(\text{c})$  of a cation  $\text{M}^{\text{z}+}$  is constant  
267 and the same in simple and double sulfates.

268 A new relationship between the enthalpy of formation of the oxides,  $\Delta\text{H}_{\text{f,ox}}^{\circ}$ , is proposed  
269 by considering the new parameter  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}^{\text{z}+}(\text{c})$ , characterizing the electronegativity of a  
270 cation in sulfate minerals and given by the following Equation 16, which is analogous to that  
271 of the enthalpy of formation (Vieillard, 1994a).

$$272 \quad \Delta\text{H}_{\text{f,ox}}^{\circ} = -N * \left[ \sum_{i=1}^{i=2} \sum_{j=i+1}^{j=3} X_i * X_j * \left( \Delta_{\text{H}}\text{O}^{\ominus} \text{M}_i^{\text{z}_i+}(\text{c}) - \Delta_{\text{H}}\text{O}^{\ominus} \text{M}_j^{\text{z}_j+}(\text{c}) \right) \right] \quad (16)$$

273  
274 The difference between Equations 12 and 16 are, first, the consideration of the parameter  
275  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}^{\text{z}+}(\text{c})$  instead of  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}^{\text{z}+}(\text{aq})$ , and second, the constant  $\alpha$  is set to -1 instead of -1.65.

276 The parameters  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}_i^{\text{z}_i+}(\text{c})$  and  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}_j^{\text{z}_j+}(\text{c})$  characterize the electronegativity of  
277 cations  $\text{M}_i^{\text{z}_i+}$  and  $\text{M}_j^{\text{z}_j+}$ , respectively, in sulfates and can be determined by minimizing the  
278 difference between the experimental and calculated enthalpy of formation from oxides.

279 In Equation 16, the interaction energy between two cations  $\text{M}_i^{\text{z}_i+}$  and  $\text{M}_j^{\text{z}_j+}$  is defined

280 by the difference  $\Delta_{\text{H}}\text{O}^- \text{M}_i^{\text{Z}_i^+}(\text{c}) - \Delta_{\text{H}}\text{O}^- \text{M}_j^{\text{Z}_j^+}(\text{c})$ . This term characterizes the short-range  
281 interactions between the different cations. Vieillard and Tardy (1988b, 1989) showed that the  
282 difference between the two  $\Delta_{\text{H}}\text{O}^-$  parameters is positive and can be assumed to be:

$$283 \left[ \Delta_{\text{H}}\text{O}^- \text{M}_i^{\text{Z}_i^+}(\text{c}) - \Delta_{\text{H}}\text{O}^- \text{M}_j^{\text{Z}_j^+}(\text{c}) \right] = 96.483 (\chi_{\text{M}_i} - \chi_{\text{M}_j})^2 \quad (17)$$

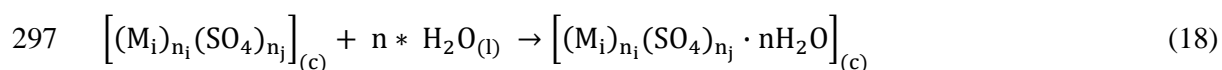
284 where  $\chi_{\text{M}}$  designates the Pauling's electronegativity of the cation  $\text{M}^{\text{Z}^+}$  (Pauling 1960) in the  
285 considered crystal structure, and the difference in the left-hand member of equation 17 should  
286 be expressed as an absolute value. When two cations sharing the same oxygen are identical,  
287 i.e., have the same oxygen affinity, the interaction energy is equal to zero. The greater the  
288 difference of oxygen affinity between two cations is, the stronger the interaction energy.

289

## 290 2.2. Enthalpy of hydration of simple and double sulfates

291 In evaluating the thermodynamic quantities, it is important to describe the standard state  
292 chosen for a given constituent. In the present study, the standard state for water is chosen as  
293 pure water at a temperature of 25°C with a vapor pressure of  $P_o=31.69\text{mbar}$  (Wagner and  
294 Pruss, 2002), and for the minerals, the dry compound is at a temperature of 25°C with a vapor  
295 pressure of  $P=0$ .

296 The hydration reaction may be expressed by the following reaction (Equation 18):



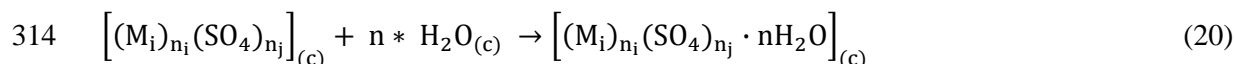
298 If we consider the standard enthalpy of hydration to be  $\Delta\text{H}_{\text{hyd},298.15\text{K}}^\circ$  for a given sulfate  
299 having  $n$  bounded molecules, the enthalpy of hydration is related to the total formation  
300 enthalpy of the sulfate,  $\Delta\text{H}_{\text{f},298.15\text{K}}^\circ$ , by the following (Equation 19):

$$301 \Delta\text{H}_{\text{hyd},298.15\text{K}}^\circ = \Delta\text{H}_{\text{f},298.15\text{K}}^\circ \left[ (\text{M}_i)_{n_i} (\text{SO}_4)_{n_j} \cdot n\text{H}_2\text{O} \right]_{(\text{c})} - \Delta\text{H}_{\text{f},298.15\text{K}}^\circ \left[ (\text{M}_i)_{n_i} (\text{SO}_4)_{n_j} \right]_{(\text{c})} - n * \Delta\text{H}_{\text{f},298.15\text{K}}^\circ (\text{H}_2\text{O}_{(\text{l})})$$

302 (19)

303 where  $\Delta H_{f,298.15K}^{\circ} \left[ (M_i)_{n_i} (SO_4)_{n_j} \cdot nH_2O \right]_{(c)}$  and  $\Delta H_{f,298.15K}^{\circ} \left[ (M_i)_{n_i} (SO_4)_{n_j} \right]_{(c)}$  are the standard  
304 enthalpy of formation of a sulfate in the hydrated and dehydrated states, respectively, and  
305  $\Delta H_{f,298.15K}^{\circ} (H_2O_{(l)})$  stands for the enthalpy of formation of bulk water. The unit of the  
306 enthalpy of formation,  $\Delta H_{hyd,298}^{\circ}$ , is based per n moles of bound water or per mole of an  
307 anhydrous sulfate.

308 The standard enthalpy of the hydration of the hydration water can be calculated if the  
309 enthalpies of formation of the anhydrous and hydrous end members are available in  
310 thermochemical tables or calculated from calorimetric measurements. Enthalpies of hydrated  
311 sulfates are compiled and given in column I of Appendix B.  
312 However, the thermodynamic properties of the hydration water can be estimated by  
313 considering the hypothetical intra-crystalline reaction (Equation 20):



315 where  $H_2O_{(c)}$  represents the hydration water. For the Equation 20 we can write (Equation 21):

$$316 \Delta H_{r,298.15K}^{\circ} = \Delta H_{f,298.15K}^{\circ} \left[ (M_i)_{n_i} (SO_4)_{n_j} \cdot nH_2O \right]_{(c)} - \Delta H_{f,298.15K}^{\circ} \left[ (M_i)_{n_i} (SO_4)_{n_j} \right]_{(c)} - n * \Delta H_{f,298.15K}^{\circ} [H_2O_{(c)}] \quad (21)$$

317 By assuming that  $\Delta H_{r,298.15K}^{\circ} = 0$ , the standard values of the  $\Delta H_{f,298.15K}^{\circ} (H_2O_{(c)})$ , is  
318 finally obtained from Equations 19 and 21 and presented in Equation 22:

$$319 \Delta H_{f,298.15K}^{\circ} (H_2O_{(c)}) = \frac{n * \Delta H_{f,298.15K}^{\circ} (H_2O_{(l)}) + \Delta H_{hyd,298.15K}^{\circ}}{n} \quad (22)$$

320 Mercury et al. (2001) proposed a model of prediction built on a simple additive scheme  
321 for all sulfate minerals and yielded a constant value of  $\Delta H_{f,298.15K}^{\circ} (H_2O_{(c)}) = -301.4 \pm 7.7$   
322  $\text{kJ.mol}^{-1}$ . The additive model gave errors ranging from -1.75% to +1.87% with an average of  
323 0.53%. The high error in the enthalpy of ice-like water in sulfate minerals does not allow a  
324 discussion on the impact of errors on variations of stability fields between hydrous sulfates.

325 To improve the accuracy of the prediction, Vieillard (2012) and Vieillard and Jenkins

326 (1986a, 1986b, 1986c) developed a model to predict the enthalpy of hydration from 349  
327 different hydrate salts and showed that the enthalpy of hydration is closely related to the  
328 nature of the cation in the anhydrous salt, the number of water molecules in the chemical  
329 formula and the nature of the salt. This formalism has been reassessed using the new value of  
330 ice standard enthalpy, compared to the model of Vieillard and Jenkins (1986a), set to  
331  $\Delta H_{f,298.15K}^{\circ}(\text{H}_2\text{O}_{(\text{ice})}) = -292.75 \text{ kJ}\cdot\text{mol}^{-1}$  (Vieillard 2012).

332 Because the previous model of prediction was initially tested on different salts of the  
333 same cation, we propose a new model for the prediction of the enthalpy of hydration for a  
334 whole family (i.e., sulfates) but with different cations.

335 Two parameters are required in this model of prediction. The first is the previously  
336 defined enthalpy of hydration (Equation 19), and the second is the parameter  $\Delta H_{\text{diss},298.15K}^{\circ}$ ,  
337 called enthalpy of dissolution and expressed as follows (Equation 23):

$$338 \Delta H_{\text{diss},298.15K}^{\circ} = n_j * \Delta H_{f,298.15K}^{\circ}[\text{SO}_4^{2-}] + n_i * \Delta H_{f,298.15K}^{\circ}[\text{M}_i^{z_i+}] - \Delta H_{f,298.15K}^{\circ}[(\text{M}_i)_{n_i}(\text{SO}_4)_{n_j}]_{(\text{c})} \quad (23)$$

339 in which  $\Delta H_{f,298.15K}^{\circ}[\text{SO}_4^{2-}]$  stands for the enthalpy of formation of the sulfate ion and is equal  
340 to  $-909.34 \text{ kJ}\cdot\text{mol}^{-1}$  (Cox et al. 1989). The proposed relationship of the enthalpy of hydration  
341 of a salt to the number of the molecules of water and the nature of the salt is (Vieillard (2012);  
342 Vieillard and Jenkins (1986a, 1986b, 1986c)):

$$343 \Delta H_{\text{hyd},298.15K}^{\circ} = A * n^{\alpha} * (\Delta H_{\text{diss},298.15K}^{\circ} + B) \quad (24)$$

344 where A,  $\alpha$  and B are constants, and n designates the number water molecules in the hydrate.  
345 This relationship is analogous to those given by Vieillard and Jenkins (1986a, 1986b, 1986c)  
346 and by Vieillard (2012) for different salts of the same cation. Values A,  $\alpha$ , B and  $\Delta H_{f,298.15K}^{\circ}$   
347 ( $\text{H}_2\text{O}_{(\text{c})}$ ) are determined by minimizing the difference between the experimental and  
348 calculated enthalpy of hydration for all data presented in figure 4 and Appendix B.

349



### 350 3. RESULTS

#### 351 3.1. Enthalpy of formation of anhydrous sulfates

352 By considering the following cations:  $\text{NH}_4^+$ ,  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  
353  $\text{Sr}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{S}^{6+}$ , the parameter  $\Delta_{\text{H}}\text{O}^- \text{M}^{\text{z}+}(\text{c})$  of 16 cations involved  
354 in simple and double sulfates were determined by minimizing the difference between the  
355 calculated enthalpy of formation from oxides (Equation 3) and those computed by Equation  
356 16.

357 The values obtained by minimization are given in Table 2 and contribute to the  
358 determination of the enthalpy of formation from constituent oxides. Each value of the  
359 parameter  $\Delta_{\text{H}}\text{O}^- \text{M}^{\text{z}+}(\text{c})$  for the 16 cations, characterize the electronegativity of a cation  
360 having a specific coordination number. With the help of the knowledge of crystal chemistry of  
361 sulfate minerals (Hawthorne et al. 2000), the coordination chemistry of each cation can be  
362 related to the mineral structure. The ion  $\text{S}^{6+}$  is in the fourfold coordination in all involved  
363 sulfates. Divalent and trivalent ions (by excluding  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ ) are in the sixfold  
364 coordination. Cations  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  are more often coordinated by eight or nine oxygen  
365 atoms,  $\text{Pb}^{2+}$  is in the tenfold coordination in palmierite. Among the monovalent cations, only  
366  $\text{Na}^+$  is in sixfold coordination and the two other cations  $\text{NH}_4^+$  and  $\text{K}^+$  exhibit different  
367 coordination numbers ranging from 8 to 12. Consequently, the determined enthalpy of  
368 formation of simple and double sulfates (Column V of Appendix A) may be compared with  
369 experimental values. The difference between the predicted and the measured values ranges  
370 between  $-2.27\%$  and  $3.46\%$ , with an average of  $0.55\%$  (or approximately 2 log units or  
371  $\pm 6.7 \text{kJ}\cdot\text{mol}^{-1}$  per 1 mole of  $\text{SO}_4$ ) for 49 different anhydrous sulfates (Column V of Appendix  
372 A).

373 Figure 2 displays the improvements of the predictive model of the enthalpy of formation  
374 based on the parameter  $\Delta_{\text{H}}\text{O}^- \text{M}^{\text{z}+}(\text{c})$  better than ones using  $\Delta_{\text{H}}\text{O}^- \text{M}^{\text{z}+}(\text{aq})$ . The cause of this

375 improvement is related to the new scale of the electronegativity of cations in sulfates and the  
376 involvement of interaction energy between any two cations in a double sulfate.

377 It seems important to point out that the high deviations between experimental and  
378 predicted enthalpy of formation are observed for potassium (and in less extent for ammonium)  
379 bearing double sulfates. The existence of positive deviations (>1%) for arcanite (K<sub>2</sub>SO<sub>4</sub>) and  
380 negative deviation (<-1%) for compounds belonging to the langbeinite group and to the  
381 leonite-type compounds, indicate the presence of two different states of coordination of the  
382 cation K<sup>+</sup> in these minerals and should lead to a new set of different electronegativity values  
383 for K<sup>+</sup> with different coordination numbers.

384 The relationship between  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}^{\text{Z}^+}(\text{c})$  and  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}^{\text{Z}^+}(\text{aq})$  is displayed in Figure 3 and is  
385 expressed as follows (Equation 25):

$$386 \quad \Delta_{\text{H}}\text{O}^{\ominus} \text{M}^{\text{Z}^+}(\text{c}) = 1.6551 \Delta_{\text{H}}\text{O}^{\ominus} \text{M}^{\text{Z}^+}(\text{aq}) + 253.63 \quad (\text{R}^2=0.9504) \quad (25)$$

387 By taking into account of the crystal chemistry of sulfates, a relationship between  $\Delta_{\text{H}}\text{O}^{\ominus}$   
388  $\text{M}^{\text{Z}^+}(\text{c})$  and  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}^{\text{Z}^+}(\text{aq})$  for cations in the sixfold coordination is proposed (Equation 26)  
389 and displayed in Figure 3 (dotted line):

$$390 \quad \Delta_{\text{H}}\text{O}^{\ominus} \text{M}^{\text{Z}^+}(\text{c}) = 1.7147 \Delta_{\text{H}}\text{O}^{\ominus} \text{M}^{\text{Z}^+}(\text{aq}) + 239.28 \quad (\text{R}^2=0.9657) \quad (26)$$

391 This useful relationship allows the evaluation of the electronegativity of any cation in  
392 sixfold coordination in a double sulfate from the available electronegativity of the cation in  
393 the aqueous state (Equation 1). Values that are not estimated by minimization, can be  
394 calculated by the relation illustrated in Figure 3 (values of Fe<sup>2+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup> in italics in  
395 Table 2).

396 Using the new set of  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}^{\text{Z}^+}(\text{c})$  values, enthalpies of formation for some anhydrous  
397 double sulfates can be evaluated from Equations 16 and 3 (Table 3) and will be used for the  
398 prediction of hydrous analogs.

399

400 3.2. Enthalpy of hydration for hydrated sulfates

401

402 Combined Equations 19 and 24 are rewritten below for one SO<sub>4</sub>, and a new equation for

403 the predicted  $\Delta H^\circ_f$  of hydrous sulfate can be deduced:

404 
$$\frac{\Delta H^\circ_{\text{hyd},298.15\text{K}}}{n_j} = \frac{\Delta H^\circ_{f,298.15\text{K}}[(M_i)_{n_i}(\text{SO}_4)_{n_j} \cdot n\text{H}_2\text{O}]}{n_j} - \frac{\Delta H^\circ_{f,298.15\text{K}}[(M_i)_{n_i}(\text{SO}_4)_{n_j}]}{n_j} - \frac{n}{n_j} * \Delta H^\circ_{f,298.15\text{K}}(\text{H}_2\text{O}_{(c)}) \quad (27)$$

405 and

406 
$$\frac{\Delta H^\circ_{\text{hyd},298.15\text{K}}}{n_j} = A * \left(\frac{n}{n_j}\right)^\alpha * \left(\frac{\Delta H^\circ_{\text{diss},298.15\text{K}}}{n_j} + B\right) \quad (28)$$

407 By minimizing the difference between the experimental values (given in Appendix B)

408 of the enthalpy of formation of hydrous sulfate with the estimated values obtained with

409 Equation 29, optimal values for the constants were determined:  $A = 0.2608$ ,  $\alpha = 0.367$ ,

410  $B = 2.111$  and  $\Delta H^\circ_{f,298.15\text{K}}(\text{H}_2\text{O}_{(c)}) = -293.90$ .

