CRYSTAL CHEMISTRY OF THE JAROSITE GROUP OF MINERALS

Solid-solution and atomic structures

by

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One day Alice came to a fork in the road and saw a Cheshire cat in a tree. "Which road do I take?" she asked. "Where do you want to go?" was his response. "I don't know," Alice answered. "Then," said the cat, "it doesn't matter."

--Lewis Carroll

Abstract

The jarosite group of minerals is part of the alunite supergroup, which consists of more than 40 different mineral species that have the general formula $AB_3(TO_4)_2(OH, H_2O)_6$. There is extensive solid-solution in the A, B and T sites within the alunite supergroup. Jarosite group minerals are common in acid mine waste and there is evidence of jarosite existing on Mars. Members of the jarosite - natrojarosite – hydronium jarosite (K,Na, H_3O)Fe₃(SO₄)₂(OH)₆ solid-solution series were synthesized and investigated by Rietveld analysis of X-ray powder diffraction data. The synthesized samples have full iron occupancy, where in many previous studies there was significant vacancies in the B site. Well-defined trends can be seen in the unit cell parameters, bond lengths A – O and Fe - O across the solid-solution series in the synthetic samples. Based on unit cell parameters many natural samples appear to have full iron occupancy and correlate well with the synthetic samples from this study. In addition, the infrared spectra of the samples were analyzed. The atomic structure of ammoniojarosite,

(NH₄)Fe₃(SO₄)₂(OH)₆, has been solved using single-crystal X-ray diffraction to *wR* 3.64% and *R* 1.4%. The atomic coordinates of the hydrogen atoms of the NH₄ group have been located and it was found that the ammonium group has two different orientations with equal probability. Samples in the ammoniojarosite – hydronium jarosite solid-solution series were synthesized and analyzed using powder X-ray diffraction and Rietveld refinement. It was found that an incomplete solid-solution series exists between jarosite and plumbojarosite, Pb[Fe₃(SO₄)₂(OH)₆]₂, based on experimental and mineralogical data. At the studied synthesis conditions, lead solubility in jarosite is extremely limited with occupancy of 2% in the potassium site. Increased Pb in the starting solution resulted in no increased substitution of Pb into jarosite, but an increased substitution of H_3O^+ . The stable isotope (H) geochemistry of hydronium jarosite, $(H_3O,K)Fe_3(SO_4)_2(O,OH)_6$, and the effect that the presence of hydronium in the crystal structure has on exchange rates of stable isotope values of jarosite with hydronium substitution has been investigated in this study.

Co-Authorship

Dr. Ronald Peterson is co-author of each of the following manuscripts. The manuscripts are my own work with significant intellectual contribution from Dr. Peterson. Chapter 6 had intellectual contribution from Dr. Peterson and Dr. Kurt Kyser.

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Statement of Originality

I hereby certify that all of the work described within this thesis is the original work of the author. Any published (or unpublished) ideas and/or techniques from the work of others are fully acknowledged in accordance with the standard referencing practices.

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Chapter 1: General Introduction

Acid mine drainage (AMD) is one of the largest environmental and financial challenges of the mining industry today. Canada's mining industry spends more than \$100 million annually to control AMD

(www.nserc.ca/news/features/2007_06_06_e.htm). Currently active mines, as well as mines that have been out of production for years, produce acidic waters and secondary minerals. The resulting contaminated waters are potentially toxic to the surrounding ecosystems and to humans. AMD is formed by the oxidation of sulfide minerals, which include pyrite (FeS₂), pyrrhotite (Fe_{1-x}S), chalcopyrite (CuFeS₂) and marcasite (FeS₂). Oxidation of sulfide minerals is a natural process (acid-rock drainage) that is greatly amplified by human activities related to mining and mineral processing, which exposes these minerals to air and water. Oxidation of sulfide minerals leads to the formation of both insoluble and soluble, metal-bearing sulfates, hydroxysulfates and hydrous oxides and leads to the generation of acidic solutions. Acid mine waters commonly have pH values in the range of 2 to 4 and can have pH values as low as -3.6 (Nordstrom et al., 2000). As the pH decreases, sulfide oxidation is accelerated because mineral solubilities and metal concentrations increase (Jambor et al. 2000). A generalized reaction for the oxidation of pyrite is:

