Thermochemistry of jarosite-alunite and natrojarosite-natroalunite solid solutions

CHRISTOPHE DROUET,1 KATRINA L. PASS,1 DIRK BARON,2 SARA DRAUCKER,2 and ALEXANDRA NAVROTSKY1,∗

1Thermochemistry Facility and NEAT ORU, University of California at Davis, Davis, California 95616, USA
2Department of Physics and Geology, California State University at Bakersfield, Bakersfield, California 93311, USA

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Abstract—The thermochemistry of jarosite-alunite and natrojarosite-natroalunite solid solutions was investigated. Members of these series were either coprecipitated or synthesized hydrothermally and were characterized by XRD, FTIR, electron microprobe analysis, ICP-MS, and thermal analysis. Partial alkali substitution and vacancies on the Fe/Al sites were observed in all cases, and the solids studied can be described by the general formula K1-x-y Na y (H3O)x Fez Alw (SO4)2(OH)6-3(3-z-w) (H2O)3(3-z-w). A strong preferential incorporation of Fe over Al in the jarosite/alunite structure was observed. Heats of formation from the elements, ΔHf°, were determined by high-temperature oxide melt solution calorimetry. The solid solutions deviate slightly from thermodynamic ideality by exhibiting positive enthalpies of mixing in the range 0 to +11 kJ/mol. The heats of formation of the end members of both solid solutions were derived. The values ΔHf° = -3773.6 ± 9.4 kJ/mol, ΔHf° = -4912.2 ± 24.2 kJ/mol, ΔHf° = -3734.6 ± 9.7 kJ/mol and ΔHf° = -4979.7 ± 7.5 kJ/mol were found for K0.85 (H3O)0.15 Fe2.5 (SO4)2 (OH)4.5 (H2O)1.5, K0.85 (H3O)0.15 Al2.5 (SO4)2 (OH)4.5 (H2O)1.5, Na0.7 (H3O)0.3 Fe2.7 (SO4)2 (OH)5.1 (H2O)0.9, and Na0.7 (H3O)0.3 Al2.7 (SO4)2 (OH)5.1 (H2O)0.9, respectively. To our knowledge, this is the first experimentally-based report of ΔHf° for such nonstoichiometric alunite and natroalunite samples. These thermodynamic data should prove helpful to study, under given conditions, the partitioning of Fe and Al between the solids and aqueous solution.

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1. INTRODUCTION

Jarosites and alunites are members of the alunite supergroup of minerals and can be described by the ideal formula AB5(SO4)2(OH)6, with B-sites being occupied by Fe3+ and Al3+. Although numerous cations can occupy the A-site, potassium and sodium are incontestably the most commonly encountered in natural solids of this group as well as in synthetic phases (Dutrizac and Jambor, 2000).

Natural specimens have been found in many places on Earth, some dating from several million years (Hofstra et al., 1999; Stoffregen et al., 2000). These recent to ancient occurrences and vacancies on the Fe/Al sites were observed in all cases, and the solids studied can be described by the general formula K1-x-y Na y (H3O)x Fez Alw (SO4)2(OH)6-3(3-z-w) (H2O)3(3-z-w). A strong preferential incorporation of Fe over Al in the jarosite/alunite structure was observed. Heats of formation from the elements, ΔHf°, were determined by high-temperature oxide melt solution calorimetry. The solid solutions deviate slightly from thermodynamic ideality by exhibiting positive enthalpies of mixing in the range 0 to +11 kJ/mol. The heats of formation of the end members of both solid solutions were derived. The values ΔHf° = -3773.6 ± 9.4 kJ/mol, ΔHf° = -4912.2 ± 24.2 kJ/mol, ΔHf° = -3734.6 ± 9.7 kJ/mol and ΔHf° = -4979.7 ± 7.5 kJ/mol were found for K0.85 (H3O)0.15 Fe2.5 (SO4)2 (OH)4.5 (H2O)1.5, K0.85 (H3O)0.15 Al2.5 (SO4)2 (OH)4.5 (H2O)1.5, Na0.7 (H3O)0.3 Fe2.7 (SO4)2 (OH)5.1 (H2O)0.9, and Na0.7 (H3O)0.3 Al2.7 (SO4)2 (OH)5.1 (H2O)0.9, respectively. To our knowledge, this is the first experimentally-based report of ΔHf° for such nonstoichiometric alunite and natroalunite samples. These thermodynamic data should prove helpful to study, under given conditions, the partitioning of Fe and Al between the solids and aqueous solution.