411

412 
$$\frac{\Delta H^\circ_{f,298.15\text{K}}[(M_i)_{n_i}(\text{SO}_4)_{n_j} \cdot n\text{H}_2\text{O}]}{n_j} = \frac{\Delta H^\circ_{f,298.15\text{K}}[(M_i)_{n_i}(\text{SO}_4)_{n_j}]}{n_j} + \frac{n}{n_j} * [\Delta H^\circ_{f,298.15\text{K}}(\text{H}_2\text{O}_{(c)})] + \frac{\Delta H^\circ_{\text{hyd},298.15\text{K}}}{n_j} \quad (29)$$

413 Figure 4, showing the relation between  $\Delta H^\circ_{\text{diss},298.15\text{K}}$  (for 1 SO<sub>4</sub> or  $\Delta H^\circ_{\text{diss},298.15\text{K}}/n_j$ ) and

414 the calculated enthalpies of hydration  $\Delta H^\circ_{\text{hyd},298.15\text{K}}$  (for 1 SO<sub>4</sub> or  $\Delta H^\circ_{\text{hyd},298.15\text{K}}/n_j$ ), illustrates

415 the experimental data (Appendix B) used to establish the predictive model (different symbols

416 for different numbers of hydration water) with theoretical data (displayed by full lines),

417 having the following relationship (Equation 30):

418 
$$\frac{\Delta H^\circ_{\text{hyd},298.15\text{K}}}{n_j} = 0.2608 * \left(\frac{n}{n_j}\right)^{0.367} * \left(\frac{\Delta H^\circ_{\text{diss},298.15\text{K}}}{n_j} + 2.111\right) \quad (30)$$

419 From the presented graph many remarks can be made:

420 - for the same hydration state and number of moles of SO<sub>4</sub>, the enthalpy of hydration

421 becomes more exothermic when the enthalpy of dissolution decreases.

422 - for a sulfate with the same cation (or same cations), the enthalpy of hydration becomes

423 less and less negative when the number of water molecules increases and does not follow an  
424 additive scheme.

425 - the value of the enthalpy of formation of ice-like water,  $\Delta H_{f,298.15K}^{\circ} \text{H}_2\text{O}_{(c)} = -293.90$   
426  $\text{kJ}\cdot\text{mol}^{-1}$ , in the sulfate is slightly more negative than that of ice,  $\Delta H_{f,298.15K}^{\circ} \text{H}_2\text{O}_{(ice)} = -292.75$   
427  $\text{kJ}\cdot\text{mol}^{-1}$  (Mercury et al. 2001).

428 Figure 5 shows that the method developed in this work gives better results than that of  
429 Mercury et al. (2001) by opposing the errors of the 2 models. Indeed, it appears that all of the  
430 errors obtained in this work are less than 1% (maximum value = 0.92% and average = 0.14%,  
431 (Column VI of Appendix B), which are much lower than the errors of the additive model of  
432 Mercury et al. (2001) (maximum value = 1.87% and mean = 0.52%). In this model, the error  
433 in the predicted enthalpy of formation of the hydrated water for sulfate minerals is  $\pm 1.42 \text{ kJ}$ .  
434  $(\text{mole H}_2\text{O})^{-1}$ .

435 From the available enthalpies of formation of anhydrous double sulfates (the  
436 experimental or estimated values developed in the previous section), enthalpies of formation  
437 of hydrous sulfates can be calculated from Equation 29 and are presented in Table 4, where  
438 predictions show a mean uncertainty for enthalpy of formation of  $2.1 \text{ kJ}\cdot(\text{mole H}_2\text{O})^{-1}$ .

439 For the 6 minerals belonging to the halotrichite family, which are double sulfates with  
440 22 moles of water (Table 4), the enthalpy of hydration increases with the enthalpy of  
441 dissolution of the anhydrous analog. From Table 4, the most negative hydration enthalpy and  
442 enthalpy of dissolution concern pickeringite, and the less negative hydration enthalpy and  
443 enthalpy of dissolution is for bilinite.

444 The enthalpies of formation for  $\text{NaAl}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$  for  $n=2, 5, 6$  and  $12$  are listed in Wagman  
445 et al. (1982), but the origin of these values is unknown. To verify our predictive model, the  
446 value of  $\Delta H_{f,298.15K}^{\circ}$  for  $\text{NaAl}(\text{SO}_4)_2$ , not available in the literature, was requested. It was  
447 estimated and used to predict the  $\Delta H_{f,298.15K}^{\circ}$  of hydrous phases with 2, 5, 6 and 12  $\text{H}_2\text{O}$

448 molecules, and compared with the Wagman et al. (1982) data. The high negative deviations  
449 from values of Wagman et al. (1982) presented in Table 5 for all hydrates forms of  
450  $\text{NaAl}(\text{SO}_4)_2$  can come from the use of the parameter  $\Delta_{\text{H}}\text{O}^{\ominus} [^{61}]\text{Na}^+(\text{c})$  in the prediction of the  
451 enthalpy of formation of  $\text{NaAl}(\text{SO}_4)_2$ . Indeed, the cation  $\text{Na}^+$  in these hydrated forms is rather  
452 in twelvefold coordination and the difference between  $\Delta_{\text{H}}\text{O}^{\ominus} [^{61}]\text{Na}^+(\text{c})$  and  $\Delta_{\text{H}}\text{O}^{\ominus} [^{12}]\text{Na}^+(\text{c})$  is  
453 ignored.

454

### 455 3.3 Example of computation of a hydrous double sulfate

456 Bilinite  $\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$  and romerite  $\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$  were chosen to  
457 describe the protocol for estimating the enthalpy of formation using the model described  
458 above. The details of the computation of the enthalpy of formation from the constituent oxides  
459 of anhydrous double sulfate  $\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4$  and the enthalpy of hydration of bilinite and  
460 romerite are given in Table 6. The enthalpy of formation of bilinite from our model is  
461  $\Delta_{\text{H}}^{\circ}_{\text{f},298.15\text{K}} = -10118.89 \text{ kJ}\cdot\text{mol}^{-1}$ , a value close to the estimated value of Hemingway et al.  
462 (2002) of  $\Delta_{\text{H}}^{\circ}_{\text{f},298.15\text{K}} = -10121 \text{ kJ}\cdot\text{mol}^{-1}$ . From the enthalpy of formation of the anhydrous  
463 double sulfate,  $\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4$ , the enthalpy of formation of romerite  $\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$   
464 can be evaluated using  $n = (14/4)$  instead of  $22/4$  for the number of moles of hydration water  
465 and gives a value of  $\Delta_{\text{H}}^{\circ}_{\text{f},298.15\text{K}} = -7762.41 \text{ kJ}\cdot\text{mol}^{-1}$ , which is close to the value of  
466  $\Delta_{\text{H}}^{\circ}_{\text{f},298.15\text{K}} = -7748.56 \text{ kJ}\cdot\text{mol}^{-1}$  estimated by Hemingway et al. (2002).

467 Special attention is paid to minerals with two cations (of the same charge) for which  
468 the stoichiometric sum is equal to unity, like anhydrous form of nickelbousingaultite  
469  $(\text{NH}_4)_2\text{Ni}_{0.75}\text{Mg}_{0.25}(\text{SO}_4)_2$  or anhydrous form of loncreekite  $(\text{NH}_4)\text{Fe}^{3+}_{0.75}\text{Al}_{0.25}(\text{SO}_4)_2$ .  
470 Indeed, these minerals are considered double sulfates, and one of the sites is occupied by two  
471 different cations in different proportions,  $0.75 \text{ Ni}^{2+}$  and  $0.25 \text{ Fe}^{2+}$  or  $0.75 \text{ Fe}^{3+}$  and  $0.25 \text{ Al}^{3+}$  in  
472 nickelbousingaultite and loncreekite, respectively. The formalism of the computation of the

473 enthalpy of formation from constituent oxides is the same (Equation 16) but one of the sites  
474 (divalent or trivalent) has a parameter  $\Delta_{\text{H}}\text{O}^{\ominus} \text{M}_i^{\text{z}_i^+}(\text{c})$ , considered the stoichiometric average  
475 of the electronegativities of two different cations,  $\text{Ni}^{2+}$  and  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ , respectively,  
476 for the two minerals.

477

## 478 4. DISCUSSION

### 479 4.1. Introduction

480 To validate the model for the prediction of the enthalpy of formation for hydrated  
481 double sulfates, the determination of stability fields versus relative humidity and the solubility  
482 products, for some sulfate minerals, have been calculated with estimated data of this work and  
483 compared with experimental data from literature. These parameters are based on the Gibbs  
484 free energies of formation for sulfate minerals, a parameter calculated from the enthalpy of  
485 formation and entropy of minerals. As in the previous section, a predictive model has been  
486 used to generate the enthalpy of formation for hydrated sulfates, and this section begins with a  
487 short introduction to a simplified prediction model of entropy for sulfate minerals.

488

### 489 4.2. Estimation of entropy of formation for hydrated double sulfates

490 Various empirical algorithms have been used to estimate the standard molal entropies  
491 of minerals (Helgeson et al. 1978; Holland 1989; Vieillard 2010; Blanc et al. 2010). All these  
492 methods yield approximations in the range of  $\pm 5\%$  for certain classes of compounds. Many of  
493 such algorithms are based on corresponding state relations in models in which simple  
494 additivity rules prevail. The most classical relation for anhydrous sulfates is given by the  
495 following relationship (Equation 31):

$$496 \Delta S_{\text{ox},298.15\text{K}}^{\circ} = S_{298.15\text{K}}^{\circ} [\text{M}_{i n_i}(\text{SO}_4)_{n_j}] - \sum_{i=1}^{i=2} n_i * S_{298.15\text{K}}^{\circ} [\text{M}_i\text{O}_{x_i}] - n_j * S_{298.15\text{K}}^{\circ} [\text{SO}_3] \quad (31)$$

497 where  $n_i$  stands for the number of moles of the  $i^{\text{th}}$  oxide formula unit and  $n_j$  is the number of

498 moles of the  $\text{SO}_3$  formula unit, and  $S^\circ$  represents the standard molal entropy of the pure oxide  
499  $i$  and  $\text{SO}_3$  at  $25^\circ\text{C}$  and 1 bar. The experimental standard molal entropies of sulfate minerals  
500 are listed in Table 7 (Column I) as well as of oxides  $\text{M}_i\text{O}_{x_i}$  and  $\text{SO}_3$  (Line I of Table 8). For  
501 various ferrous sulfates and  $\text{MnSO}_4$ , only the third law entropy is used, and they are free from  
502 magnetic spin entropy (Ulbrich and Waldbaum 1976).

503 Values of  $S^\circ_{298.15\text{K},(\text{sulfates})}$  are determined by assuming that the standard molal entropy  
504 of formation of a sulfate mineral from its oxides is zero. The results of the minimization  
505 provide values of fictive  $S^\circ_{298.15\text{K},(\text{sulfates})}$  in Table 8 (Line II).

506 The standard molal entropies of hydrated sulfates  $(\text{M}_i)_{n_i}(\text{SO}_4)_{n_j} \cdot n\text{H}_2\text{O}$  can be  
507 calculated from the predicted standard molal entropies of anhydrous sulfates,  $(\text{M}_i)_{n_i}(\text{SO}_4)_{n_j}$ ,  
508 by the following Equation 32:

$$509 \quad S^\circ_{298.15\text{K}} \left[ (\text{M}_i)_{n_i}(\text{SO}_4)_{n_j} \cdot n\text{H}_2\text{O} \right] = S^\circ_{298.15\text{K}} \left[ (\text{M}_i)_{n_i}(\text{SO}_4)_{n_j} \right] + n * S^\circ_{298.15\text{K}}(\text{H}_2\text{O})_{(c)} \quad (32)$$

510 where  $n$  is the number of water molecules of the hydrated sulfate minerals. An average value  
511 of the entropy of ice-like water,  $S^\circ_{298.15\text{K}}(\text{H}_2\text{O})_{(c)}$ , of  $41.5 \text{ K}\cdot\text{J}^{-1}\cdot\text{mol}^{-1}$  for sulfate is proposed  
512 based on statistical calculations (Mercury et al. 2001).

513

#### 514 4.3. Applications to natural systems

515 The weathering of sulfide minerals allows unusual amounts of iron and toxic metals  
516 and metalloids released in the environment (Jambor et al. 2000). Large quantities of metals  
517 and sulfate ions in low pH solutions may precipitate to form sulfate minerals (Nordstrom and  
518 Alpers 1999) if environmental conditions such as temperature, air humidity (or relative  
519 humidity), activities of aqueous ions or concentrations of solutions change. The modeling of  
520 acid mine drainage may require the enthalpy, entropy and Gibbs free energies of formation of  
521 hydrated sulfates, which are not available in literature or exhibit strong inconsistency among  
522 predicted and measured values.

523 Two areas of application for our model of prediction of the thermodynamic properties  
524 of hydrated sulfate minerals with experimental measurements are proposed and developed.  
525 The first field of application will be based on the variation of the equilibrium between  
526 different hydrated sulfates of the same cation with temperature. This will be developed in this  
527 section with the help of experimental measurements and stability diagrams from Ackermann  
528 et al. (2009), Hemingway et al. (2002), Majzlan et al. (2005), Chou et al. (2013), Wang et al.  
529 (2012) and Kong et al. (2011), on the  $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$  system. The second field of application  
530 will be focused on the comparison of the solubility products of sulfate minerals predicted in  
531 this work with experimental measurements.

532

533

#### 534 4.4. The $\text{Fe}_2(\text{SO}_4)_3 - \text{H}_2\text{O}$ system

535 From Ackermann et al. (2009) and Hemingway et al. (2002), there are six minerals  
536 belonging to the  $\text{Fe}_2(\text{SO}_4)_3 - \text{H}_2\text{O}$  system: mikasaite,  $\text{Fe}_2(\text{SO}_4)_3$ ;  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ; lawsonite,  
537  $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ ; kornelite,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$  (Hemingway et al. 2002) or  $\text{Fe}_2(\text{SO}_4)_3 \cdot 7.75 \text{H}_2\text{O}$   
538 (Ackermann et al. 2009); coquimbite,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$  and quenstedtite,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 10 \text{H}_2\text{O}$ .  
539 From the predicted enthalpies of formation for hydrous ferric sulfates (Table 4) and entropies  
540 for hydrous ferric sulfates, calculated from experimental entropy of mikasaite (Majzlan et al.  
541 2005) by using the average entropy of hydration water, Gibbs free energies for these hydrated  
542 minerals are calculated and presented in Table 9 with other values from different sources.

543 All enthalpies of formation for hydrous sulfates predicted in this work exhibit  
544 overestimated but consistent values compared to the experimental ones in a range of -0.3%-  
545 0.7%. Only the enthalpy of formation of coquimbite from Majzlan et al. (2006) is too low in  
546 reason of presence of Al in the sample.

547 By assuming  $\Delta C_p = 0$  for reactions between different hydrated sulfates, reactions between the



548 6 different hydrated ferric sulfates are represented versus temperature and relative humidity  
549 (Figure 6).  
550 With the additive model of the enthalpy of hydration (Mercury et al. 2001), it is impossible to  
551 build the stability diagrams of temperature versus relative humidity for different hydrous  
552 ferric sulfates (dotted line, Figure 6A). The model of prediction of the enthalpy of hydration  
553 based on the enthalpy of dissolution developed in the previous section (full lines N° 1 to 6,  
554 Figure 6A) yields different phase boundaries for all minerals belonging to the system  
555  $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ . It appears that ferric sulfates become more hydrated with increasing relative  
556 humidity for a given temperature. The parallelism observed for different stability boundaries  
557 in the temperature-relative humidity diagram is due to the additive model of prediction for the  
558 entropy of hydration. In the mikasaite- kornelite (7  $\text{H}_2\text{O}$ ) – coquimbite system, Hemingway et  
559 al. (2002) only showed an estimation close to our model for the equilibrium kornelite-  
560 coquimbite (respectively dotted line and full line N°4, Figure 6B). These authors do not  
561 include minerals such as  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  and lawsonite,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ , which most likely  
562 explains the large deviation for the equilibrium mikasaite-kornelite (line N°7 in Figure 6B). In  
563 the system mikasaite- $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  - kornelite -coquimbite, studied by Ackermann et al.  
564 (2009) (dotted line Figure 6C), there is very good consistency at 25°C for the following 3  
565 systems: mikasaite-  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ;  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  - kornelite (7.75  $\text{H}_2\text{O}$ ) and kornelite  
566 (7.75  $\text{H}_2\text{O}$ ) - coquimbite. When the temperature increases, there is a weak divergence of the  
567 first two equilibria and a large deviation for the equilibrium kornelite-coquimbite. At low  
568 relative humidity( in particular for equilibrium 1), the transition temperature discrepancy  
569 between this work and Ackermann's one, at constant RH, is great. This is most likely due to  
570 two reasons: estimated entropy is based on the additive scheme and the heat capacity of  
571 reaction is assumed to be independent with temperature. The square represented in Figure 6B  
572 and C is the experimental observation of Chipera et al. (2007), who found that kornelite is a

573 stable phase at  $T=348\text{K}$  and  $\text{RH}=43\%$ .

574 These results provide an acceptable prediction of thermodynamic data for normal hydrous  
575 ferric sulfates. It seems evident that several authors (Wang et al. 2012; Chou et al. 2013)  
576 obtained stability fields of many hydrous ferric sulfates from experimental measurements that  
577 are very difficult to use in the presence of some basic hydrous ferric sulfates (ferricopiapite),  
578 acid hydrous ferric sulfates (rhomboclase) and amorphous ferric sulfates, compounds that are  
579 not considered to be true double sulfates and are excluded in the predictive model of the  
580 enthalpy of formation of hydrous normal double sulfates.