 $\text{FeS}_{2(aq)} + 3.75\text{O}_{2(g)} + 3.5\text{H}_2\text{O}_{(l)} \leftrightarrow \text{Fe}(\text{OH})_{3(s)} + 2\text{H}_2\text{SO}_{4(aq)}$

More detailed "steps" of pyrite oxidation are shown in Figure 1.1. The oxidation of sulfide minerals is exacerbated by the presence of Fe- and S- oxidizing bacteria such

as *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* (Bigham and Nordstrom, 2000).

The jarosite group minerals, which are the focus of this study, form after the system has very low acidity and the acid sulfate waters become fully oxidized (Figure 1.1, Eqn 1.43). The stability relations for some of the less soluble secondary minerals in the Fe-S-K-O-H system, including jarosite, are shown in Figure 1.2. The jarosite group minerals are one of the most prevalent naturally occurring iron-sulfates. They usually occur as yellow crusts and coatings within the saturated or vadose zones of mine tailings and acid sulfate soils (Bigham 1994).

The jarosite group of minerals is part of the alunite supergroup, which consists of more than 40 different mineral species that have the general formula $AB_3(TO_4)_2(OH, H_2O)_6$ (Table 1.1, Bigham and Nordstrom 2000). Minerals of the alunite-jarosite group can have Na⁺, K⁺, H₃O⁺, NH₄⁺, Ag⁺, and ½Pb²⁺ in the A site, Fe³⁺ (jarosite group) or Al³⁺ (alunite group) in the B site and S⁶⁺, P⁵⁺, or As⁵⁺ in the T site. There is extensive solid-solution in the A, B and T sites within the alunite supergroup. As the jarosite structure can incorporate a large number of elements, its chemical composition reflects the chemical compositions of the fluids from which it formed. The jarosite group plays a role in sequestering elements from the fluids thereby controlling the composition of the effluent.

Jarosite is also important in the zinc industry as a sink for iron. Jarosite is precipitated as a means of eliminating the Fe that is commonly present in Zn-sulfide (sphalerite) concentrations. Twenty-five thousand tonnes of synthetic jarosite containing 25-36 wt% Fe is produced annually (Dutrizac and Jambor 2000). This jarosite must be contained or disposed of.

Jarosite has recently been hypothesized as a mineral on Mars (Papike et al. 2006a; Papike et al. 2006b; Klingelhöfer et al. 2004; Madden et al. 2004). Jarosite on Mars may form through similar processes as it does on Earth, such as oxidation of sulfide minerals (Burns 1987, 1988; Papike et al. 2006). Jarosite is a hydrous mineral with approximately 10 weight % H₂O in the form of OH⁻ groups. The presence of jarosite on Mars would indicate the existence of specific temperature ranges and fluid compositions on the Martian surface in the past.

The basic structure of jarosite group minerals is shown in Figure 1.3. The members of the group belong to the space group $R\overline{3}m$. The structure consists of TO₄ tetrahedra and variably distorted B-cation octahedra, where the octahedra corner-share to form sheets perpendicular to the *c* axis. Substitutions of Al for Fe into the B sites mainly affect the *a* dimension, with *a* increasing as Fe substitutes for Al. The TO₄ tetrahedra, which are aligned along [001], occur as two sites related by symmetry, one set of TO₄ points upward along c, which alternate with another set pointing downward. The oxygen and hydroxyl group form an icosahedron, where the A cation is located. Substitutions in the A site mainly affect unit cell dimensions *c*.