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2. EXPERIMENTAL

2.1. Synthesis

2.1.1. Jarosite-alunite solid solution

Five compositions in the solid solution between jarosite, KFe$_3$(SO$_4$)$_2$(OH)$_6$, and alunite, KAl$_3$(SO$_4$)$_2$(OH)$_6$, were synthesized following a procedure described by Brophy et al. (1962). Varying amounts of K$_2$SO$_4$, Fe$_2$(SO$_4$)$_3$, and Al$_2$(SO$_4$)$_3$·18H$_2$O were placed in a sealed vessel and heated to 150°C for 48 h. The resulting solids were then heated to 300°C for 1 h.

2.1.2. Natrojarosite-natroalunite solid solution

Six members of the solid solution between natrojarosite, NaFe$_3$(SO$_4$)$_2$(OH)$_6$, and natroalunite, NaAl$_3$(SO$_4$)$_2$(OH)$_6$, were synthesized from varying weights of reagent grade Na$_2$SO$_4$, Fe$_2$(SO$_4$)$_3$, and Al$_2$(SO$_4$)$_3$·18H$_2$O using two synthesis methods (Table 1). The first synthesis route consisted of a coprecipitation of the above reactants at 90°C for 4 h, with sulfuric acid 0.1 N. The precipitate was then filtered, washed with deionized water, and dried at 110°C for 24 h.

2.1.3. Alunite-natroalunite solid solution

To cross-check the results obtained for the jarosite-alunite and natrojarosite-natroalunite solid solutions, we prepared three solids from the alunite-natroalunite solid solution, with varying Na/K ratios. These jarosite-natroalunite solid solutions, we prepared three solids from the alunite-natroalunite solid solution, with varying Na/K ratios.

Table 1. Composition of starting synthesis solutions.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Vol. (mL)</th>
<th>K$_2$SO$_4$ (g)</th>
<th>Na$_2$SO$_4$ (g)</th>
<th>Fe$_2$(SO$_4$)$_3$ (g)</th>
<th>Al$_2$(SO$_4$)$_3$·18H$_2$O (g)</th>
<th>Synthesis method</th>
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<tbody>
<tr>
<td>K series: jarosite-alunite solid solution</td>
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<tr>
<td>II-2*</td>
<td>100</td>
<td>4.4</td>
<td>0</td>
<td>10.5</td>
<td>40.5</td>
<td>Brophy et al. (1962)</td>
</tr>
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<td>0</td>
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<tr>
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<td>49.0</td>
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<td>3.1</td>
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<td>1.3</td>
<td>51.5</td>
<td>Brophy et al. (1962)</td>
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<tr>
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<td>3.6</td>
<td>2.0</td>
<td>Coprecipitation</td>
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<td>Coprecipitation</td>
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<td>0</td>
<td>0.60</td>
<td>Hydrothermal</td>
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<tr>
<td>Alunite-natroalunite solid solution</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T-1</td>
<td>90</td>
<td>0.84</td>
<td>0.60</td>
<td>0</td>
<td>4.8</td>
<td>Stoffregen and Cygan (1990)</td>
</tr>
<tr>
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<td>0</td>
<td>4.8</td>
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<td>90</td>
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<td>1.35</td>
<td>0</td>
<td>5.4</td>
<td>Stoffregen and Cygan (1990)</td>
</tr>
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</table>

* Same sample names as those given by Brophy et al. (1962).

2.2. Characterization

Powder X-ray diffraction patterns were recorded on a Rigaku BIP-Plane diffractometer for the jarosite-alunite and the alunite-natroalunite series and on a Scintag PAD-V diffractometer for the natrojarosite-natroalunite series. In all cases, Cu Kα radiation was used (λ = 1.54056 Å). Before each experiment, the diffractometer was calibrated with quartz as a standard.