581

582

583 4.5. Solubility products of some hydrous sulfates

584

585 Table 10 displays a comparison between experimental or available solubility products  
586 (Column I of Table 10) with calculated ones (values given in column V, Table 10) from the  
587 predicted enthalpy of formation (Column II of Table 10) and entropy (Column III of Table  
588 10) developed in this work. Calculated solubility products are obtained with Gibbs free  
589 energies of ions from Robie and Hemingway (1995). The differences between measured and  
590 predicted solubility products are approximately 1-2 log units per mole of S. Some large  
591 deviations are observed for minerals such as arcanite (+3.27 log units); coquimbite (-5.64 log  
592 units), halotrichite (-3.49 log units),  $\text{K}_2\text{SO}_4\cdot\text{FeSO}_4\cdot 6\text{H}_2\text{O}$  (-2.64 log units);  
593  $\text{Na}_2\text{SO}_4\cdot\text{FeSO}_4\cdot 4\text{H}_2\text{O}$  (-3.70 log units); yavapaiite (-3.49 log units); romerite (-6.90 log units),  
594 bilinite (-2.67 log units), apthitalite (+9.28).

595 The mineral arcanite and the potassium bearing double sulfates yavapaiite, apthitalite and  
596  $\text{K}_2\text{SO}_4\cdot\text{FeSO}_4\cdot 6\text{H}_2\text{O}$  have the same magnitude of deviation than for predicted enthalpy of  
597 formation. This is related to a lack of accuracy of the electronegativity of  $\text{K}^+$  in sulfates,  $\Delta_{\text{H}}\text{O}^-$

598  $K^+(c)$  for a given coordination number. Indeed, by discarding yavapaiite (twelvefold  
599 coordination), the other minerals exhibit two distinct coordination for the K polyhedron.

600 The iron-bearing minerals coming from Hemingway et al. (2002) have a predicted  
601 enthalpy and free energy of formation and have been used by Marion et al. (2008) in  
602 solubility diagrams for  $Fe_2(SO_4)_3 - FeSO_4 - H_2SO_4$ . From Hemingway et al. (2002), the  
603 enthalpy and free energy of each water hydration (except the first  $H_2O$  molecule) in different  
604 hydrous sulfate compounds are constant. Assuming an absence of excess free enthalpy of  
605 mixing, the enthalpy of formation and free energy of these four minerals are predicted by the  
606 summation of the properties of simple sulfate compounds and the contribution of each  $H_2O$   
607 molecule. This explain probably why the enthalpy of hydration water predicted in this work is  
608 more closely related to the nature of cations bound to sulfates and to the number of molecules  
609 of hydration water.

610

## 611 CONCLUSIONS

612 Two different models for the prediction of the enthalpy of formation of hydrous double  
613 sulfates are necessary to obtain reasonable agreement with experimental values. For  
614 anhydrous simple sulfates, the enthalpy of formation of the compound from its constituent  
615 oxides per one oxygen atom is proportional to the product of the molar fraction of oxygen  
616 bound to the cation and to  $S^{6+}$  and also to the interaction energy  $[\Delta_H O^- M_i^{Z_i+}(c) - \Delta_H O^-$   
617  $S^{6+}(c)]$  characterizing the difference in electronegativity between the cations  $M_i^{Z_i+}$  and  $S^{6+}$ . In  
618 anhydrous double sulfates, there are three interaction energies between the cations  $M_i^{Z_i+}$ ,  
619  $M_j^{Z_j+}$  and  $S^{6+}$  because we assume that oxygen atoms are common to all three cations.  
620 Therefore, the enthalpy of formation of anhydrous double sulfates per one oxygen atom  
621 contains three terms, with each term having the same formalism, i.e., the product of the molar

622 fraction of oxygen bound to cation 1 and to cation 2 and also to the interaction energy  $[\Delta_{\text{H}}\text{O}^-$   
623 cation 1(c) -  $\Delta_{\text{H}}\text{O}^-$  cation 2(c)].

624 The model of prediction for anhydrous double sulfates provides good results because  
625 the model is based on the difference in electronegativities among three cations with common  
626 oxygen. This model, initially developed in silicates (Vieillard and Tardy 1988a), clearly  
627 shows that Pauling's concept of electronegativity is fully justified for any anhydrous double  
628 sulfate. Improvements can be brought by considering in some minerals the coordination  
629 number for potassium and ammonium sulfates minerals, in order to set relationships between  
630  $\Delta_{\text{H}}\text{O}^- \text{M}^{z+}(\text{c})$  with coordination number. In this view, the presence of two distinct  
631 coordination numbers for some cation ( $\text{K}^+$ ,  $\text{NH}_4^+$ ) leads us to reformulate the Equation 16  
632 with six interactions energy terms. For basic anhydrous double sulfates, this method is not  
633 wholly valid because the presence of a hydroxyl indicates the existence of four cations and the  
634 existence of six theoretical interactions energy terms between the four cations. In such  
635 compounds, the existence of non-common oxygen between the four cations may exist, and  
636 some interaction energy terms between any two cations may not contribute to the  
637 computation of the enthalpy of formation of a mineral from constituent oxides using a short  
638 range approach. This is why Gaboreau and Vieillard (2004) used a predictive model of the  
639 free energies based on the electronegativity difference and short range approach and have  
640 demonstrated the presence of non-common oxygen between two cations (or sites) in minerals  
641 belonging to the alunite family.

642 The model of prediction of the enthalpy of hydration proposed by Vieillard (2012) and  
643 by Vieillard and Jenkins (1986a, 1986c) on salts with the same cation has been applied here  
644 within a same family, namely sulfates with one or two cations, for the first time. This model  
645 of prediction provides very good results for simple and double sulfates and shows that the  
646 enthalpy of hydration water (for the same number of  $\text{SO}_4$ ) in sulfates of the same cation (or 2

647 different cations) is not constant but instead increases with the increasing number of hydration  
648 waters. A second point of this model of prediction is the fact that for the same number of  
649 hydration waters and for one mole of  $\text{SO}_4$ , the enthalpy of formation of hydration water  
650 increases (i.e. becomes less negative) when the enthalpy of dissolution of the anhydrous  
651 analogue becomes less negative.

652 The predicted enthalpies and entropies for many hydrous sulfates belonging to the  
653 system anhydrous double sulfate – water have been calculated, and some minerals have been  
654 chosen to compare with the experimental observations and numerical modeling. Stability  
655 fields of hydrous minerals versus temperature and relative humidity and solubility products  
656 have been used as a test for some predicted values for hydrous sulfate and provide acceptable  
657 results with experimental observations made at 25°C. With increasing temperature,  
658 divergences between the predicted and experimental values for hydrous sulfates obviously  
659 increase due to the additive model for the entropy of hydration and the non-involvement of  
660 heat capacity in computations.

661 To increase the accuracy of the predictive models of thermodynamic data for  
662 temperatures over or below 25°C, further studies should be planned, such as calorimetric  
663 measurements for the enthalpy of formation but also for entropy and heat capacity for some  
664 hydrous sulfates. These measurements will contribute to the improvement of a predictive  
665 model for entropy and heat capacity of hydration water based on the molar volume of the  
666 hydration water, available from crystallographic parameters and structure refinements.

667

## 668 IMPLICATIONS

669 Sulfate minerals occur in various environments, as noted in the introduction part, and are also  
670 subject of current works, where their thermodynamic parameters are needed but not always  
671 available.

672 Thermodynamic parameters, for simple anhydrous and hydrous sulfates, are well-  
673 documented, but it is not the case for double heavy metal and rare earth bearing sulfates in  
674 anhydrous and hydrous form. The models of prediction developed here, try to provide missing  
675 enthalpy of formation for anhydrous sulfates and its hydrous analogs, for simple or double  
676 form.

677 Indeed, evaporite deposits, weathering of sulfide minerals, mineral processing (uranium for  
678 example), or composition of Mars' surface, are all environments where various common and  
679 uncommon sulfates formed; the knowledge of thermodynamic parameters, estimated from  
680 their chemical formula, would contribute to a better understanding of the stability of these  
681 minerals. Furthermore, an increasing interest in geochemical modeling is recognized in the  
682 fields cited above and requires thermodynamic values for these sulfate minerals, to simulate,  
683 for example:

684 -reactions between acid solution and uraniferous ore for uranium recovery

685 -evaporation of hypothetical Mars Ocean

686 -weathering of metallic sulfides deposits.

687

688

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690

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875

### 876 Figures Captions

877  
878 Figure 1. Relation between  $\Delta H_{f,ox}^\circ$  and  $\Delta_{\text{H}}\text{O}^- \text{M}^{\text{Z}^+}(\text{aq})$ .

879 Figure 2. Comparison of error between  $\Delta H_f^\circ$  calculated in this study and  $\Delta H_f^\circ$  from literature  
880 ( $\Delta H_{f,(lit)}^\circ$ ) induced one part using  $\Delta_{\text{H}}\text{O}^- \text{M}^{\text{Z}^+}(\text{aq})$  and in the other hand  $\Delta_{\text{H}}\text{O}^- \text{M}^{\text{Z}^+}(\text{c})$ .

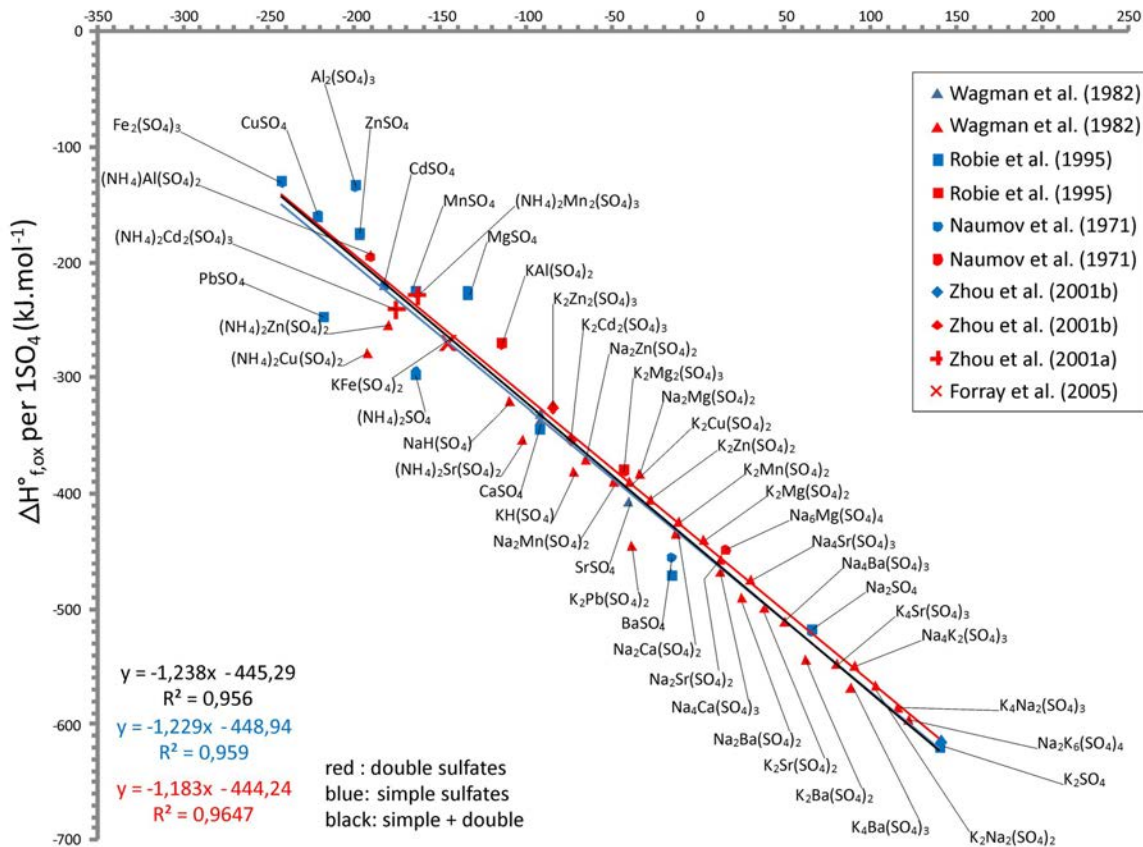
881 Figure 3. Linear correlation between  $\Delta_{\text{H}}\text{O}^- \text{M}^{\text{Z}^+}(\text{aq})$  and  $\Delta_{\text{H}}\text{O}^- \text{M}^{\text{Z}^+}(\text{c})$ .

882 Figure 4. Relation between enthalpy of hydration ( $\Delta H_{\text{hyd},298.15\text{K}}^\circ$ ) and enthalpy of dissolution  
883 ( $\Delta H_{\text{diss},298.15\text{K}}^\circ$ ) of hydrated sulfates (reported for  $1\text{SO}_4$  per formula).

884 Figure 5. Comparison of error between  $\Delta H_f^\circ$  from literature ( $\Delta H_{f,(lit)}^\circ$ ) and  $\Delta H_f^\circ$  estimated one  
885 part using the model presented in this work and in the other hand the additive model of  
886 Mercury et al. (2001).

887 Figure 6. Comparison of estimated and experimental data for reactions in the system  
888  $\text{Fe}_2(\text{SO}_4)_3 - \text{H}_2\text{O}$  as a function of temperature and water activity. A – This work and  
889 additive model (Mercury et al., 2001); B – System mikasaite- kornelite ( $7 \text{H}_2\text{O}$ ) –  
890 coquimbite; C – System mikasaite -  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  - kornelite ( $7.75 \text{H}_2\text{O}$ ) -  
891 coquimbite.

$$\Delta_{\text{H}}\text{O}^{\ominus} = \text{M}^{\text{Z}+} (\text{aq}) \text{ (kJ}\cdot\text{mol}^{-1}\text{)}$$



Error (%): column VI appendix A

$(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2$  ◆

$\text{K}_2\text{SO}_4$  ×

$\text{K}_2\text{Zn}(\text{SO}_4)_2$  ◆

$\text{K}_2\text{Mn}(\text{SO}_4)_2$  ◆

$\text{K}_2\text{Cd}_2(\text{SO}_4)_3$  ◆

$\text{K}_2\text{Cu}(\text{SO}_4)_2$  ◆

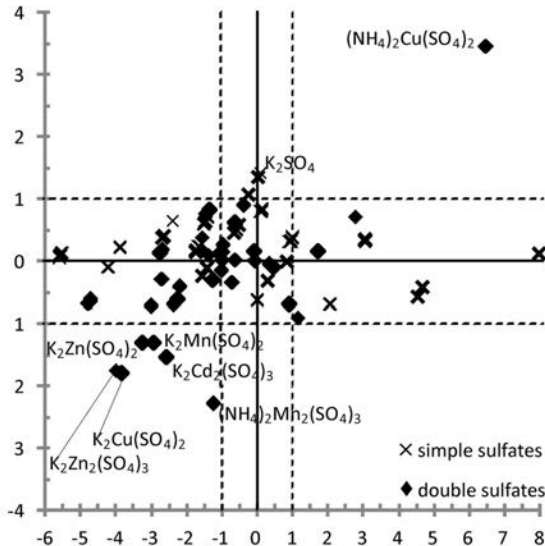
$\text{K}_2\text{Zn}_2(\text{SO}_4)_3$  ◆