Non-stoichiometry of the jarosite group

Synthetic jarosite and alunite group minerals are commonly non-stoichiometric, with deficiencies in the B site. Studies which address the iron/aluminum deficiency are:

Hendricks 1937, Ripmeester *et al.* 1986, Drouet and Navrotsky 2003 and Drouet *et al.* 2004. It is thought that charge neutrality for the iron/aluminum deficient samples is maintained by protonation of the hydroxyl groups in the structure, creating water molecules (Ripmeester *et al.* 1986). Recently, Nielson et al. 2007 reinvestigated structural defects in the alunite structure of natural and synthetic alunites with multi-nuclear solid-state NMR spectroscopy, including B site deficiencies and hydronium substitution in the A site. They found that the hydronium ion (H_3O^+) is observed in hydronium alunite but was not detected in the spectra of alunite and natroalunite that had less than 100% A site occupancy of K or Na. They suggest that a vacancy at the B site is compensated by the addition of 4 H⁺. The H_3O^+ in the A site would then not be necessary for charge balance resulting in the A site vacancy that is commonly seen.

Jarosite group members in this study were grown with full iron occupancy by a variety of methods in stainless steel pressure bombs (Figure 1.4). Through the carefully controlled experiments on well characterized materials all other variables were avoided that complicate natural samples. The bombs are a large enough size so that an appropriate amount of resultant jarosite is produced for all accurate powder X-ray diffraction data to be collected that is suitable for Rietveld refinement.

Solid-solution between jarosite, natrojarosite and hydronium jarosite (K, Na, H₃O)Fe₃(SO₄)₂(OH)₆

Jarosite and natrojarosite are the most common naturally occurring jarosite group minerals. Their prevalence is due to the abundance of potassium and sodium in natural

environments. Jarosite has a much lower solubility than natrojarosite and hydronium jarosite, making it the first jarosite group mineral to precipitate when potassium is available (at 25°C) (Glynn, 2000). End-member hydronium jarosite is rare, though hydronium substitutes readily into the A site and is common in natural samples and previously synthesized samples. The solid-solution series between $Na - K - H_3O$ jarosite have been studied previously by Brophy and Sheridon (1965), Brown (1970), Kubisz (1970, 1972), Dutrizac (1983), and Drouet and Navrotsky (2003). The majority of the synthesized jarosite and natrojarosite in these previous studies were not fully occupied with iron and there were varying amounts of hydronium substitution in the A site. This has led to discrepancies in the literature with regards to the unit cell parameters of jarosite and natrojarosite. The effect that iron deficiency has on the jarosite crystal structure was investigated in Chapter 2. Samples in the jarosite – natrojarosite – hydronium jarosite solid-solution series were synthesized and analyzed using X-ray diffraction and Rietveld refinement to determine changes in unit cell parameters and atomic positions. The jarosite – hydronium jarosite series is discussed in Chapter 2 and the natrojarosite – jarosite and natrojarosite – hydronium jarosite series are discussed in Chapter 3. The synthetic samples in this current study have full iron occupancy and the samples in the Na – K jarosite series have no hydronium substitution. The unit cell parameters are significantly different than those reported in the majority of previous synthetic studies and follow well defined trends. Natural samples were also analyzed in the jarosite – natrojarosite – hydronium jarosite solid-solution with the synthetic samples. Many of the natural samples are stoichiometric with respect to iron and correlate well with the synthetic samples from this study. The data from these solid-solution studies

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can be used as a guide in subsequent studies on natural jarosite samples to roughly determine the composition of the sample.

This study as well as other recent advances in the knowledge of the jarosite group of minerals (Glynn 2000; Papike et al. 2007; Nielson et al. 2007) will aid in the interpretation of jarosite group minerals analyzed in future Mars missions where the combined XRD/XRF (CheMin) instrument will be used.

Ammoniojarosite (NH₄)Fe₃(SO₄)₂(OH)₆

Ammoniojarosite is an important by-product of the zinc industry (Salinas *et al.*, 2001). It is produced as result of the Jarosite Method which is used to precipitate dissolved iron from the hot acid leach solutions prior to subsequent zinc recovery.