The chemical composition of the jarosite-alunite and alunite-natroalunite samples was determined by ICP-MS. Small amounts of the precipitates were digested in 20% trace-metal grade HNO$_3$, and analyzed for K, Na, Al, Fe, and S using a Perkin Elmer Elan 6100. The instrument was calibrated using NIST-traceable standards. The uncertainty associated with such measurements is 5%. The composition of the natrojarosite-natroalunite samples was drawn from electron microprobe analysis. The measurements were carried out with a Cameca SX-50 apparatus. Each sample was pressed into a 5 mg pellet and immobilized with epoxy resin. The microprobe results were used to determine the potassium, sodium, iron, aluminum, and sulfur contents, assuming that each unit formula contains two sulfate groups. The standard deviation on each determination (not reported here for the sake of clarity) was close to 5%. For all experiments, total weight percents of the analyzed elements are in good agreement with expected totals.

Thermal analyses (TG/DSC) were performed on a Netzsch STA 449 C, with argon as the carrier gas. The heating rate was 10°C/min, and the gas phase was constantly monitored by Fourier transform infrared spectroscopy using a Bruker EQUINOX 55 spectrometer (MCT detector). Transmission infrared spectra were recorded on the same spectrometer, but using a DTGS detector. Pellets of 13 mm diameter (150 mg) were pressed under 300 bar for 1 min. The spectrometer was flushed with nitrogen to avoid contamination. Spectra were collected in the 400–4000 cm$^{-1}$ range with a resolution of 4 cm$^{-1}$. A baseline correction was made before interpretation.

2.3. High-temperature Calorimetry

High temperature drop solution calorimetry was carried out at 700°C in a custom-built Tian-Calvet twin calimeter. The technique was described in detail elsewhere (Navrotsky, 1977 and 1997). In this work, sodium molybdate, 3Na$_2$O·4MoO$_3$, was used as solvent. The pelletized samples (5–15 mg) were dropped into a platinum crucible containing the solvent, located in the hot zone of the calorimeter (700°C). The end of the reaction was judged by the return of the baseline to its initial value. The final state in these calorimetric experiments is a dilute solution in 3Na$_2$O·4MoO$_3$ of the sulfates of Na, K, and Fe.
Al and Fe$^{3+}$ (as ions in the melt) and gaseous H$_2$O, all at 700°C. Indeed, preliminary studies on simple sulfates and jarosite phases (Majzlan et al., 2002; Drouet and Navrotsky, 2003) have shown that all the sulfur was retained in the melt rather than emitted in the gas phase. During the experiments, oxygen is flushed through the gas space above the melt (~35 mL/min) and bubbled through the solvent (~5 mL/min) to maintain oxidizing conditions, stir the melt, and remove the evolved water.

Throughout the text, the notation $\Delta H^\circ_f$ will represent the enthalpy of formation from the elements of a given species. For heats of formation determined from the oxides/sulfates, the corresponding notation will be $\Delta H^\circ_{\text{ox}}$.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization

The X-ray diffraction patterns obtained with the samples precipitated in this work were compared to the PDF (powder diffraction file) standard files 22–0827 for jarosite, 71–1776 for alunite, 36–0425 for natrojarosite, and 41–1467 for natroalunite. Figure 1 is related to samples C-2 and H-3, which are close in composition to natrojarosite and natroalunite respectively. In all cases, the Fe-rich samples could easily be identified as jarosite group minerals, and Al-rich samples as alunite group minerals. Evolution of the XRD patterns from jarosite-like to alunite-like was observed as the aluminum content increased, as expected for solid solutions.

The unit cell parameters were determined for all samples (Table 2). For both the jarosite-alunite and natrojarosite-natroalunite solid solutions, the unit cell parameter “a” was found to increase monotonically with the iron content. In contrast, the parameter “c” remained almost constant for these series, close to 17.1 Å for the potassium-containing samples and 16.6 Å for the Na samples, regardless of the Fe/Al ratio. These results are consistent with those reported by Stoffregen et al. (2000) for Fe-Al substitution in jarosite-like species.

The unit cell parameters obtained for the samples from the alunite-natroalunite solid solution (Table 2) show, on the contrary, constant “a” values, close to 6.98 Å, but increasing “c” values in the range 16.7–17.2 Å as the sodium content increases. This is in accord with reported data on alunites and natroalunites (Stoffregen et al., 2000), and the “a” and “c” variations observed here also agree with earlier results on A-site potassium-sodium substitution in jarosites (Drouet and Navrotsky, 2003).