$(\text{NH}_4)_2\text{Mh}_2(\text{SO}_4)_3$  ◆

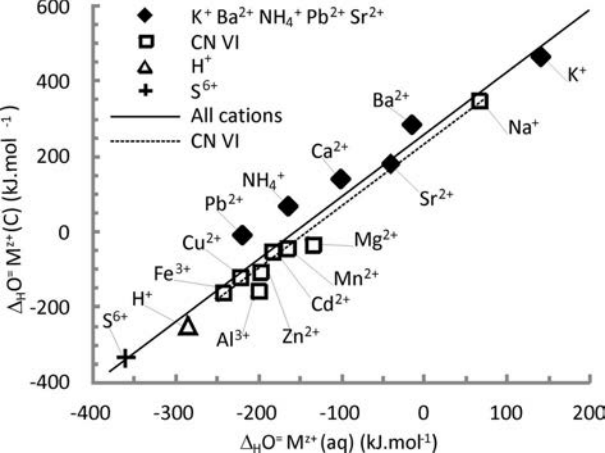
× simple sulfates

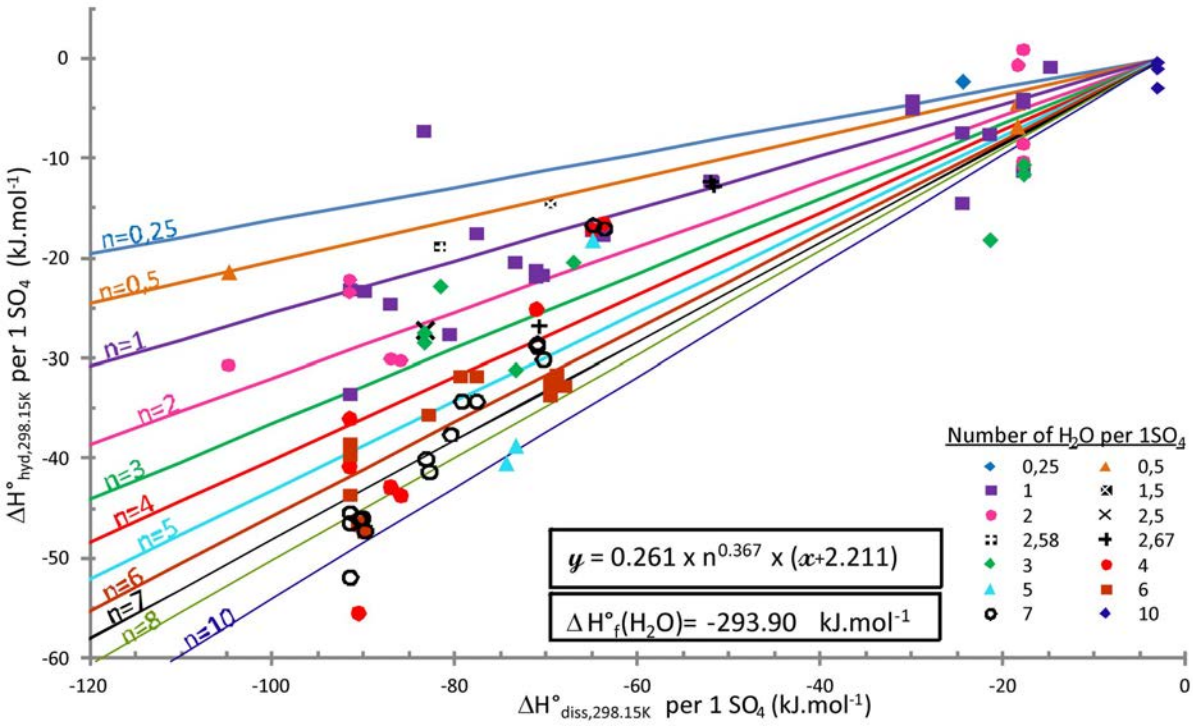
◆ double sulfates

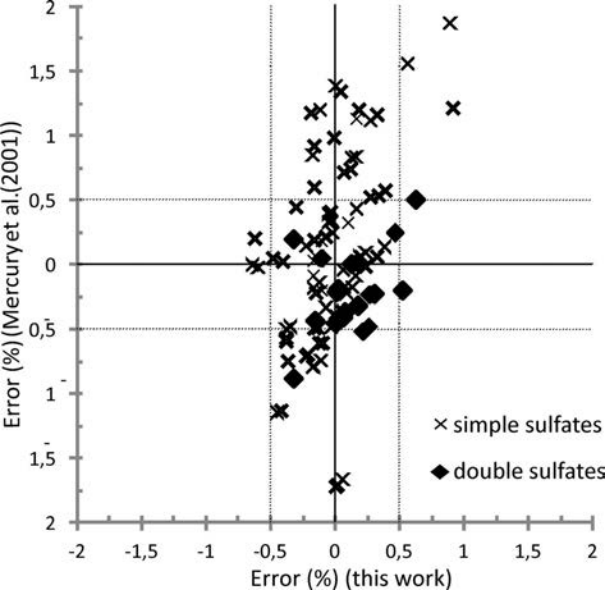
Error (%): column IV appendix A

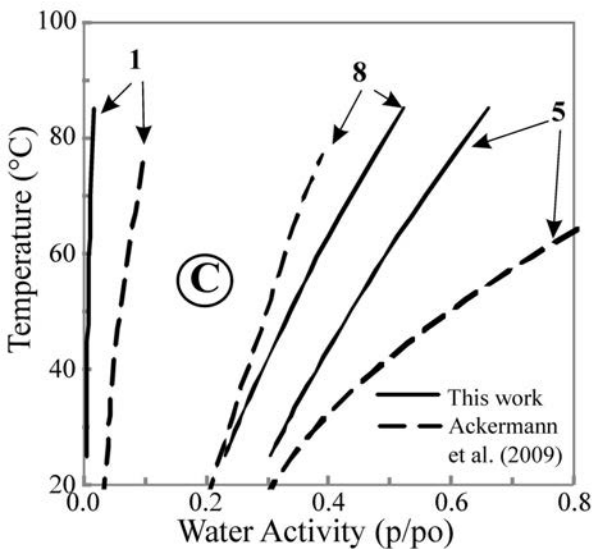
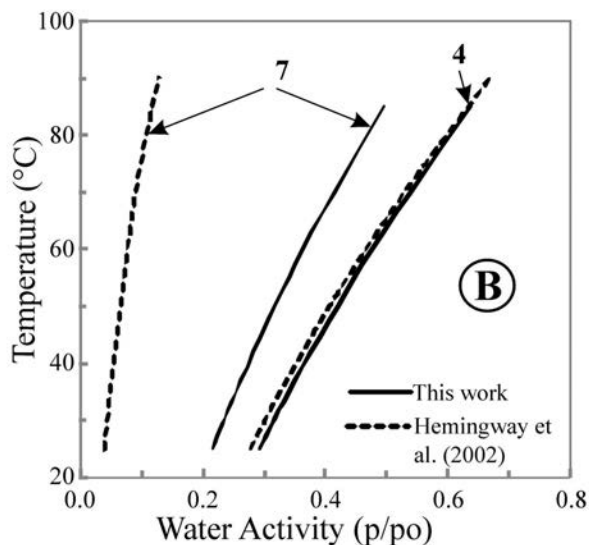
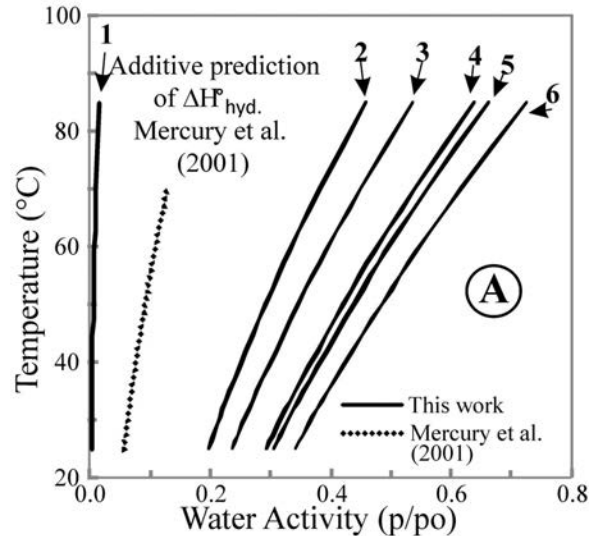












Numbers of lines

- 1 :  $\text{Mikasaite} + 5 \text{H}_2\text{O} \rightarrow \text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$
- 2 :  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{Lausenite}$
- 3 :  $\text{Lausenite} + \text{H}_2\text{O} \rightarrow \text{Kornelite}$
- 4 :  $\text{Kornelite} + 2 \text{H}_2\text{O} \rightarrow \text{Coquimbite}$
- 5 :  $\text{Kornelite} + 1.25 \text{H}_2\text{O} \rightarrow \text{Coquimbite}$
- 6 :  $\text{Coquimbite} + \text{H}_2\text{O} \rightarrow \text{Quenstedtite}$
- 7 :  $\text{Mikasaite} + 7 \text{H}_2\text{O} \rightarrow \text{Kornelite}$
- 8 :  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O} + 2.75 \text{H}_2\text{O} \rightarrow \text{Kornelite}$

Table 1. Values of  $\Delta H_{f,298.15K}^{\circ}$  for oxides and cations used for calculation of  $\Delta_H O^{\ominus} M^{Z+}(aq)$ .

oxides	$\Delta H_{f,298.15K}^{\circ}$ (kJ.mol <sup>-1</sup> )	ref	cations	$\Delta H_{f,298.15K}^{\circ}$ (kJ.mol <sup>-1</sup> )	ref	$\Delta_H O^{\ominus} M^{Z+}(aq)$ (kJ.mol <sup>-1</sup> )
SO <sub>3</sub>	-454.51	1	S <sup>6+</sup>	-	5	-359.77
K <sub>2</sub> O	-363.20	4	K <sup>+</sup>	-252.10	4	141.00
CaO	-635.10	3	Ca <sup>2+</sup>	-543.00	3	-92.10
MgO	-601.60	3	Mg <sup>2+</sup>	-467.00	3	-134.60
Al <sub>2</sub> O <sub>3</sub>	-1675.70	3	Al <sup>3+</sup>	-538.40	3	-199.63
FeO	-272.00	4	Fe <sup>2+</sup>	-91.10	4	-180.90
Fe <sub>2</sub> O <sub>3</sub>	-826.20	4	Fe <sup>3+</sup>	-49.90	4	-242.13
Na <sub>2</sub> O	-414.80	4	Na <sup>+</sup>	-240.30	4	65.80
BaO	-548.10	4	Ba <sup>2+</sup>	-532.50	4	-15.60
MnO	-385.20	4	Mn <sup>2+</sup>	-220.80	4	-164.40
(NH <sub>4</sub> ) <sub>2</sub> O	-430.70	2	NH <sub>4</sub> <sup>+</sup>	-133.30	4	-164.10
H <sub>2</sub> O	-285.83	3	H <sup>+</sup>	0.00	3	-285.83
CdO	-258.35	3	Cd <sup>2+</sup>	-75.92	3	-182.43
CoO	-237.94	4	Co <sup>2+</sup>	-58.20	1	-179.74
CuO	-156.10	4	Cu <sup>2+</sup>	64.90	4	-221.00
NiO	-239.30	4	Ni <sup>2+</sup>	-54.00	4	-185.30
PbO	-219.00	4	Pb <sup>2+</sup>	0.90	4	-219.90
SrO	-591.30	4	Sr <sup>2+</sup>	-550.90	4	-40.40
ZnO	-350.50	3	Zn <sup>2+</sup>	-153.39	3	-197.11

Footnote added at the end of Table 1

ref: references. 1- Wagman et al. (1982); 2 - Wilcox and Bromley (1963); 3 - Cox et al.

(1989); 4 - Robie and Hemingway (1995); 5 - this work

Table 2. Values of  $\Delta_{\text{H}}\text{O}^- \text{M}^{z+}(\text{c})$  obtained by minimization or by calculation for values in italic ( $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ ).

cations	$\Delta_{\text{H}}\text{O}^- \text{M}^{z+}(\text{c})$ (kJ.mol <sup>-1</sup> )	cations	$\Delta_{\text{H}}\text{O}^- \text{M}^{z+}(\text{c})$ (kJ.mol <sup>-1</sup> )
$\text{S}^{6+}$	-333.07	$\text{NH}_4^+$	70.11
$\text{K}^+$	467.61	$\text{H}^+$	-247.20
$\text{Ca}^{2+}$	120.20	$\text{Cd}^{2+}$	-49.20
$\text{Mg}^{2+}$	-31.88	$\text{Co}^{2+}$	<i>-73.00</i>
$\text{Al}^{3+}$	-155.62	$\text{Cu}^{2+}$	-117.58
$\text{Fe}^{2+}$	<i>-74.90</i>	$\text{Ni}^{2+}$	-82.27
$\text{Fe}^{3+}$	-160.71	$\text{Pb}^{2+}$	-5.59
$\text{Na}^+$	348.72	$\text{Sr}^{2+}$	183.26
$\text{Ba}^{2+}$	287.91	$\text{Zn}^{2+}$	-104.57
$\text{Mn}^{2+}$	-40.83		

Table 3. Enthalpies of formation of simple and double anhydrous sulfates, estimated in this work (anh.: anhydrous)

Mineral/Compound	Formula	$\Delta H_{f,298.15K}^{\circ}$ estimated (kJ.mol <sup>-1</sup> )	Mineral/Compound	Formula	$\Delta H_{f,298.15K}^{\circ}$ estimated (kJ.mol <sup>-1</sup> )
Eldfellite	NaFe(SO <sub>4</sub> ) <sub>2</sub>	-2026.86	Romerite anh., Bilinite anh.	Fe <sup>2+</sup> Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub>	-3513.77
Tamarugite anh., Mendozite anh.	NaAl(SO <sub>4</sub> ) <sub>2</sub>	-2456.85	Halotrichite anh.	Fe <sup>2+</sup> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub>	-4373.76
Sabieite	(NH <sub>4</sub> )Fe <sup>3+</sup> (SO <sub>4</sub> ) <sub>2</sub>	-1904.21	Apjohnite anh.	Mn <sup>2+</sup> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub>	-4518.90
Tschemigite anh.	(NH <sub>4</sub> )Al(SO <sub>4</sub> ) <sub>2</sub>	-2334.20	Dietrichite anh.	(d)	-4548.95
Lonecreekite anh.	(a)	-2010.40	Wupatkiite anh.	(e)	-4542.14
Na-Palmierite	Na <sub>2</sub> Pb(SO <sub>4</sub> ) <sub>2</sub>	-2343.81	Lishizhenite anh.	ZnFe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub>	-3564.46
Kalistrontite	K <sub>2</sub> Sr(SO <sub>4</sub> ) <sub>2</sub>	-2886.82	Ransomite anh.	CuFe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub>	-3357.86
Krohnkite anh.	Na <sub>2</sub> Cu(SO <sub>4</sub> ) <sub>2</sub>	-2211.16	IMA2008-029	(NH <sub>4</sub> ) <sub>3</sub> Fe(SO <sub>4</sub> ) <sub>3</sub>	-3113.44
Nickelblodite anh.	(b)	-2436.65	Ferrinatrite anh.	Na <sub>3</sub> Fe <sup>3+</sup> (SO <sub>4</sub> ) <sub>3</sub>	-3455.26
Mereiterite anh.	K <sub>2</sub> Fe <sup>2+</sup> (SO <sub>4</sub> ) <sub>2</sub>	-2406.17	Letovicite	(NH <sub>4</sub> ) <sub>3</sub> H(SO <sub>4</sub> ) <sub>2</sub>	-2213.51
Syngenite anh.	K <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub>	-2891.21	Misenite	K <sub>8</sub> H <sub>6</sub> (SO <sub>4</sub> ) <sub>7</sub>	-8393.46
Mohrite anh.	(NH <sub>4</sub> ) <sub>2</sub> Fe <sup>2+</sup> (SO <sub>4</sub> ) <sub>2</sub>	-2125.85	Millosevichite	Al <sub>1.5</sub> Fe <sup>3+</sup> <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub>	-3223.97
Boussingaultite anh.	(NH <sub>4</sub> ) <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub>	-2482.34	Loweite anh.	Na <sub>12</sub> Mg <sub>7</sub> (SO <sub>4</sub> ) <sub>13</sub>	-17565.30
Koktaite anh.	(NH <sub>4</sub> ) <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub>	-2623.41	Lecontite anh.	(f)	-1324.15
Ni-boussingaultite anh.	(c)	-2208.77	Gorgeyite anh.	K <sub>2</sub> Ca <sub>5</sub> (SO <sub>4</sub> ) <sub>6</sub>	-8638.40
Efremovite	(NH <sub>4</sub> ) <sub>2</sub> Mg <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	-3768.59	Omongwaite anh.	Na <sub>2</sub> Ca <sub>5</sub> (SO <sub>4</sub> ) <sub>6</sub>	-8576.05
Pickeringite anh.	MgAl <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub>	-4743.69			

Footnote added at the end of table 3

(a) - (NH<sub>4</sub>)Fe<sup>3+</sup><sub>0.75</sub>Al<sub>0.25</sub>(SO<sub>4</sub>)<sub>2</sub>; (b) - Na<sub>2</sub>Ni<sub>0.75</sub>Mg<sub>0.25</sub>(SO<sub>4</sub>)<sub>2</sub>; (c) - (NH<sub>4</sub>)<sub>2</sub>Ni<sub>0.75</sub>Mg<sub>0.25</sub>(SO<sub>4</sub>)<sub>2</sub>; (d) - (Zn<sub>0.6</sub>Fe<sup>2+</sup><sub>0.4</sub>Al<sub>2</sub>)(SO<sub>4</sub>)<sub>4</sub>; (e) - (Co<sub>0.6</sub>Mg<sub>0.4</sub>)Al<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>; (f) - ((NH<sub>4</sub>)<sub>0.75</sub>K<sub>0.25</sub>)Na(SO<sub>4</sub>).

Table 4. Enthalpies of formation of some hydrous sulfates predicted in this work.

Data for sulfate whose formula has been reported at ISO <sub>4</sub>				Estimation of $\Delta H^\circ_{f,298.15K}$ for hydrated sulfates			
Formula / number of SO <sub>4</sub>	(I)	(II)	(III)	Mineral	Formula	$\Delta H^\circ_{f,298.15K}$	Uncert.
	$\Delta H^\circ_{f,298.15K}$ (kJ.mol <sup>-1</sup> )	$\Delta H^\circ_{diss}$ (kJ.mol <sup>-1</sup> )	$\Delta H^\circ_{hyd}$ (kJ.mol <sup>-1</sup> )			Pred.	
NaHSO <sub>4</sub> ·H <sub>2</sub> O	-1125.50 <sup>a</sup>	-24.14	-5.75	Matteuccite	NaHSO <sub>4</sub> ·H <sub>2</sub> O	-1425.15	± 8.8
NaMg <sub>0.5</sub> (SO <sub>4</sub> ) <sub>2</sub> ·2(H <sub>2</sub> O)	-1345.55 <sup>a</sup>	-37.59	-11.60	Blodite	Na <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·4(H <sub>2</sub> O)	-3889.91	± 21.8
NaMg <sub>0.5</sub> (SO <sub>4</sub> ) <sub>2</sub> ·2.5(H <sub>2</sub> O)	-1345.55 <sup>a</sup>	-37.59	-12.48	Konyaite	Na <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·5(H <sub>2</sub> O)	-4185.57	± 23.9
NaCa <sub>0.5</sub> (SO <sub>4</sub> ) <sub>2</sub> ·2(H <sub>2</sub> O)	-1414.60 <sup>a</sup>	-6.54	-1.45	Wattevilleite	Na <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub> ·4(H <sub>2</sub> O)	-4007.70	± 21.8
NaCu <sub>0.5</sub> (SO <sub>4</sub> ) <sub>2</sub> ·(H <sub>2</sub> O)	-1105.58 <sup>b</sup>	-11.61	-2.48	Krohnkite	Na <sub>2</sub> Cu(SO <sub>4</sub> ) <sub>2</sub> ·2(H <sub>2</sub> O)	-2803.92	± 17.6
NaZn <sub>0.5</sub> (SO <sub>4</sub> ) <sub>2</sub> ·2(H <sub>2</sub> O)	-1209.00 <sup>a</sup>	-17.34	-4.98	Changoite	Na <sub>2</sub> Zn(SO <sub>4</sub> ) <sub>2</sub> ·4(H <sub>2</sub> O)	-3603.57	± 21.8
NaNi <sub>0.375</sub> Mg <sub>0.125</sub> (SO <sub>4</sub> ) <sub>2</sub> ·2(H <sub>2</sub> O)	-1218.33 <sup>b</sup>	-9.94	-2.56	Nickelblodite	Na <sub>2</sub> Ni <sub>0.75</sub> Mg <sub>0.25</sub> (SO <sub>4</sub> ) <sub>2</sub> ·4(H <sub>2</sub> O)	-3617.38	± 21.8
Na <sub>0.5</sub> Al <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·3(H <sub>2</sub> O)	-1228.43 <sup>b</sup>	-70.26	-25.45	Tamarugite	NaAl(SO <sub>4</sub> ) <sub>2</sub> ·6(H <sub>2</sub> O)	-4271.15	± 26.0
Na <sub>0.5</sub> Al <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·5.5(H <sub>2</sub> O)	-1228.43 <sup>b</sup>	-70.26	-31.02	Mendozite	NaAl(SO <sub>4</sub> ) <sub>2</sub> ·11(H <sub>2</sub> O)	-5751.81	± 36.5
Na <sub>0.5</sub> Fe <sup>3+</sup> <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·3(H <sub>2</sub> O)	-1057.67 <sup>b</sup>	3.23	1.99	Amarillite	NaFe <sup>3+</sup> (SO <sub>4</sub> ) <sub>2</sub> ·6(H <sub>2</sub> O)	-3874.76	± 26.0
KFe <sup>2+</sup> <sub>0.5</sub> (SO <sub>4</sub> ) <sub>2</sub> ·2(H <sub>2</sub> O)	-1203.09 <sup>b</sup>	-3.90	-0.59	Mereiterite	K <sub>2</sub> Fe <sup>2+</sup> (SO <sub>4</sub> ) <sub>2</sub> ·4(H <sub>2</sub> O)	-3582.95	± 21.8
KMg <sub>0.5</sub> (SO <sub>4</sub> ) <sub>2</sub> ·2(H <sub>2</sub> O)	-1377.35 <sup>a</sup>	-17.59	-5.06	Leonite	K <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·4(H <sub>2</sub> O)	-3940.43	± 21.8
KMg <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·3(H <sub>2</sub> O)	-1377.35 <sup>a</sup>	-17.59	-5.78	Picromerite	K <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·6(H <sub>2</sub> O)	-4529.67	± 26.0
KCa <sub>0.5</sub> (SO <sub>4</sub> ) <sub>2</sub> ·0.5(H <sub>2</sub> O)	-1445.60 <sup>b</sup>	12.66	3.07	Syngenite	K <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub> ·(H <sub>2</sub> O)	-3178.96	± 15.5
KCu <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·3(H <sub>2</sub> O)	-1104.80 <sup>a</sup>	-24.19	-8.24	Cyanochroite	K <sub>2</sub> Cu(SO <sub>4</sub> ) <sub>2</sub> ·6(H <sub>2</sub> O)	-3989.50	± 26.0
K <sub>0.5</sub> Al <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·5.5(H <sub>2</sub> O)	-1235.10 <sup>a</sup>	-69.49	-30.66	Kalinite	KAl(SO <sub>4</sub> ) <sub>2</sub> ·11(H <sub>2</sub> O)	-5764.45	± 36.5
K <sub>0.5</sub> Al <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·6(H <sub>2</sub> O)	-1235.10 <sup>a</sup>	-69.49	-31.55	Alum-K	KAl(SO <sub>4</sub> ) <sub>2</sub> ·12(H <sub>2</sub> O)	-6060.12	± 38.6
K <sub>0.5</sub> Fe <sup>3+</sup> <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·0.5(H <sub>2</sub> O)	-1021.40 <sup>a</sup>	-38.94	-7.66	Krausite	KFe <sup>3+</sup> (SO <sub>4</sub> ) <sub>2</sub> ·(H <sub>2</sub> O)	-2352.02	± 15.5
K <sub>0.5</sub> Fe <sup>3+</sup> <sub>0.5</sub> (SO <sub>4</sub> ) <sub>2</sub> ·2(H <sub>2</sub> O)	-1021.40 <sup>a</sup>	-38.94	-12.05	Goldichite	KFe <sup>3+</sup> (SO <sub>4</sub> ) <sub>2</sub> ·4(H <sub>2</sub> O)	-3242.50	± 21.8
NH <sub>4</sub> Fe <sup>2+</sup> <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·3(H <sub>2</sub> O)	-1062.93 <sup>b</sup>	-25.26	-8.64	Mohrite	(NH <sub>4</sub> ) <sub>2</sub> Fe <sup>2+</sup> (SO <sub>4</sub> ) <sub>2</sub> ·6(H <sub>2</sub> O)	-3906.55	± 26.0
NH <sub>4</sub> Mg <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·3(H <sub>2</sub> O)	-1241.17 <sup>b</sup>	-34.97	-12.27	Boussingaultite	(NH <sub>4</sub> ) <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·6(H <sub>2</sub> O)	-4270.29	± 26.0
(NH <sub>4</sub> ) <sub>0.5</sub> Al <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·6(H <sub>2</sub> O)	-1167.10 <sup>b</sup>	-78.09	-35.57	Tschermigite	(NH <sub>4</sub> )Al(SO <sub>4</sub> ) <sub>2</sub> ·12(H <sub>2</sub> O)	-5932.17	± 38.6
NH <sub>4</sub> Ca <sub>0.5</sub> (SO <sub>4</sub> ) <sub>2</sub> ·0.5(H <sub>2</sub> O)	-1311.71 <sup>b</sup>	-2.43	-0.07	Koktaite	(NH <sub>4</sub> ) <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub> ·(H <sub>2</sub> O)	-2917.45	± 15.5
(NH <sub>4</sub> ) <sub>0.5</sub> Fe <sup>3+</sup> <sub>0.375</sub> Al <sub>0.125</sub> (SO <sub>4</sub> ) <sub>3</sub> ·6(H <sub>2</sub> O)	-1046.96 <sup>b</sup>	-15.04	-6.06	Lonecreekite	(NH <sub>4</sub> )Fe <sup>3+</sup> <sub>0.75</sub> Al <sub>0.25</sub> (SO <sub>4</sub> ) <sub>2</sub> ·12(H <sub>2</sub> O)	-5632.85	± 38.6
NH <sub>4</sub> Ni <sub>0.375</sub> Mg <sub>0.125</sub> (SO <sub>4</sub> ) <sub>3</sub> ·3(H <sub>2</sub> O)	-1104.38 <sup>b</sup>	-16.88	-5.51	-	(NH <sub>4</sub> ) <sub>2</sub> Ni <sub>0.75</sub> Mg <sub>0.25</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6(H <sub>2</sub> O)	-3983.21	± 26.0
Fe <sup>2+</sup> <sub>0.25</sub> Fe <sup>3+</sup> <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·5(H <sub>2</sub> O)	-878.44 <sup>b</sup>	-78.62	-30.04	Romerite	Fe <sup>2+</sup> Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·14(H <sub>2</sub> O)	-7748.56	± 56.2
Fe <sup>2+</sup> <sub>0.25</sub> Fe <sup>3+</sup> <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·5.5(H <sub>2</sub> O)	-878.44 <sup>b</sup>	-78.62	-34.82	Bilinite	Fe <sup>2+</sup> Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·22(H <sub>2</sub> O)	-10118.89	± 73.0
Mg <sub>0.25</sub> Al <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·5(H <sub>2</sub> O)	-1185.92 <sup>b</sup>	-109.37	-48.81	Pickeringite	MgAl <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·22(H <sub>2</sub> O)	-11404.78	± 73.0
Fe <sup>2+</sup> <sub>0.25</sub> Al <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·5.5(H <sub>2</sub> O)	-1093.44 <sup>b</sup>	-107.87	-48.13	Halotrichite	Fe <sup>2+</sup> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·22(H <sub>2</sub> O)	-11032.14	± 73.0
Mn <sup>2+</sup> <sub>0.25</sub> Al <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·5.5(H <sub>2</sub> O)	-1129.73 <sup>b</sup>	-104.01	-46.38	Apjohnite	Mn <sup>2+</sup> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·22(H <sub>2</sub> O)	-11170.25	± 73.0
Zn <sub>0.15</sub> Fe <sup>2+</sup> <sub>0.1</sub> Al <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·5.5(H <sub>2</sub> O)	-1117.34 <sup>b</sup>	-93.32	-41.51	Dietrichite	Zn <sub>0.6</sub> Fe <sup>2+</sup> <sub>0.4</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·22(H <sub>2</sub> O)	-11101.24	± 73.0
Co <sub>0.15</sub> Mg <sub>0.1</sub> Al <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·5.5(H <sub>2</sub> O)	-1135.53 <sup>b</sup>	-98.44	-43.84	Wupatkiite	Co <sub>0.6</sub> Mg <sub>0.4</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·22(H <sub>2</sub> O)	-11183.33	± 73.0
Na <sub>0.92</sub> Mg <sub>0.54</sub> (SO <sub>4</sub> ) <sub>3</sub> ·1.15(H <sub>2</sub> O)	-1351.18 <sup>b</sup>	-31.44	-8.02	Loweite	Na <sub>1.2</sub> Mg <sub>7</sub> (SO <sub>4</sub> ) <sub>13</sub> ·15(H <sub>2</sub> O)	-22078.02	± 118.6
NaFe <sup>3+</sup> <sub>0.33</sub> (SO <sub>4</sub> ) <sub>3</sub> ·(H <sub>2</sub> O)	-1151.75 <sup>b</sup>	-14.52	-3.24	Ferrinaitrite	Na <sub>3</sub> Fe <sup>3+</sup> (SO <sub>4</sub> ) <sub>3</sub> ·3(H <sub>2</sub> O)	-4346.68	± 26.4
Na <sub>1.33</sub> Ca <sub>0.33</sub> (SO <sub>4</sub> ) <sub>3</sub> ·0.67(H <sub>2</sub> O)	-1410.00 <sup>a</sup>	-0.74	0.31	Hydroglauberite /Eugsterite	Na <sub>4</sub> Ca(SO <sub>4</sub> ) <sub>3</sub> ·2(H <sub>2</sub> O)	-4816.86	± 24.3
Zn <sub>0.25</sub> Fe <sup>3+</sup> <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·5.5(H <sub>2</sub> O)	-891.12 <sup>b</sup>	-81.52	-31.18	Lishizhenite	ZnFe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·14(H <sub>2</sub> O)	-7803.81	± 24.3
Cu <sub>0.25</sub> Fe <sup>3+</sup> <sub>0.5</sub> (SO <sub>4</sub> ) <sub>3</sub> ·1.5(H <sub>2</sub> O)	-839.46 <sup>b</sup>	-78.60	-22.77	Ransomite	CuFe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·6(H <sub>2</sub> O)	-5212.36	± 56.2
(NH <sub>4</sub> ) <sub>0.75</sub> K <sub>0.25</sub> Na(SO <sub>4</sub> ) <sub>2</sub> ·2(H <sub>2</sub> O)	-1324.15 <sup>b</sup>	11.51	4.46	Lecontite	(NH <sub>4</sub> ) <sub>0.75</sub> K <sub>0.25</sub> Na(SO <sub>4</sub> ) <sub>2</sub> ·2(H <sub>2</sub> O)	-1907.50	± 39.4
K <sub>0.33</sub> Ca <sub>0.83</sub> (SO <sub>4</sub> ) <sub>3</sub> ·0.17(H <sub>2</sub> O)	-1439.73 <sup>b</sup>	-6.14	-0.59	Gorgeyite	K <sub>2</sub> Ca <sub>5</sub> (SO <sub>4</sub> ) <sub>6</sub> ·(H <sub>2</sub> O)	-8935.81	± 10.9
Na <sub>0.33</sub> Ca <sub>0.83</sub> (SO <sub>4</sub> ) <sub>3</sub> ·0.5H <sub>2</sub> O	-1429.34 <sup>b</sup>	-12.60	-2.18	Omongwaite	Na <sub>2</sub> Ca <sub>5</sub> (SO <sub>4</sub> ) <sub>6</sub> ·3H <sub>2</sub> O	-9470.84	± 42.3
Fe <sup>3+</sup> <sub>0.67</sub> (SO <sub>4</sub> ) <sub>3</sub> ·5/3(H <sub>2</sub> O)	-860.50 <sup>a</sup>	-82.11	-24.65	-	Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·5(H <sub>2</sub> O)	-4124.96	± 46.5
Fe <sup>3+</sup> <sub>0.67</sub> (SO <sub>4</sub> ) <sub>3</sub> ·2(H <sub>2</sub> O)	-860.50 <sup>a</sup>	-82.11	-26.16	Lausenite	Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·6(H <sub>2</sub> O)	-4423.40	± 30.6
Fe <sup>3+</sup> <sub>0.67</sub> (SO <sub>4</sub> ) <sub>3</sub> ·2.33(H <sub>2</sub> O)	-860.50 <sup>a</sup>	-82.11	-27.51	Kornelite	Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·7(H <sub>2</sub> O)	-4721.35	± 32.7
Fe <sup>3+</sup> <sub>0.67</sub> (SO <sub>4</sub> ) <sub>3</sub> ·2.58(H <sub>2</sub> O)	-860.50 <sup>a</sup>	-82.11	-28.44	Kornelite	Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·7.75(H <sub>2</sub> O)	-4944.57	± 34.8
Fe <sup>3+</sup> <sub>0.67</sub> (SO <sub>4</sub> ) <sub>3</sub> ·3(H <sub>2</sub> O)	-860.50 <sup>a</sup>	-82.11	-29.87	Coquimbite	Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·9(H <sub>2</sub> O)	-5316.22	± 36.4
Fe <sup>3+</sup> <sub>0.67</sub> (SO <sub>4</sub> ) <sub>3</sub> ·3.33(H <sub>2</sub> O)	-860.50 <sup>a</sup>	-82.11	-30.91	Quenstedtite	Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·10(H <sub>2</sub> O)	-5613.26	± 39.0
Al <sub>0.67</sub> (SO <sub>4</sub> ) <sub>3</sub> ·5.67(H <sub>2</sub> O)	-1146.95 <sup>a</sup>	-121.32	-54.79	Alunogen	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·17(H <sub>2</sub> O)	-8601.54	± 41.1
Mg(SO <sub>4</sub> ) <sub>3</sub> ·5(H <sub>2</sub> O)	-1282.00 <sup>b</sup>	-94.34	-40.69	Pentahydrate	Mg(SO <sub>4</sub> ) <sub>3</sub> ·5(H <sub>2</sub> O)	-2792.20	± 55.8
Fe <sup>2+</sup> (SO <sub>4</sub> ) <sub>3</sub> ·5(H <sub>2</sub> O)	-920.14 <sup>b</sup>	-80.30	-34.50	Siderotil	Fe <sup>2+</sup> (SO <sub>4</sub> ) <sub>3</sub> ·5(H <sub>2</sub> O)	-2424.14	± 17.2

Footnote added at the end of table 4:

- Column (I): enthalpy of formation (per one mole of SO<sub>4</sub>) of anhydrous double sulfate (<sup>a</sup>Wagman et al. (1982); <sup>b</sup>estimated in anhydrous double sulfate model);
- Column (II): Enthalpy of dissolution (per one mole of SO<sub>4</sub>) of the anhydrous double sulfate
- Column (III): Enthalpy of hydration (per one SO<sub>4</sub>) of the hydrous double sulfate



Table 5. Comparison of predicted enthalpy of formation of  $\text{NaAl}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$  with values from literature.

	$\Delta H_{f, 298.15\text{K}}^\circ$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )		
	Wagman et al. (1982)	This work	error (%)
$\text{NaAl}(\text{SO}_4)_2$		-2456.85	
$\text{NaAl}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$	-3025.45	-3080.20	-1.81
$\text{NaAl}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$	-3934.84	-3974.31	-1.00
$\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	-4233.45	-4271.15	-0.89
$\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	-6002.74	-6047.49	-0.75

Table 6. Example of bilinite and romerite  $\Delta H_f^\circ$  estimation with models presented in this work.