The chemical compositions of the solids synthesized were determined from ICP-MS and/or electron microprobe analyses (Table 2). The K + Na content of all solids was lower than 1 mol/2 mol of sulfate, implying some substitution of hydronium ions for potassium and sodium. For the sodium-containing samples, the hydronium content was not a simple function of the amount of sodium in the reactant mixture. It was affected by

### Table 2. Chemical composition and unit cell parameters of the samples prepared in this work.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Chemical composition$^a$</th>
<th>Unit cell parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K$^+$</td>
<td>Na$^+$</td>
</tr>
<tr>
<td><strong>K series: jarosite-alunite solid solution</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II-2</td>
<td>0.79</td>
<td>0</td>
</tr>
<tr>
<td>II-10</td>
<td>0.79</td>
<td>0</td>
</tr>
<tr>
<td>II-7</td>
<td>0.83</td>
<td>0</td>
</tr>
<tr>
<td>II-4</td>
<td>0.89</td>
<td>0</td>
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<tr>
<td>II-5</td>
<td>0.99</td>
<td>0</td>
</tr>
<tr>
<td><strong>Na series: natrojarosite-natroalunite solid solution</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-1</td>
<td>0</td>
<td>0.68</td>
</tr>
<tr>
<td>C-2</td>
<td>0</td>
<td>0.69</td>
</tr>
<tr>
<td>C-3</td>
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<td>0.70</td>
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<td>H-1</td>
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<tr>
<td>H-2</td>
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<td>0.68</td>
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<tr>
<td>H-3</td>
<td>0</td>
<td>0.66</td>
</tr>
<tr>
<td><strong>Alunite-natroalunite solid solution</strong></td>
<td></td>
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</tr>
<tr>
<td>T-1</td>
<td>0.70</td>
<td>0.08</td>
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<td>T-2</td>
<td>0.48</td>
<td>0.29</td>
</tr>
<tr>
<td>T-3</td>
<td>0.24</td>
<td>0.59</td>
</tr>
</tbody>
</table>

$^a$ Normalized composition, containing two SO$_4^{2-}$ ions per unit formula. Standard deviation on each value is close to 5%.

$^b$ Derived from K + Na$^+$ + H$_2$O = 1 in A-site.

$^c$ Derived from Fe = 3-z and OH = 6-3z and H$_2$O = 3z.
the Fe/Al ratio: the amount of H$_2$O$^+$ decreases for higher iron contents. In a similar way, the sum Fe + Al was generally smaller than 3 mol/2 mol of sulfate, indicating B-site vacancies and the associated substitution of water molecules for part of the OH$^-$ groups (protonation). The amount of such vacancies decreased with increasing iron content, especially for samples synthesized hydrothermally.

We focused our syntheses on the preparation of two series of Fe-Al compounds. Samples from the first series were members of the jarosite-natroalunite solid solution having similar potassium contents and amounts of B-site vacancies. To a first approximation, the only compositional variable was the iron-to-aluminum ratio. This series will be referred to as the “potassium series.” The second family of compounds was the parallel to the first one, but with sodium replacing potassium (i.e., natrojarosite-natrosulafite solid solution), therefore leading to a “sodium series.” The general chemical formulas of the potassium and sodium series can be approximated to K$_{0.85}$ (H$_3$O)$_{0.15}$ Fe$_{2.5}$w Al$_w$ (SO$_4$)$_{2}$ (OH)$_{4.5}$ (H$_2$O)$_{1.5}$ and Na$_{0.7}$ (H$_3$O)$_{0.3}$ Fe$_{2.7}$w Al$_w$ (SO$_4$)$_{2}$ (OH)$_{5.1}$ (H$_2$O)$_{0.9}$, although some variations in the K series are observed. Figure 2 shows the composition of the samples synthesized in this work for both series, in the plane Fe/Al/B-site vacancies.

The composition of the intermediate solids from the potassium series (jarosite-alunite solid solution) shows that Fe is incorporated preferentially over Al into the crystal structure. This is apparent from comparison of the Al/Fe ratios in the starting solutions and the resulting solids. For example, the synthesis solution for sample II-4 has an Al/Fe mole ratio of ~10:1, but leads to a precipitate with an Al/Fe ratio close to 1:2:1 (Tables 1 and 2). Such preferential incorporation of Fe has been reported by Brophy et al. (1962) for similar compositions.

The Fe-rich samples from the sodium series were synthesized by coprecipitation. We experienced some difficulty in the preparation of Al-rich samples with this technique, even when using elevated Al/Fe ratios in the starting solutions. We succeeded in preparing Al-rich samples in the natrojarosite-natrosulafite series by using a hydrothermal synthesis route. As a general observation, Fe was incorporated preferentially to Al in B-sites, as for the potassium series. Hydrothermal synthesis enabled us to synthesize Al-rich samples with Al/Fe ratios close to the target compositions. These findings are in agreement with the observations made by Brophy et al. (1962) showing that increasing the temperature and the pressure and lowering the acidity of the starting solutions may lead to higher Al/Fe ratios.

The solids were analyzed by transmission FTIR spectroscopy. Infrared spectra for jarosite species have been reported and discussed elsewhere (Powers et al., 1975; Baron and Palmer, 1996; Drouet and Navrotsky, 2003). In particular, the FTIR spectra obtained here for Fe-rich samples were similar to those obtained with K-Na-H$_2$O jarosites in the literature. In the case of Al-rich samples, however, slight differences were observed, especially below 600 cm$^{-1}$. Figure 3 gives the FTIR spectrum obtained with our sample H-3, that is close to natroalunite, as compared to a typical spectrum obtained for the natrojarosite sample Na$_{0.71}$ (H$_3$O)$_{0.29}$ Fe$_{2.63}$ (SO$_4$)$_2$ (OH)$_{4.89}$ (H$_2$O)$_{1.11}$ during a previous study (Drouet and Navrotsky, 2003). The number of absorption bands is the same for both spectra: only the position and, to some extent, the intensity of some of these bands differ. This is indeed often the case for solid solutions, where the progression from one structure to the next is related to ion substitutions in equivalent crystallographic sites. It was, therefore, possible to assign the absorption bands observed here by comparison with the natrojarosite sample (Fig. 3). The differences observed between the two spectra in the region 400–600 cm$^{-1}$ are most likely due to changes in octahedra vibrations between FeO$_6$ and AlO$_6$. Indeed, absorption bands assigned to FeO$_6$ vibrations were reported at 477, 513, and 575 cm$^{-1}$ for jarosite (Baron and Palmer, 1996), and similar bands have been observed for the jarosite-natrosulafite solid solution (Drouet and Navrotsky, 2003). In the present case, three bands are seen below 600 cm$^{-1}$ for Al-rich samples (Fig. 3), at ca. 490, 515, and 592 cm$^{-1}$, Taking into account the above, these bands are most likely assignable to AlO$_6$ octahedra vibrations. Although the band at 592 cm$^{-1}$ is surprisingly intense, the positions of these three bands (490, 515, and 592 cm$^{-1}$) are close to those (486, 528, and 595 cm$^{-1}$) reported by Powers et al. (1975) for alunite.

In the region above 3000 cm$^{-1}$, the broad band corresponding to OH stretching (3456 cm$^{-1}$) appears at higher frequencies.
than for K-Na jarosites (ca. 3360–3390 cm$^{-1}$, Drouet and Navrotsky, 2003). This is in accord with literature data for a K-Na alunite sample (Okada et al., 1982) as well as with previous results comparing alunite and jarosite spectral features (Powers et al., 1975).

Thermal analyses of the samples showed the presence of "excess water," indicated by a peak close to 250°C (Fig. 4). Also, the two intense endothermic peaks that are typical during jarosite thermal decomposition were also observed here for both the K series and the Na series. Considering earlier works on the thermal decomposition of jarosites (Kubisz, 1971; Drouet and Navrotsky, 2003; and references therein) and alunites (Pysiak and Glinka, 1981; Bohmhammel et al., 1987; Stoffregen and Alpers, 1992), one can assign the first of these intense peaks (peak 1) in the range 400–600°C to dehydroxylation, leading among other phases to yavapaiite-like compounds (AB(SO$_4$)$_2$, A = K, Na, B = Fe, Al). The second intense peak (peak 2), at 700–820°C, can be attributed to the thermal decomposition of such yavapaiite-type structures.