Estimation of enthalpy of formation of anhydrous phase $\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4$						
	$\Delta H_f^\circ$ (kJ.mol <sup>-1</sup> )	$\Delta_{\text{H}}\text{O}^\circ \text{M}^{z+}$ (c) (kJ.mol <sup>-1</sup> )	Number O	$X_i$	number oxide	
<b>FeO</b>	-272.00	-74.90	1	0.0625	1	
<b>Fe<sub>2</sub>O<sub>3</sub></b>	-826.20	-160.71	3	0.1875	1	
<b>SO<sub>3</sub></b>	-454.51	-333.07	12	0.7500	4	
<b>total</b>	-	-	16	1	-	
<hr/>						
$\text{M}_i^{z_i+}$	-	$\text{M}_j^{z_j+}$	$[\Delta_{\text{H}}\text{O}^\circ \text{M}^{z_i+}(\text{c})] - [\Delta_{\text{H}}\text{O}^\circ \text{M}^{z_j+}(\text{c})]$ (kJ.mol <sup>-1</sup> )			
Fe <sup>2+</sup>	-	Fe <sup>3+</sup>	$\frac{(1 \times 8)}{16} *  \Delta_{\text{H}}\text{O}^\circ(\text{Fe}^{2+}) - \Delta_{\text{H}}\text{O}^\circ(\text{Fe}^{3+})  = 85.80$			
Fe <sup>2+</sup>	-	S <sup>6+</sup>	$\frac{(1 \times 12)}{16} *  \Delta_{\text{H}}\text{O}^\circ(\text{Fe}^{2+}) - \Delta_{\text{H}}\text{O}^\circ(\text{S}^{6+})  = 258.17$			
Fe <sup>3+</sup>	-	S <sup>6+</sup>	$\frac{(3 \times 12)}{16} *  \Delta_{\text{H}}\text{O}^\circ(\text{Fe}^{3+}) - \Delta_{\text{H}}\text{O}^\circ(\text{S}^{6+})  = 172.36$			
<hr/>						
$\Delta H_{f,ox}^\circ$ (kJ.mol <sup>-1</sup> ) Equation 15	$\Delta H_{f,ox}^\circ = \frac{(1 \times 3)}{16} *  \Delta_{\text{H}}\text{O}^\circ(\text{Fe}^{2+}) - \Delta_{\text{H}}\text{O}^\circ(\text{Fe}^{3+})  + \frac{(1 \times 12)}{16} *  \Delta_{\text{H}}\text{O}^\circ(\text{Fe}^{2+}) - \Delta_{\text{H}}\text{O}^\circ(\text{S}^{6+})  + \frac{(3 \times 12)}{16} *  \Delta_{\text{H}}\text{O}^\circ(\text{Fe}^{3+}) - \Delta_{\text{H}}\text{O}^\circ(\text{S}^{6+})  = -597.53$					
$\Delta H_f^\circ$ anhydrous (kJ.mol <sup>-1</sup> ) Equation 3 (modified)	$\Delta H_f^\circ(\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4) = \Delta H_{f,ox}^\circ(\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4) + \Delta H_f^\circ(\text{FeO}) + \Delta H_f^\circ(\text{Fe}_2\text{O}_3) + 4 * \Delta H_f^\circ(\text{SO}_3) = -3513.77$					
<hr/>						
Estimation of $\Delta H_f^\circ$ of bilinite $\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ and romerite $\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$						
	$\Delta H_f^\circ$ (kJ.mol <sup>-1</sup> )	Fe <sup>2+</sup>	Fe <sup>3+</sup>	SO <sub>4</sub> <sup>2-</sup>		
		-91.10	-49.90	-909.34		
<hr/>						
<b>Fe<sup>2+</sup><sub>0.25</sub>Fe<sup>3+</sup><sub>0.5</sub>(SO<sub>4</sub>)<sub>4</sub> · 5.5H<sub>2</sub>O</b>			<b>Fe<sup>2+</sup><sub>0.25</sub>Fe<sup>3+</sup><sub>0.5</sub>(SO<sub>4</sub>)<sub>4</sub> · 3.5H<sub>2</sub>O</b>			
number SO <sub>4</sub>	1			number SO <sub>4</sub>	1	
$\Delta H_f^\circ$ anhydrous (kJ.mol <sup>-1</sup> )	-878.44			$\Delta H_f^\circ$ anhydrous (kJ.mol <sup>-1</sup> )	-878.44	
$\Delta H_{diss}^\circ$ (kJ.mol <sup>-1</sup> )	-78.62			$\Delta H_{diss}^\circ$ (kJ.mol <sup>-1</sup> )	-78.62	
number of H <sub>2</sub> O	5.5			Number of H <sub>2</sub> O	3.5	
$\Delta H_{hyd}^\circ$ (kJ.mol <sup>-1</sup> )	-34.82			$\Delta H_{hyd}^\circ$ (kJ.mol <sup>-1</sup> )	-30.04	
$\Delta H_f^\circ$ hydrated (kJ.mol <sup>-1</sup> )	-2529.72			$\Delta H_f^\circ$ hydrated (kJ.mol <sup>-1</sup> )	-1937.14	
<b>Fe<sup>2+</sup>Fe<sup>3+</sup><sub>2</sub>(SO<sub>4</sub>)<sub>4</sub> · 22H<sub>2</sub>O</b>			<b>Fe<sup>2+</sup>Fe<sup>3+</sup><sub>2</sub>(SO<sub>4</sub>)<sub>4</sub> · 14H<sub>2</sub>O</b>			
$\Delta H_f^\circ$ Bilinite (kJ.mol <sup>-1</sup> )	<b>-10118.89</b>			$\Delta H_f^\circ$ Romerite (kJ.mol <sup>-1</sup> )	<b>-7748.56</b>	
Combination of Equations 28 and 29 :						
$\Delta H_f^\circ[\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}] = \Delta H_f^\circ[\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4] + 4 * \{5.5 * \Delta H_f^\circ[\text{H}_2\text{O}_{(l)}] + 0.2608 * 5.5^{2.227} * (\Delta H_{f,diss}^\circ[\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4] + 2.111)\}$						
$\Delta H_f^\circ[\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}] = \Delta H_f^\circ[\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4] + 4 * \{3.5 * \Delta H_f^\circ[\text{H}_2\text{O}_{(l)}] + 0.2608 * 3.5^{2.227} * (\Delta H_{f,diss}^\circ[\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4] + 2.111)\}$						

Table 7. Standard molal entropy ( $S^{\circ}_{298.15}$ ) for sulfates used for the calculation of fictive entropies values for oxides ( $J.K^{-1}.mol^{-1}$ ).

Formula	(I)		(II)		Formula	(I)		(II)	
	$S^{\circ}_{298.15K}$	ref	$\Delta S^{\circ}_{ox,298.15K}$			$S^{\circ}_{298.15K}$	ref	$\Delta S^{\circ}_{ox,298.15K}$	
Na <sub>2</sub> SO <sub>4</sub>	149.58	1	-0.11		CdSO <sub>4</sub>	123.13	3	-0.95	
	149.60	2	-0.09		MgSO <sub>4</sub>	91.60	1	-7.66	
	149.59	3	-0.10			91.40	2	-7.86	
K <sub>2</sub> SO <sub>4</sub>	175.56	1	-3.25			91.69	3	-7.57	
	175.60	2	-3.21		MnSO <sub>4</sub>	112.10	1	-0.29	
	175.58	3	-3.23			112.10 <sup>a</sup>	2	-0.29	
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	220.23	3	4.20			112.21	3	-0.18	
CaSO <sub>4</sub>	106.70	1	-0.82		Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	282.80 <sup>a</sup>	5	0.17	
	108.40	1	0.88		Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	239.30	1	3.45	
	108.40	1	0.88			239.30	2	3.45	
	107.40	2	-0.12			239.48	3	3.63	
	106.76	3	-0.76		KAl(SO <sub>4</sub> ) <sub>2</sub>	204.60	1	-2.73	
BaSO <sub>4</sub>	132.20	1	-0.45			204.60	2	-2.73	
	132.20	2	-0.45			204.73	3	-2.60	
	132.30	3	-0.35		K <sub>2</sub> Mg <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	389.30	2	11.98	
FeSO <sub>4</sub>	107.50	1	-0.73		Cd(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub>	486.05	3	0.06	
	107.60	3	-0.63		NH <sub>4</sub> Al(SO <sub>4</sub> ) <sub>2</sub>	216.46	3	-9.48	

Footnote added at the end of table 7:

1- Wagman et al. (1982); 2- Robie and Hemingway (1995); 3- Naumov et al. (1971); 4- Pankratz and Weller (1969); Majzlan et al. (2005). <sup>a</sup>Spin magnetic entropy ( $S^{\circ}_m$ ) of cations Mn<sup>2+</sup> and Fe<sup>3+</sup> have not been taken into account and are subtracted from listed values.

Table 8. Values of  $S^{\circ}_{298.15K}$  ( $J.K^{-1}.mol^{-1}$ ) (line I) and fictive  $S^{\circ}_{298.15K}$  (sulf) ( $J.K^{-1}.mol^{-1}$ ) (line II) for oxides.

		SO <sub>3</sub>	K <sub>2</sub> O	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	FeO	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	BaO	MnO	CdO	(NH <sub>4</sub> ) <sub>2</sub> O
(I)	$S^{\circ}_{298.15K}$ 3rd law, <sup>a</sup>	256.80	94.14	38.21	26.94	59.80	46.42	57.60	75.27	72.07	44.80	54.80	267.52
(II)	$S^{\circ}_{298.15K}$ (sulf) <sup>b</sup>	72.94	105.87	34.59	26.32	17.04	35.29	63.82	76.76	59.71	39.46	51.14	143.09

Foot note added at the end of table 8:

<sup>a</sup>Spin Magnetic entropy ( $S^{\circ}_m$ ) of cations Fe<sup>2+</sup>, Fe<sup>3+</sup> and Mn<sup>2+</sup> have been subtracted from entropies of formation ( $S^{\circ}$ ) of oxides given by Robie and Hemingway (1995), to obtain third-law entropy. <sup>b</sup>fictive  $S^{\circ}_{(sulfates)}$  ( $J.K^{-1}.mol^{-1}$ ) calculated by minimization of  $\Delta S^{\circ}_{ox}$ .

Table 9. Thermodynamic values (experimental and predicted in this study) for different hydrous sulfates belonging to the system  $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ .

Mineral	Formula	$\Delta H_{f,298.15\text{K}}^\circ$ (kJ.mol <sup>-1</sup> )	ref	$S_{298.15\text{K}}^\circ$ (J.K <sup>-1</sup> .mol <sup>-1</sup> )	ref	$\Delta G_{f,298.15\text{K}}^\circ$ (kJ.mol <sup>-1</sup> )	ref
Mikasaite	$\text{Fe}_2(\text{SO}_4)_3$	-2585.20	(1)	305.60	(1)	-2260.79	(1)
	$\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$	-4124.96 ( $\pm 30.6$ )	(2)	513.1	(2)	-3518.39	calc
		-4115.80	(3)	488.2	(3)	-3499.7	(3)
Lausenite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$	-4423.40 ( $\pm 32.7$ )	(2)	554.6	(2)	-3759.66	calc
Kornelite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$	-4721.35 ( $\pm 34.8$ )	(2)	596.1	(2)	-4000.44	calc
		-4692.20	(4)	590.6	(4)	-3793.7	(4)
	$\text{Fe}_2(\text{SO}_4)_3 \cdot 7.75 \text{H}_2\text{O}$	-4944.57 ( $\pm 36.4$ )	(2)	627.2	(2)	-4180.78	calc
	-4916.20	(5)	586.9	(5)			
Coquimbite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$	-5316.22 ( $\pm 39.0$ )	(2)	679.1	(2)	-4480.96	calc
		-5295.40	(5)	632.3	(5)		
		-5738.00	(3)	638.3	(3)	-4845.60	(3)
		-5288.20	(4)	670.1	(4)	-4250.60	(4)
Quenstedtite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 10 \text{H}_2\text{O}$	-5613.26 ( $\pm 41.1$ )	(2)	720.6	(2)	-4720.83	calc

Footnote added at the end of table 9:

ref: references. calc: calculated in this work. 1 - Majzlan et al. (2005); 2 - this work (Table 5);

3 - Majzlan et al. (2006); 4 - Hemingway et al. (2002); 5 - Ackermann et al. (2009).

Table 10. Experimental solubility product, predicted enthalpy of formation and entropy, calculated Gibbs free energy of formation and solubility products for some sulfate minerals.

Mineral	Formula	I log K Meas.	II Pred. $\Delta H_f^\circ$ (kJ.mol <sup>-1</sup> )	III Pred. $S^\circ$ (J.K <sup>-1</sup> .mol <sup>-1</sup> )	IV $\Delta G_f^\circ$ calc. (kJ.mol <sup>-1</sup> )	V log K calc.	VI V - I
Blodite	Na <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	-2.64 <sup>1</sup>	-3889.91	415.03	-3431.30	-2.76	-0.12
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	-4.6 <sup>2</sup>	-2027.19	190.52	-1800.24	-5.18	-0.58
Pentahydrate	Mg(SO <sub>4</sub> )·5H <sub>2</sub> O	-1.27 <sup>3</sup>	-2793.82	306.80	-2395.97	-1.92	-0.65
Syngenite	K <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	-7.67 <sup>1</sup>	-3178.96	327.75	-2892.02	-8.69	-1.02
Leonite	K <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	-4.13 <sup>1</sup>	-3940.43	444.02	-3482.59	-4.52	-0.39
Coquimbite	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	-8.98 <sup>4</sup>	-5316.22	685.97	-4483.08	-14.62	-5.64
Epsomite	Mg(SO <sub>4</sub> )·7H <sub>2</sub> O	-1.93 <sup>1</sup>	-3386.20	389.80	-2874.02	-2.58	-0.65
Mirabilite	Na <sub>2</sub> (SO <sub>4</sub> )·10H <sub>2</sub> O	-1.56 <sup>1</sup>	-4326.51	564.74	-3636.93	0.37	1.93
Picromerite	K <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	-4.50 <sup>1</sup>	-4529.67	527.02	-3957.49	-4.63	-0.13
Rozenite	Fe <sup>2+</sup> (SO <sub>4</sub> )·4H <sub>2</sub> O	-1.7 <sup>5</sup>	-2127.81	287.67	-1795.46	-2.26	-0.56
Bassanite	Ca(SO <sub>4</sub> )·0.5H <sub>2</sub> O	-3.92 <sup>6</sup>	-1584.41	128.27	-1443.21	-4.95	-1.03
Hexahydrate	Mg(SO <sub>4</sub> )·6H <sub>2</sub> O	-1.69 <sup>1</sup>	-3090.14	348.30	-2635.12	-2.28	-0.59
Melanterite	Fe(SO <sub>4</sub> )·7H <sub>2</sub> O	-2.31 <sup>7</sup>	-3015.95	412.17	-2512.10	-3.18	-0.87
Szomolnokite	Fe(SO <sub>4</sub> )·H <sub>2</sub> O	-1.66 <sup>4</sup>	-1234.43	163.17	-1073.58	-0.42	1.24
	CdSO <sub>4</sub> ·8/3H <sub>2</sub> O	-1.72 <sup>8</sup>	-1734.93	234.65	-1472.12	-3.17	-1.45
Kornelite	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	-7.87 <sup>4</sup>	-4721.35	602.97	-4002.55	-13.52	-5.65
Siderotil	Fe(SO <sub>4</sub> )·5H <sub>2</sub> O	-2.23 <sup>4</sup>	-2424.14	329.17	-2034.62	-2.62	-0.39
Halotrichite	Fe <sup>2+</sup> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·22H <sub>2</sub> O	-8.24 <sup>4</sup>	-11032.14	1270.60	-9328.62	-11.73	-3.49
Kieserite	Mg(SO <sub>4</sub> )·H <sub>2</sub> O	-0.14 <sup>1</sup>	-1602.10	140.80	-1432.91	0.62	0.76
	K <sub>2</sub> SO <sub>4</sub> FeSO <sub>4</sub> ·6H <sub>2</sub> O	-4.61 <sup>9</sup>	-4170.92	549.39	-3607.08	-7.25	-2.64
	Na <sub>2</sub> SO <sub>4</sub> FeSO <sub>4</sub> ·4H <sub>2</sub> O	-3.21 <sup>9</sup>	-3539.95	437.41	-3089.67	-6.91	-3.70
Ferrohexahydrate	Fe(SO <sub>4</sub> )·6H <sub>2</sub> O	-2.52 <sup>4</sup>	-2720.16	370.67	-2273.48	-2.92	-0.40
Yavapaiite	KFe(SO <sub>4</sub> ) <sub>2</sub>	-5.57 <sup>10</sup>	-2056.79	245.60	-1838.88	-9.06	-3.49
Glauberite	Na <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub>	-5.6 <sup>1</sup>	-2838.77	257.26	-2608.23	-7.73	-2.13
Thenardite	Na <sub>2</sub> (SO <sub>4</sub> )	-0.54 <sup>1</sup>	-1380.65	149.74	-1262.72	0.87	1.41
Anhydrite	Ca(SO <sub>4</sub> )	-4.47 <sup>1</sup>	-1429.56	107.52	-1316.94	-3.60	0.87
Mikasaite	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.81 <sup>11</sup>	-2577.55	312.47	-2258.90	1.15	0.34
Glaserite	Na <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·3K <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub>	-8.19 <sup>1</sup>	-5657.60	685.92	-5188.19	1.02	9.28
Arcanite	K <sub>2</sub> (SO <sub>4</sub> )	-1.89 <sup>1</sup>	-1418.22	178.73	-1301.06	1.38	3.27
Labile Salt	Na <sub>4</sub> Ca(SO <sub>4</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	-6.30 <sup>1</sup>	-4816.05	490.00	-4353.24	-8.27	-1.97
Romerite	Fe <sup>2+</sup> Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·14H <sub>2</sub> O	-11.77 <sup>4</sup>	-7748.56	1015.14	-6525.91	-18.67	-6.90
Bilinite	Fe <sup>2+</sup> Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·22H <sub>2</sub> O	-16.54 <sup>4</sup>	-10118.89	1303.97	-8426.04	-19.21	-2.67

Footnote added at the end of table 10

Meas.: measure. Pred. : predicted. Column VI (V – I): difference between column I and Column V.

Reference of log k in exponent in column I: 1- Harvie et al. (1984); 2- Garvin and White (1987); 3-

Harvie and Weare (1980); 4- Hemingway et al. (2002); 5- Chou et al. (2002); 6- Blanc et al. (2006); 7-

Parker and Khodakovskii (1995); 8- Cox et al. (1989); 9- Christov (2004); 10- Forray et al. (2005); 11-

Calculated from  $\Delta G_f^\circ$  given by Majzlan et al. (2005);

Appendix A (part 1/2): Data used to establish  $\Delta H_{f, 298.15K}^{\circ}$  estimation model of anhydrous sulfates.