The temperature dependence of these DSC peaks was followed as a function of the Fe/Al ratio in the sodium series, which is less documented than the potassium series in the literature. As shown in Table 3, the temperature of the maxima of these peaks increases as the samples become richer in aluminum, and differences of up to 113°C are seen between Al-rich and Fe-rich samples. This is in agreement with earlier results (Brophy et al., 1962), showing that the dehydroxylation of alunites requires higher temperatures than the dehydroxylation of jarosites. Note that the same general trend is observed for Fe and Al oxyhydroxides (Wolska et al., 1992; Kloprogge et al., 2002; Mitov et al., 2002): the higher the Al content, the higher the decomposition temperatures. According to Brophy et al. (1962), these observations may be indicative of stronger bonds formed between Al and hydroxyl groups. This has indeed been confirmed by Menchetti and Sabelli (1976), in the case of jarosite/alunite: these authors showed that Al-OH bond lengths in alunites were close to 1.879 Å as compared to 1.975 for Fe-OH in jarosites.

It is, moreover, possible to estimate, in a semiquantitative way, the enthalpy of decomposition of the (dehydrated) natrojarosite/natroalunite samples from integration of peak 1, after calibration of the DSC. The corresponding values of $\Delta H_{\text{decomp}}$ range between 193 and 235 kJ/mol (Table 3). $\Delta H_{\text{decomp}}$ becomes more endothermic as the Al content increases, confirming that the decomposition of the jarosite/alunite network requires more energy as the samples become richer in Al. Thus, the higher decomposition temperature for Al-rich samples has a thermodynamic basis.

### 3.2. Calorimetry

The enthalpies of formation from the elements ($\Delta H_f^\circ$) of the samples prepared in this work were obtained from high-temperature oxide melt calorimetric experiments as was done earlier for K-Na-H$_2$O jarosites (Drouet and Navrotsky, 2003). The values of $\Delta H_f^\circ$ were determined from experimental drop solution enthalpies ($\Delta H_{\text{sol}}$) by application of the thermodynamic cycle described in Table 4.

In this cycle, $x$, $y$, $z$, and $w$ respectively stand for the hydronium, sodium, iron, and aluminum contents in the solids, the potassium content being 1-$x$-$y$. As was mentioned above, the sum $z + w$ was generally lower than 3, leading to modifications in the OH sites as compared to the theoretical composition $\text{AB}_y(\text{SO}_4)_x(\text{OH})_6$, where B represents Fe or Al. In this regard, the general chemical formula of these compounds is $\text{K}_{1-x-y}\text{Na}_y(\text{H}_3\text{O})_x\text{Fe}_z\text{Al}_w(\text{SO}_4)_2(\text{OH})_{6-3(z+w)}(\text{H}_2\text{O})_{3(z+w)}$.

In addition to the enthalpies of drop solution of these solids, the thermodynamic cycle given in Table 3 involves the phases K$_2$SO$_4$, Na$_2$SO$_4$, $\alpha$-Fe$_2$O$_3$ (hematite), $\alpha$-Al$_2$O$_3$ (corundum), SO$_3$(g), and H$_2$O(l). Thermodynamic data for these compounds were taken from the literature (Robie and Hemingway, 1995; Majzlan et al., 2002; Drouet and Navrotsky, 2003), and they are given in Table 5. Numerical values for the enthalpies of drop solution $\Delta H_{\text{sol}}$ measured in this work, as well as the derived enthalpies of formation $\Delta H_f^\circ$, have also been included in this table. Note that each of these $\Delta H_f^\circ$ values have been determined using the actual $x$, $y$, $z$, and $w$ values corresponding to each sample. Therefore, the uncertainties in $\Delta H_f^\circ$ take into account the variations in chemical composition as well as the uncertainties on the experimental determination of $\Delta H_{\text{decomp}}$.

### Table 3. DSC peak maxima for the natrojarosite-natroalunite solid solution, and enthalpy of decomposition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe/Al</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>$\Delta H_{\text{decomp}}$ (kJ/mol)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>38.0</td>
<td>435.6</td>
<td>730.3</td>
</tr>
<tr>
<td>C-2</td>
<td>37.1</td>
<td>438.1</td>
<td>729.2</td>
</tr>
<tr>
<td>C-3</td>
<td>12.2</td>
<td>444.1</td>
<td>731.2</td>
</tr>
<tr>
<td>H-1</td>
<td>0.9</td>
<td>494.4</td>
<td>750.8</td>
</tr>
<tr>
<td>H-2</td>
<td>0.4</td>
<td>507.7</td>
<td>769.2</td>
</tr>
<tr>
<td>H-3</td>
<td>0</td>
<td>548.3</td>
<td>812.7</td>
</tr>
</tbody>
</table>

$^a$ Estimated from area of DSC peak 1.
deviations of the mean).

Formation of a (K, Na)-jarosite-alunite:

\[
\text{Na}_{0.7} \text{(H}_3\text{O})_{0.3} \text{Fe}_{2.7-w} \text{Al}_w \text{(SO}_4\text{)}_2 \text{(OH)}_{6.1} \text{(H}_2\text{O})_{0.9} \rightarrow (1-x-y)/2 \text{K}_2\text{O (solvn, 973)} + y/2 \text{Na}_2\text{O (solvn, 973)} + (15+3x-3y)/2 \text{H}_2\text{O (g, 973)}
\]

\[
\Delta H_f^\circ (\text{K}_2\text{SO}_4) = -377.2 \pm 10.1 \text{ kJ/mol}
\]

The ratio Fe/Al decreases, \( \Delta H_f^\circ \) varies from -3963 to -3760 kJ/mol for the potassium series, and from -3760 to -4980 kJ/mol for the sodium series. In other words, the enthalpies of formation from the elements become less exothermic as samples become richer in iron. However, because the heats of formation (from the elements) of corundum and hematite themselves differ by a factor two (Table 5), it is interesting to calculate the enthalpies of formation from the oxides/sulfates, \( \Delta H_f^{\circ, \text{ox}} \). For the K series, \( \Delta H_f^{\circ, \text{ox}} \) is defined here as the enthalpy accompanying the reaction (at 298 K):

As the ratio Fe/Al decreases, \( \Delta H_f^\circ \) varies from -3963 to -4778 kJ/mol for the potassium series, and from -3760 to -4980 kJ/mol for the sodium series.
By definition, the enthalpy of mixing for an intermediate composition $KFe_{3-w}Al_w(SO_4)_{2}(OH)_{6}$ between the end-members jarosite, $KFe(SO_4)_{2}(OH)_{6}$ and alunite, $KAl(SO_4)_{2}(OH)_{6}$, is given by the equation:

$$
\Delta H_{\text{mix}}(Fe_{3-w}Al_w) = \Delta H_f(Fe_{3-w}Al_w)
$$

$$
- \frac{(3w)\Delta H_f(\text{jarosite}) - w/3 \cdot \Delta H_f(\text{alunite})}{(3-w)/3} \quad (5)
$$

or, equivalently:

$$
\Delta H_{\text{mix}}(Fe_{3-w}Al_w) = \frac{(3-w)\Delta H_f(\text{jarosite}) + w/3 \cdot \Delta H_f(\text{alunite})}{(3-w)/3} \quad (6)
$$

The use of Eqn. 6 is preferred to that of Eqn. 5 because the magnitude of the heats of formation is often very large; in addition, the drop solution enthalpies are the experimental values directly measured here, and thus calculation using Eqn. 6 gives smaller uncertainties.

Application of Eqn. 6 to the potassium and sodium series studied in this work requires the knowledge of the enthalpies of drop solution of four end members: jarosite, natrojarosite, alunite, and natroaluminate. However, because our samples show deviations from the theoretical stoichiometric formulas, as many natural samples do, we consider here end members with A- and B-site contents close to those of the samples studied.

Values of the enthalpies of drop solution (in sodium molybdate) of the jarosite $K_{0.72}(H_2O)_{0.28}Fe_{2.60}(SO_4)_{2}(OH)_{4.80}(H_2O)_{1.20}$ ($\Delta H_{ds} = 504.1 \pm 3.9$ kJ/mol) and the natrojarosite $Na_{0.68}(H_2O)_{0.32}Fe_{2.83}(SO_4)_{2}(OH)_{5.49}(H_2O)_{0.51}$ ($\Delta H_{ds} = 477.7 \pm 5.0$ kJ/mol) have been reported in a previous study (Drouet and Navrotsky, 2003). Taking into account their chemical compositions, these compounds can be chosen as the nonstoichiometric jarosite and natrojarosite end members needed here. The remaining two end members, namely nonstoichiometric alunite $K_{0.8-x}Na_{x}(H_2O)_{0.2}Al_{2.7}(SO_4)_{2}(OH)_{4.9}$ and natroaluminate $Na_{0.8}(H_2O)_{0.2}Al_{2.7}(SO_4)_{2}(OH)_{4.9}(H_2O)_{0.9}$, were extrapolated from the linear variation of $\Delta H_{ds}$ with the sodium content for the alunite-natroaluminate solid solution $K_{0.8-x}Na_{x}(H_2O)_{0.2}Al_{2.7}(SO_4)_{2}(OH)_{4.9}(H_2O)_{0.9}$ (samples T-1, T-2, T-3, Fig. 7). The numerical values are $\Delta H_{ds} = 593.3 \pm 2.9$ kJ/mol for the K-Al end member and $\Delta H_{ds} = 616.4 \pm 5.9$ kJ/mol for the Na-Al end member.