Mineral/Compound	Formula	(I)	(II)	(III)	(IV)	(V)	(VI)
		$\Delta H_{f, 298.15K}^{\circ}$ (kJ.mol <sup>-1</sup> )	$\Delta H_{f,ox}^{\circ}$ (kJ.mol <sup>-1</sup> )	$\Delta H_{f(es, aq)}^{\circ}$ (kJ.mol <sup>-1</sup> )	error (%)	$\Delta H_{f(es, cr)}^{\circ}$ (kJ.mol <sup>-1</sup> )	error (%)
Thenardite	Na <sub>2</sub> SO <sub>4</sub>	-1387.08 <sup>1</sup>	-517.77	-1395.95	-0.64	-1380.65	0.46
		-1387.80 <sup>2</sup>	-518.49	-1395.95	-0.59	-1380.65	0.52
		-1388.80 <sup>3</sup>	-519.49	-1395.95	-0.52	-1380.65	0.59
Arcanite	K <sub>2</sub> SO <sub>4</sub>	-1437.79 <sup>1</sup>	-620.08	-1437.41	0.03	-1418.22	1.36
		-1437.70 <sup>2</sup>	-619.99	-1437.41	0.02	-1418.22	1.35
		-1433.69 <sup>7</sup>	-615.98	-1437.41	-0.26	-1418.22	1.08
		-1438.65 <sup>3</sup>	-620.94	-1437.41	0.09	-1418.22	1.42
Mascagnite	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	-1180.85 <sup>1</sup>	-295.64	-1127.35	4.53	-1187.59	-0.57
		-1182.70 <sup>2</sup>	-297.49	-1127.35	4.68	-1187.59	-0.41
		-1180.80 <sup>3</sup>	-295.59	-1127.35	4.53	-1187.59	-0.58
Anhydrite	CaSO <sub>4</sub>	-1434.11 <sup>1</sup>	-344.5	-1420.85	0.92	-1429.56	0.32
		-1425.24 <sup>1</sup>	-335.63	-1420.85	0.31	-1429.56	-0.30
		-1420.80 <sup>1</sup>	-331.19	-1420.85	0.00	-1429.56	-0.62
		-1434.40 <sup>2</sup>	-344.79	-1420.85	0.94	-1429.56	0.34
		-1435.15 <sup>3</sup>	-345.54	-1420.85	1.00	-1429.56	0.39
Baryte	BaSO <sub>4</sub>	-1473.20 <sup>1</sup>	-470.59	-1428.52	3.03	-1468.34	0.33
		-1473.60 <sup>2</sup>	-470.99	-1428.52	3.06	-1468.34	0.36
		-1458.35 <sup>3</sup>	-455.74	-1428.52	2.05	-1468.34	-0.69
Mg-sulfate	MgSO <sub>4</sub>	-1284.90 <sup>1</sup>	-228.79	-1334.76	-3.88	-1282.00	0.23
		-1284.90 <sup>2</sup>	-228.79	-1334.76	-3.88	-1282.00	0.23
		-1280.83 <sup>3</sup>	-224.72	-1334.76	-4.21	-1282.00	-0.09
Mn-sulfate	MnSO <sub>4</sub>	-1065.25 <sup>1</sup>	-225.54	-1081.48	-1.52	-1058.89	0.60
		-1065.70 <sup>2</sup>	-225.99	-1081.48	-1.48	-1058.89	0.64
		-1066.50 <sup>3</sup>	-226.79	-1081.48	-1.40	-1058.89	0.71
Anglesite	PbSO <sub>4</sub>	-919.94 <sup>1</sup>	-246.43	-846.60	7.97	-918.82	0.12
		-920.00 <sup>2</sup>	-246.49	-846.60	7.98	-918.82	0.13
		-919.92 <sup>3</sup>	-246.41	-846.60	7.97	-918.82	0.12
Zincosite	ZnSO <sub>4</sub>	-982.80 <sup>1</sup>	-177.79	-1006.30	-2.39	-976.39	0.65
		-980.10 <sup>2</sup>	-175.09	-1006.30	-2.67	-976.39	0.38
		-980.46 <sup>3</sup>	-175.45	-1006.30	-2.64	-976.39	0.42
Cd-sulfate	CdSO <sub>4</sub>	-933.28 <sup>1</sup>	-220.42	-932.32	0.10	-925.76	0.81
		-933.57 <sup>3</sup>	-220.71	-932.32	0.13	-925.76	0.84
Chalcocyanite	CuSO <sub>4</sub>	-771.36 <sup>1</sup>	-160.75	-782.34	-1.42	-772.23	-0.11
		-771.40 <sup>2</sup>	-160.79	-782.34	-1.42	-772.23	-0.11
		-770.37 <sup>3</sup>	-159.76	-782.34	-1.55	-772.23	-0.24
	SrSO <sub>4</sub>	-1453.10 <sup>1</sup>	-407.29	-1441.03	0.83	-1453.08	0.00
Mikasaite	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	-2581.50 <sup>1</sup>	-130.59	-2626.46	-1.74	-2577.55	0.15
		-2581.90 <sup>2</sup>	-130.72	-2626.46	-1.73	-2577.55	0.17
		-2583.67 <sup>3</sup>	-131.31	-2626.46	-1.66	-2577.55	0.24
Millosevichite	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	-3440.84 <sup>1</sup>	-133.87	-3633.74	-5.61	-3438.49	0.07
		-3441.80 <sup>2</sup>	-134.19	-3633.74	-5.58	-3438.49	0.10
		-3443.15 <sup>3</sup>	-134.64	-3633.74	-5.54	-3438.49	0.14
Godovikovite	NH <sub>4</sub> Al(SO <sub>4</sub> ) <sub>2</sub>	-2352.20 <sup>1</sup>	-194.99	-2386.04	-1.44	-2334.20	0.77
		-2353.82 <sup>3</sup>	-195.8	-2386.04	-1.37	-2334.20	0.83
Yavapaiite	KFe(SO <sub>4</sub> ) <sub>2</sub>	-2042.80 <sup>6</sup>	-269.54	-2091.20	-2.37	-2056.79	-0.68
Steklite	KAl(SO <sub>4</sub> ) <sub>2</sub>	-2470.20 <sup>1</sup>	-270.86	-2588.27	-4.78	-2486.78	-0.67
		-2470.90 <sup>2</sup>	-271.25	-2588.27	-4.75	-2486.78	-0.64
		-2471.64 <sup>3</sup>	-271.58	-2588.27	-4.72	-2486.78	-0.61
Zn-glauberite	Na <sub>2</sub> Zn(SO <sub>4</sub> ) <sub>2</sub>	-2418.00 <sup>1</sup>	-371.84	-2456.48	-1.59	-2413.70	0.18
Glauberite	Na <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub>	-2829.20 <sup>1</sup>	-435.14	-2849.37	-0.71	-2838.77	-0.34
Mn-glauberite	Na <sub>2</sub> Mn(SO <sub>4</sub> ) <sub>2</sub>	-2490.70 <sup>1</sup>	-390.84	-2524.91	-1.37	-2488.23	0.10
Mg-glauberite	Na <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub>	-2691.10 <sup>1</sup>	-382.84	-2772.04	-3.01	-2710.22	-0.71

Appendix A (part 2/2): Data used to establish  $\Delta H_{f, 298.15K}^{\circ}$  estimation model of anhydrous sulfates.

Mineral/Compound	Formula	(I)	(II)	(III)	(IV)	(V)	(VI)
		$\Delta H_{f, 298.15K}^{\circ}$ (kJ.mol <sup>-1</sup> )	$\Delta H_{f,ox}^{\circ}$ (kJ.mol <sup>-1</sup> )	$\Delta H_{f (es,aq)}^{\circ}$ (kJ.mol <sup>-1</sup> )	error (%)	$\Delta H_{f (es,cr)}^{\circ}$ (kJ.mol <sup>-1</sup> )	error (%)
	Na <sub>2</sub> Sr(SO <sub>4</sub> ) <sub>2</sub>	-2830.10 <sup>1</sup>	-457.49	-2858.89	-1.02	-2834.39	-0.15
	Na <sub>2</sub> Ba(SO <sub>4</sub> ) <sub>2</sub>	-2853.90 <sup>1</sup>	-490.99	-2841.26	0.44	-2856.59	-0.09
	(NH <sub>4</sub> ) <sub>2</sub> Sr(SO <sub>4</sub> ) <sub>2</sub>	-2639.30 <sup>1</sup>	-354.14	-2593.90	1.72	-2634.80	0.17
	(NH <sub>4</sub> ) <sub>2</sub> Cu(SO <sub>4</sub> ) <sub>2</sub>	-2054.30 <sup>1</sup>	-279.24	-1921.43	6.47	-1983.28	3.46
	(NH <sub>4</sub> ) <sub>2</sub> Zn(SO <sub>4</sub> ) <sub>2</sub>	-2201.60 <sup>1</sup>	-255.69	-2140.46	2.78	-2185.81	0.72
	K <sub>2</sub> Sr(SO <sub>4</sub> ) <sub>2</sub>	-2887.40 <sup>1</sup>	-511.94	-2915.86	-0.99	-2886.82	0.02
	K <sub>2</sub> Ba(SO <sub>4</sub> ) <sub>2</sub>	-2907.90 <sup>1</sup>	-543.79	-2898.23	0.33	-2909.03	-0.04
	K <sub>2</sub> Na <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>	-2821.30 <sup>1</sup>	-567.14	-2848.88	-0.98	-2813.73	0.27
Palmierite	K <sub>2</sub> Pb(SO <sub>4</sub> ) <sub>2</sub>	-2379.90 <sup>1</sup>	-444.34	-2358.45	0.90	-2396.24	-0.69
	K <sub>2</sub> Zn(SO <sub>4</sub> ) <sub>2</sub>	-2434.30 <sup>1</sup>	-405.79	-2513.45	-3.25	-2466.13	-1.31
Cyanochroite anh.	K <sub>2</sub> Cu(SO <sub>4</sub> ) <sub>2</sub>	-2209.60 <sup>1</sup>	-397.74	-2294.41	-3.84	-2263.60	-1.79
	K <sub>2</sub> Mn(SO <sub>4</sub> ) <sub>2</sub>	-2508.30 <sup>1</sup>	-425.44	-2581.88	-2.93	-2540.66	-1.29
Leonite anh.	K <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub>	-2754.70 <sup>1</sup>	-440.44	-2829.01	-2.70	-2762.66	-0.29
Langbeinite	K <sub>2</sub> Mg <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	-4071.00 <sup>2</sup>	-380.36	-4182.72	-2.74	-4065.47	0.14
		-4073.00 <sup>3</sup>	-381.02	-4182.72	-2.69	-4065.47	0.18
Zn-langbeinite	K <sub>2</sub> Zn <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	-3406.85 <sup>4</sup>	-326.37	-3543.00	-4.00	-3466.36	-1.75
Cd-langbeinite	K <sub>2</sub> Cd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	-3305.52 <sup>4</sup>	-354.03	-3390.99	-2.59	-3355.88	-1.52
Cd-effremovite	(NH <sub>4</sub> ) <sub>2</sub> Cd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	-3031.74 <sup>5</sup>	-240.27	-2997.03	1.14	-3059.00	-0.90
Mn-effremovite	(NH <sub>4</sub> ) <sub>2</sub> Mn <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	-3250.16 <sup>5</sup>	-228.51	-3290.39	-1.24	-3323.86	-2.27
Vanthoffite	Na <sub>6</sub> Mg(SO <sub>4</sub> ) <sub>4</sub>	-5461.81 <sup>3</sup>	-449.44	-5584.62	-2.25	-5495.31	-0.61
Eugsterite anh.	Na <sub>4</sub> Ca(SO <sub>4</sub> ) <sub>3</sub>	-4230.00 <sup>1</sup>	-467.26	-4256.18	-0.62	-4228.94	0.02
	Na <sub>4</sub> Sr(SO <sub>4</sub> ) <sub>3</sub>	-4209.10 <sup>1</sup>	-474.89	-4262.14	-1.26	-4221.93	-0.30
	Na <sub>4</sub> Ba(SO <sub>4</sub> ) <sub>3</sub>	-4240.10 <sup>1</sup>	-499.62	-4242.81	-0.06	-4239.77	0.01
	K <sub>4</sub> Sr(SO <sub>4</sub> ) <sub>3</sub>	-4323.30 <sup>1</sup>	-547.36	-4365.74	-0.98	-4316.89	0.15
	K <sub>4</sub> Ba(SO <sub>4</sub> ) <sub>3</sub>	-4342.20 <sup>1</sup>	-568.06	-4346.41	-0.10	-4334.74	0.17
	Na <sub>4</sub> K <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	-4204.50 <sup>1</sup>	-549.39	-4250.00	-1.08	-4199.33	0.12
	K <sub>4</sub> Na <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	-4263.90 <sup>1</sup>	-586.39	-4291.46	-0.65	-4236.91	0.63
	Na <sub>2</sub> K <sub>6</sub> (SO <sub>4</sub> ) <sub>4</sub>	-5709.24 <sup>1</sup>	-596.70	-5731.46	-0.39	-5657.60	0.90
Mercallite	KHSO <sub>4</sub>	-1160.60 <sup>1</sup>	-381.58	-1178.64	-1.55	-1156.16	0.38
Na-mercallite	NaHSO <sub>4</sub>	-1125.50 <sup>1</sup>	-320.68	-1150.16	-2.19	-1129.94	-0.39

Footnote added at the end of Appendix A:

Anh.: Anhydrous form

Column (I): enthalpy of formation of anhydrous salt from reference (in exponent) 1 - Wagman et al. (1982); 2 -Robie and Hemingway (1995); 3 - Naumov et al. (1971); 4 - Zhou et al. (2001b); 5 - Zhou et al. (2001a); 6 - Forray et al. (2005); 7 – Barin (1985)

Column (II): enthalpy of formation of anhydrous salt from constituent oxides per one mole of SO<sub>4</sub>;

Column (III): predicted enthalpy of formation of anhydrous salt with parameters  $\Delta_H O^{\circ} = M_i^{Z_i+}$  (aq) ;

Column (IV): % error between predicted enthalpy of formation (Column III) and experimental enthalpy of formation (Column I) ;

Column (V): predicted enthalpy of formation of anhydrous salt with parameters  $\Delta_H O^{\circ} = M_i^{Z_i+}$  (c) ;



Column (VI): % error between predicted enthalpy of formation (Column V) and experimental enthalpy of formation (Column I).

Appendix B (part 1/2) : Data used for establish  $\Delta H_{f, 298.15K}^{\circ}$  estimation model for hydrated sulfates. (formula and all values are per one  $SO_4$ ).