Figures 5 and 6 depict the variation of the enthalpies of drop solution and of formation (from the elements) for the potassium and sodium series respectively, as a function of the Al content in B-sites. In both cases, a deviation from linearity is observed and the curves can best be fitted to second-degree polynomials. This trend points out that these solid solutions depart from thermodynamic ideality, and it is indicative of non-zero enthalpies of mixing, $\Delta H_{\text{mix}}$. 

Fig. 5. $\Delta H_{f}$ and $\Delta H_{f}^{o}$ for the potassium series (jarosite-alunite solid solution) and for end members (this work, Drouet and Navrotsky, 2003).

Fig. 6. $\Delta H_{f}$ and $\Delta H_{f}^{o}$ for the sodium series (natrojarosite-natroaluminate solid solution) and for end members (this work, Drouet and Navrotsky, 2003).
This linearity of $\Delta H_{\text{mix}}$ versus Na content for the aluninonatoalunite solid solution is not surprising as it parallels what was observed in previous work (Drouet and Navrotvsky, 2003) on the jarosite-natrojarosite solid solution. This suggests that the enthalpies of mixing for substitutions in A-sites are negligible regardless of the nature of the cation located in B-sites. In contrast, a recent study (Drouet et al., in press) on the solid solution between jarosite and its chromate analog, KFe$_2$(CrO$_4$)$_2$(OH)$_5$, showed non-zero (negative) enthalpies of mixing for the substitution of chromium (VI) for sulfur.

The above values of $\Delta H_{\text{mix}}$ for the four end members were then used to calculate the enthalpies of mixing for all intermediate compositions in the potassium and the sodium series using Eqn. 6. Numerical values of $\Delta H_{\text{mix}}$ are given in Table 5. Despite fairly large uncertainties, mostly originating from ex-

Table 6. Equation of curves $\Delta H_{\text{mix}} = f (\text{Al mole fraction})$ for the K and Na series.

| y = A + Bx + Cx$^2$, y = $\Delta H_{\text{mix}}$ and x = Al mole fraction |
|------------------|--------------------|------------------|
| K series:        | A = 504.4, B = 44.8, C = 78.2 |
| Na series:       | A = 479.9, B = 113.9, C = 39.3 |

The corresponding additional uncertainties on the heats of formation of the corresponding end members. The parabolic curves $\Delta H_{\text{mix}}$ vs. Al mole fraction are described by second-order polynomials $y = A + Bx + Cx^2$ (Table 6).

The thermochemistry of the jarosite-alunite and natrojarosite phases.

4. CONCLUSIONS

The thermochemistry of the jarosite-alunite and natrojarosite-natroalunite solid solutions was investigated by oxide melt solution calorimetry. The enthalpies of formation from the elements of 11 samples from these series and 3 samples from the aluninonatoalunite solid solution series were determined. $\Delta H_{\text{mix}}$ becomes more endothermic with the iron content. Slightly positive enthalpies of mixing were found, indicating that these solid solutions involving B-site Fe/Al substitutions are not thermodynamically ideal.

The heats of formation of the end members of the series were extrapolated from the experimental data. These thermodynamic data should enable the estimation/prediction of the heats of formation of natural (K-Na-H$_2$O)-jarosite-alunite samples, encountered, for example, in acid rock drainage environments, which generally depart from the AB$_3$(SO$_4$)$_2$(OH)$_b$ stoichiometry. Also, under given conditions, the partitioning of Fe and Al between the solids and the aqueous solution may be estimated
using these thermodynamic data and aqueous speciation programs, which were beyond the scope of the present paper.

The strong affinity of the jarosite-alunite structure for Fe, observed in this work, is consistent with observed metal uptake in industrial applications using jarosite precipitation, e.g., in zinc hydrometallurgy, to eliminate iron impurities from raw minerals (Dutrizac and Jambor, 2000).

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