Mineral	Formula	(I)	(II)	(III)	(IV)	(V)	(VI)
		$\Delta H_{f, 298.15K}^{\circ}$ (kJ.mol <sup>-1</sup> )	$\Delta H_{hyd}^{\circ}$ (kJ.mol <sup>-1</sup> )	n H <sub>2</sub> O	$\Delta H_{diss}^{\circ}$ (kJ.mol <sup>-1</sup> )	$\Delta H_f^{\circ}$ calc (kJ.mol <sup>-1</sup> )	Error (%)
	KCu <sub>0.5</sub> (SO <sub>4</sub> ) · 0.25H <sub>2</sub> O	-1180.70 <sup>1</sup>	-2.42	0.25	-24.19	-1181.93	-0.10
Bassanite	CaSO <sub>4</sub> · 0.5H <sub>2</sub> O	-1576.74 <sup>1</sup>	-4.55	0.5	-18.23	-1584.40	-0.49
Bassanite	CaSO <sub>4</sub> · 0.5H <sub>2</sub> O	-1574.65 <sup>1</sup>	-6.90	0.5	-18.23	-1584.40	-0.62
Zr-Sulfate	Zr <sub>0.5</sub> (SO <sub>4</sub> ) · 0.5H <sub>2</sub> O	-1276.95 <sup>1</sup>	-21.45	0.5	-104.69	-1276.90	0.00
Kieserite	MgSO <sub>4</sub> · H <sub>2</sub> O	-1602.10 <sup>1</sup>	-23.29	1	-91.44	-1602.15	0.00
Kieserite	MgSO <sub>4</sub> · H <sub>2</sub> O	-1612.40 <sup>4</sup>	-33.59	1	-91.44	-1598.08	0.89
	NaMn <sub>0.5</sub> (SO <sub>4</sub> ) · H <sub>2</sub> O	-1540.15 <sup>1</sup>	-0.89	1	-14.69	-1542.51	-0.15
	KMg <sub>0.5</sub> (SO <sub>4</sub> ) · H <sub>2</sub> O	-1675.70 <sup>1</sup>	-4.44	1	-17.59	-1675.27	0.03
	KMn <sub>0.5</sub> (SO <sub>4</sub> ) · H <sub>2</sub> O	-1559.40 <sup>1</sup>	-11.34	1	-17.69	-1552.09	0.47
	KZn <sub>0.5</sub> (SO <sub>4</sub> ) · H <sub>2</sub> O	-1518.80 <sup>1</sup>	-7.74	1	-20.99	-1515.96	0.19
	KCu <sub>0.5</sub> (SO <sub>4</sub> ) · H <sub>2</sub> O	-1413.35 <sup>1</sup>	-14.64	1	-24.19	-1404.45	0.63
	KCu <sub>0.5</sub> (SO <sub>4</sub> ) · H <sub>2</sub> O	-1413.35 <sup>1</sup>	-7.54	1	-24.19	-1411.55	0.13
	NaZn <sub>0.5</sub> (SO <sub>4</sub> ) · H <sub>2</sub> O	-1507.10 <sup>1</sup>	-4.19	1	-17.34	-1506.85	0.02
	ZnSO <sub>4</sub> · H <sub>2</sub> O	-1304.49 <sup>1</sup>	-27.78	1	-79.94	-1297.04	0.57
	CdSO <sub>4</sub> · H <sub>2</sub> O	-1239.55 <sup>1</sup>	-12.36	1	-51.96	-1240.20	-0.05
	CdSO <sub>4</sub> · H <sub>2</sub> O	-1240.05 <sup>3</sup>	-12.57	1	-51.67	-1240.41	-0.03
	CuSO <sub>4</sub> · H <sub>2</sub> O	-1085.83 <sup>1</sup>	-20.56	1	-73.08	-1083.80	0.19
	NiSO <sub>4</sub> · H <sub>2</sub> O	-1190.89 <sup>3</sup>	-23.45	1	-89.81	-1190.35	0.05
Cobaltkieserite	CoSO <sub>4</sub> · H <sub>2</sub> O	-1201.53 <sup>1</sup>	-17.67	1	-77.59	-1203.57	-0.17
Szomolnokite	FeSO <sub>4</sub> · H <sub>2</sub> O	-1243.69 <sup>1</sup>	-21.38	1	-72.04	-1240.57	0.25
Szomolnokite	FeSO <sub>4</sub> · H <sub>2</sub> O	-1244.30 <sup>2</sup>	-21.99	1	-72.04	-1240.57	0.30
Szomolnokite	FeSO <sub>4</sub> · H <sub>2</sub> O	-1244.82 <sup>3</sup>	-21.86	1	-71.39	-1241.05	0.30
Szmlkite	MnSO <sub>4</sub> · H <sub>2</sub> O	-1376.50 <sup>1</sup>	-17.34	1	-64.89	-1375.55	0.07
Szmlkite	MnSO <sub>4</sub> · H <sub>2</sub> O	-1378.13 <sup>3</sup>	-17.72	1	-63.64	-1376.47	0.12
	UO <sub>2</sub> SO <sub>4</sub> · H <sub>2</sub> O	-2146.40 <sup>1</sup>	-7.39	1	-83.24	-2160.20	-0.64
	BeSO <sub>4</sub> · H <sub>2</sub> O	-1523.80 <sup>1</sup>	-24.69	1	-86.94	-1521.27	0.17
	Li <sub>2</sub> SO <sub>4</sub> · H <sub>2</sub> O	-1735.50 <sup>1</sup>	-5.10	1	-29.85	-1737.62	-0.12
	Li <sub>2</sub> SO <sub>4</sub> · H <sub>2</sub> O	-1735.05 <sup>3</sup>	-4.32	1	-29.85	-1737.95	-0.17
	K <sub>0.5</sub> Al <sub>0.5</sub> (SO <sub>4</sub> ) · 1.5H <sub>2</sub> O	-1690.55 <sup>7</sup>	-14.59	1.5	-69.49	-1696.04	-0.32
	Al <sub>2/3</sub> (SO <sub>4</sub> ) · 2H <sub>2</sub> O	-1770.57 <sup>1</sup>	-35.81	2	-121.33	-1773.82	-0.18
	Al <sub>2/3</sub> (SO <sub>4</sub> ) · 2H <sub>2</sub> O	-1771.76 <sup>3</sup>	-36.23	2	-121.33	-1773.82	-0.12
Sanderite	MgSO <sub>4</sub> · 2H <sub>2</sub> O	-1896.20 <sup>1</sup>	-23.49	2	-91.44	-1901.97	-0.30
Sanderite	MgSO <sub>4</sub> · 2H <sub>2</sub> O	-1894.90 <sup>4</sup>	-22.19	2	-91.44	-1897.90	-0.16
Gypsum	CaSO <sub>4</sub> · 2H <sub>2</sub> O	-2022.63 <sup>1</sup>	-0.71	2	-18.23	-2027.16	-0.22
Gypsum	CaSO <sub>4</sub> · 2H <sub>2</sub> O	-2023.00 <sup>2</sup>	-0.79	2	-18.23	-2027.45	-0.22
Gypsum	CaSO <sub>4</sub> · 2H <sub>2</sub> O	-2023.82 <sup>3</sup>	-0.86	2	-18.23	-2028.20	-0.22
Leonite	KMg <sub>0.5</sub> (SO <sub>4</sub> ) · 2H <sub>2</sub> O	-1973.80 <sup>1</sup>	-8.64	2	-17.59	-1970.19	0.18
Leonite	KMg <sub>0.5</sub> (SO <sub>4</sub> ) · 2H <sub>2</sub> O	-1975.50 <sup>3</sup>	-10.33	2	-17.59	-1970.19	0.27
	KMn <sub>0.5</sub> (SO <sub>4</sub> ) · 2H <sub>2</sub> O	-1852.70 <sup>1</sup>	-10.74	2	-17.69	-1847.02	0.31
	NaZn <sub>0.5</sub> (SO <sub>4</sub> ) · 2H <sub>2</sub> O	-1796.00 <sup>1</sup>	0.81	2	-17.34	-1801.76	-0.32
Zicosulfate	Zr <sub>0.5</sub> (SO <sub>4</sub> ) · 2H <sub>2</sub> O	-1727.15 <sup>1</sup>	-30.79	2	-104.69	-1729.97	-0.16
	BeSO <sub>4</sub> · 2H <sub>2</sub> O	-1823.14 <sup>1</sup>	-30.13	2	-86.94	-1820.79	0.13
	BeSO <sub>4</sub> · 2H <sub>2</sub> O	-1824.40 <sup>3</sup>	-30.25	2	-85.80	-1821.56	0.16
	UO <sub>2</sub> SO <sub>4</sub> · 2.5H <sub>2</sub> O	-2607.10 <sup>1</sup>	-27.24	2.5	-83.24	-2608.44	-0.05
	UO <sub>2</sub> SO <sub>4</sub> · 2.5H <sub>2</sub> O	-2607.50 <sup>5</sup>	-27.64	2.5	-83.24	-2608.48	-0.04
Kornelite	Fe <sub>2/3</sub> (SO <sub>4</sub> ) · 2.58H <sub>2</sub> O	-1638.73 <sup>6</sup>	-18.98	2.58	-82.11	-1648.95	-0.62
	Sm <sub>2/3</sub> (SO <sub>4</sub> ) · 8/3H <sub>2</sub> O	-2110.27 <sup>1</sup>	-26.82	2.67	-70.71	-2108.11	0.10
	CdSO <sub>4</sub> · 8/3H <sub>2</sub> O	-1729.40 <sup>1</sup>	-12.37	2.67	-51.96	-1735.92	-0.38
	CdSO <sub>4</sub> · 8/3H <sub>2</sub> O	-1730.11 <sup>3</sup>	-12.79	2.67	-51.67	-1736.11	-0.35
Picromerite	KMg <sub>0.5</sub> (SO <sub>4</sub> ) · 3H <sub>2</sub> O	-2269.80 <sup>1</sup>	-10.73	3	-17.59	-2264.81	0.22
Picromerite	KMg <sub>0.5</sub> (SO <sub>4</sub> ) · 3H <sub>2</sub> O	-2270.73 <sup>3</sup>	-11.66	3	-17.59	-2264.81	0.26
	KZn <sub>0.5</sub> (SO <sub>4</sub> ) · 3H <sub>2</sub> O	-2117.10 <sup>1</sup>	-18.23	3	-20.99	-2105.88	0.53

Mineral	Formula	(I)	(II)	(III)	(IV)	(V)	(VI)
		$\Delta H_{f,298.5K}^{\circ}$ (kJ.mol <sup>-1</sup> )	$\Delta H_{hyd}^{\circ}$ (kJ.mol <sup>-1</sup> )	n H <sub>2</sub> O	$\Delta H_{diss}^{\circ}$ (kJ.mol <sup>-1</sup> )	$\Delta H_f^{calc}$ (kJ.mol <sup>-1</sup> )	Error (%)
Banattite	CuSO <sub>4</sub> · 3H <sub>2</sub> O	-1684.31 <sup>1</sup>	-31.23	3	-73.08	-1679.59	0.28
Coquimbite	Fe <sub>2/3</sub> (SO <sub>4</sub> ) · 3H <sub>2</sub> O	-1765.13 <sup>6</sup>	-22.92	3	-82.11	-1772.84	-0.44
	La <sub>2/3</sub> (SO <sub>4</sub> ) · 3 H <sub>2</sub> O	-2216.00 <sup>1</sup>	-20.52	3	-66.97	-2219.71	-0.17
	UO <sub>2</sub> SO <sub>4</sub> · 3H <sub>2</sub> O	-2754.30 <sup>1</sup>	-27.48	3	-83.24	-2757.14	-0.10
	UO <sub>2</sub> SO <sub>4</sub> · 3H <sub>2</sub> O	-2755.29 <sup>5</sup>	-28.47	3	-83.24	-2757.18	-0.07
	UO <sub>2</sub> SO <sub>4</sub> · 3.5H <sub>2</sub> O	-2900.80 <sup>1</sup>	-27.03	3.5	-83.24	-2905.65	-0.17
	UO <sub>2</sub> SO <sub>4</sub> · 3.5H <sub>2</sub> O	-2901.60 <sup>5</sup>	-27.83	3.5	-83.24	-2905.69	-0.14
Starkeyite	MgSO <sub>4</sub> · 4H <sub>2</sub> O	-2496.60 <sup>1</sup>	-36.08	4	-91.44	-2497.20	-0.02
Starkeyite	MgSO <sub>4</sub> · 4H <sub>2</sub> O	-2497.30 <sup>3</sup>	-40.85	4	-91.44	-2493.13	0.17
	NiSO <sub>4</sub> · 4H <sub>2</sub> O	-2104.10 <sup>1</sup>	-55.57	4	-90.43	-2084.79	0.92
Rozenite	FeSO <sub>4</sub> · 4H <sub>2</sub> O	-2129.20 <sup>1</sup>	-25.18	4	-72.04	-2132.72	-0.17
	MnSO <sub>4</sub> · 4H <sub>2</sub> O	-2258.10 <sup>1</sup>	-17.23	4	-64.89	-2266.63	-0.38
	MnSO <sub>4</sub> · 4H <sub>2</sub> O	-2258.74 <sup>3</sup>	-16.62	4	-63.64	-2267.36	-0.38
	BeSO <sub>4</sub> · 4H <sub>2</sub> O	-2423.75 <sup>1</sup>	-42.93	4	-86.94	-2415.64	0.33
	BeSO <sub>4</sub> · 4H <sub>2</sub> O	-2425.75 <sup>3</sup>	-43.79	4	-85.80	-2416.32	0.39
Chalcanthite	CuSO <sub>4</sub> · 5H <sub>2</sub> O	-2279.62 <sup>1</sup>	-38.73	5	-73.08	-2272.21	0.33
Chalcanthite	CuSO <sub>4</sub> · 5H <sub>2</sub> O	-2279.70 <sup>2</sup>	-38.77	5	-73.04	-2272.23	0.33
Chalcanthite	CuSO <sub>4</sub> · 5H <sub>2</sub> O	-2280.47 <sup>3</sup>	-40.57	5	-74.07	-2271.65	0.39
Jokokuite	MnSO <sub>4</sub> · 5H <sub>2</sub> O	-2553.10 <sup>1</sup>	-18.32	5	-64.89	-2562.47	-0.37
	Al <sub>2/3</sub> (SO <sub>4</sub> ) · 6H <sub>2</sub> O	-2959.63 <sup>1</sup>	-49.25	6	-121.33	-2966.26	-0.22
	Al <sub>2/3</sub> (SO <sub>4</sub> ) · 6H <sub>2</sub> O	-2961.60 <sup>3</sup>	-50.45	6	-121.33	-2966.26	-0.16
Hexahydrite	MgSO <sub>4</sub> · 6H <sub>2</sub> O	-3087.00 <sup>1</sup>	-38.67	6	-91.44	-3090.19	-0.10
Hexahydrite	MgSO <sub>4</sub> · 6H <sub>2</sub> O	-3088.06 <sup>3</sup>	-43.80	6	-91.44	-3086.12	0.06
Hexahydrite	MgSO <sub>4</sub> · 6H <sub>2</sub> O	-3088.10 <sup>4</sup>	-39.77	6	-91.44	-3086.12	0.06
Alum-K	K <sub>0.5</sub> Al <sub>0.5</sub> (SO <sub>4</sub> ) · 6H <sub>2</sub> O	-3030.90 <sup>1</sup>	-32.37	6	-69.49	-3030.08	0.03
Alum-K	K <sub>0.5</sub> Al <sub>0.5</sub> (SO <sub>4</sub> ) · 6H <sub>2</sub> O	-3030.90 <sup>7</sup>	-32.55	6	-69.49	-3027.67	0.03
Alum-K	K <sub>0.5</sub> Al <sub>0.5</sub> (SO <sub>4</sub> ) · 6H <sub>2</sub> O	-3033.00 <sup>3</sup>	-33.75	6	-69.49	-3030.80	0.07
Tschermigite	(NH <sub>4</sub> ) <sub>0.5</sub> Al <sub>0.5</sub> (SO <sub>4</sub> ) · 6H <sub>2</sub> O	-2971.19 <sup>1</sup>	-31.65	6	-69.09	-2970.90	0.01
Tschermigite	(NH <sub>4</sub> ) <sub>0.5</sub> Al <sub>0.5</sub> (SO <sub>4</sub> ) · 6H <sub>2</sub> O	-2973.17 <sup>3</sup>	-32.83	6	-68.28	-2971.33	0.06
Bianchite	ZnSO <sub>4</sub> · 6 H <sub>2</sub> O	-2779.65 <sup>3</sup>	-35.76	6	-82.28	-2781.45	-0.06
Retgersite	NiSO <sub>4</sub> · 6H <sub>2</sub> O	-2682.82 <sup>1</sup>	-46.48	6	-90.43	-2677.72	0.19
Retgersite	NiSO <sub>4</sub> · 6H <sub>2</sub> O	-2683.40 <sup>2</sup>	-46.77	6	-90.14	-2677.88	0.21
Retgersite	NiSO <sub>4</sub> · 6H <sub>2</sub> O	-2684.41 <sup>3</sup>	-47.45	6	-89.81	-2678.05	0.24
	CoSO <sub>4</sub> · 6H <sub>2</sub> O	-2683.60 <sup>1</sup>	-31.87	6	-79.24	-2687.86	-0.16
	CoSO <sub>4</sub> · 6H <sub>2</sub> O	-2685.29 <sup>3</sup>	-31.91	6	-77.59	-2688.74	-0.13
Epsomite	MgSO <sub>4</sub> · 7H <sub>2</sub> O	-3388.71 <sup>1</sup>	-46.47	7	-91.44	-3386.25	0.07
Epsomite	MgSO <sub>4</sub> · 7H <sub>2</sub> O	-3388.70 <sup>2</sup>	-46.46	7	-91.44	-3386.25	0.07
Epsomite	MgSO <sub>4</sub> · 7H <sub>2</sub> O	-3390.05 <sup>3</sup>	-51.88	7	-91.44	-3382.18	0.23
Epsomite	MgSO <sub>4</sub> · 7H <sub>2</sub> O	-3387.70 <sup>4</sup>	-45.46	7	-91.44	-3382.18	0.16
Goslarite	ZnSO <sub>4</sub> · 7 H <sub>2</sub> O	-3077.75 <sup>1</sup>	-37.61	7	-79.94	-3078.47	-0.02
Goslarite	ZnSO <sub>4</sub> · 7 H <sub>2</sub> O	-3077.50 <sup>2</sup>	-40.06	7	-82.64	-3077.10	0.01
Goslarite	ZnSO <sub>4</sub> · 7 H <sub>2</sub> O	-3079.14 <sup>3</sup>	-41.34	7	-82.28	-3077.29	0.06
Morenosite	NiSO <sub>4</sub> · 7H <sub>2</sub> O	-2976.33 <sup>1</sup>	-46.08	7	-90.43	-2973.76	0.09
Morenosite	NiSO <sub>4</sub> · 7H <sub>2</sub> O	-2976.50 <sup>2</sup>	-45.96	7	-90.14	-2973.91	0.09
Morenosite	NiSO <sub>4</sub> · 7H <sub>2</sub> O	-2978.11 <sup>3</sup>	-47.24	7	-89.81	-2974.07	0.14
Bieberite	CoSO <sub>4</sub> · 7H <sub>2</sub> O	-2979.93 <sup>1</sup>	-34.29	7	-79.24	-2983.63	-0.12
Bieberite	CoSO <sub>4</sub> · 7H <sub>2</sub> O	-2981.59 <sup>3</sup>	-34.30	7	-77.59	-2984.46	-0.10
Melanterite	FeSO <sub>4</sub> · 7H <sub>2</sub> O	-3014.57 <sup>1</sup>	-28.83	7	-72.04	-3020.17	-0.19
Melanterite	FeSO <sub>4</sub> · 7H <sub>2</sub> O	-3014.30 <sup>2</sup>	-28.56	7	-72.04	-3020.17	-0.19
Melanterite	FeSO <sub>4</sub> · 7H <sub>2</sub> O	-3016.51 <sup>3</sup>	-30.12	7	-71.39	-3020.50	-0.13
Mallardite	MnSO <sub>4</sub> · 7H <sub>2</sub> O	-3139.30 <sup>1</sup>	-16.71	7	-64.89	-3153.49	-0.45
Mallardite	MnSO <sub>4</sub> · 7H <sub>2</sub> O	-3140.90 <sup>3</sup>	-17.06	7	-63.64	-3154.13	-0.42
Mirabilite	Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O	-4327.26 <sup>1</sup>	-1.13	10	-2.86	-4326.47	0.02
Mirabilite	Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O	-4327.30 <sup>2</sup>	-0.45	10	-2.86	-4327.19	0.00
Mirabilite	Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O	-4330.83 <sup>3</sup>	-2.98	10	-2.86	-4328.19	0.06

Footnote added at the end of Appendix B

Colonne (I) : experimental values of  $\Delta H_{f,298.15K}^{\circ}$  (for one  $\text{SO}_4$ ) for hydrous sulfates from references (in exponent): 1- Wagman et al. (1982); 2- Robie and Hemingway (1995); 3- Naumov et al. (1971); 4- Grevel and Majzlan (2011); 5- Grenthe et al. (1992); 6- Ackermann et al. (2009); 7- Barin (1985)

Column (II):  $\Delta H_{\text{hyd}}^{\circ}$ . Enthalpy of hydration of hydrous sulfate per one  $\text{SO}_4$ ;

Column (III): number of moles of hydration water ( per one  $\text{SO}_4$ )

Column (IV): Enthalpy of dissolution (per one  $\text{SO}_4$ ) of anhydrous analogue;

Column (V):  $\Delta H_{\text{ox}}^{\circ}$ . Predicted enthalpy of formation of hydrous sulfate (Eqn. (26));

Column (VI): % error between predicted enthalpy of formation (Column V) and experimental enthalpy of formation (Column I) for hydrous sulfates