Natural ammoniojarosite is quite rare as ammonium-bearing solutions that have the necessary attributes to produce jarosite are not common. The ammonium must come from the decomposition of organic substances or biologic activity associated with organic matter (Frost et al. 2006). Natural ammoniojarosite is most often found in lignitic shale associated with other ammonium-bearing minerals.

Unit cell parameters of ammoniojarosite have been determined previously by Smith and Lampert (1973) and Dutrizac and Kaiman (1976). Both samples were not endmember ammoniojarosite, with presumably H₃O substitution in the A site. The structure of ammoniojarosite has been solved in the current study using single crystal X-ray diffraction as discussed in Chapter 4. The synthetic sample has full iron occupancy and no H₃O substitution in the A site. As a result the unit cell parameter is different than previously analyzed samples. In addition to end-member ammoniojarosite, the complete solid-solution series between ammoniojarosite and hydronium jarosite was synthesized and analyzed using powder X-ray diffraction and Rietveld refinement.

Plumbojarosite Pb_{0.5}Fe₃(SO₄)₂(OH)₆

Plumbojarosite is primarily found in gossans, which overlie massive sulfide deposits. Gossans are the residues of an intense acidic leaching and are commonly enriched in some trace elements with respect to the original sulfide, such as Au, Ag, As and Pb. Gossan deposits can be important because they fix toxic elements such as Pb and As and restrict their release into the environment (Nieto et al. 2003).

As a result of the difference in charge of Pb^{2+} from other jarosite group minerals where the A site is filled with a univalent cation, unit cell parameter *c* is doubled. For every one potassium cation in jarosite there are half Pb cations in plumbojarosite. The Pb cations and A site vacancies are ordered, causing the doubling of the unit cell (Symański, 1985). Based on the complete solid solution between other members of the jarosite group, it was thought that there was complete solid-solution between jarosite and plumbojarosite. As discussed in Chapter 5 it was found in this study that there is an incomplete solid-solution between end-members. There is little substitution of either potassium or lead in plumbojarosite or jarosite at the synthesis temperatures investigated in this study.

Stable isotope geochemistry of hydronium jarosite

The stable isotope geochemistry of hydronium jarosite has not been investigated previously. As hydronium readily substitutes into potassium jarosite, the influence of hydronium on the isotopic values of potassium jarosite needs to be known to properly evaluate isotopic values for natural samples that contain hydronium in the A site. The stable isotope geochemistry of potassium jarosite has been studied by Rye and Stoffregen (1995). The effect of hydronium substitution in jarosite increases the number of oxygen isotope sites from two (sulfate group and a hydroxyl group) to three, and the hydrogen sites from one to two. Preliminary isotopic data was collected on hydronium jarosite in this study. Additionally, data were collected to determine if isotopic exchange occurs between hydronium jarosite, air and water. These preliminary results are discussed in Chapter 6.

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Table 1.1: Minerals of the Alunite Supergroup

NAME

FORMULA

NAME

FORMULA

Alunite Group Al>Fe alunite natroalunite ammonioalunite schlossmacherite minamiite osarizawaite walthierite huangite	$\begin{array}{l} KAI_3(SO_4)_2(OH)_6\\ NaAI_3(SO_4)_2(OH)_6\\ (NH)_4AI_3(SO_4)_2(OH)_6\\ (H_3O,Ca)AI_3(SO_4)_2(OH)_6\\ (Na,K,Ca,\bar{1})AI_3(SO_4)_2(OH)_6\\ PbCuAI_2(SO_4)_2(OH)_6\\ Ba_{0.5}\square_{0.5}AI_3(SO_4)_2(OH)_6\\ Ca_{0.5}\square_{0.5}AI_3(SO_4)_2(OH)_6\\ \end{array}$	Jarosite Group Fe>AI jarosite natrojarosite hydronium jarosite ammoniojarosite argentojarosite plumbojarosite beaverite dorallcharite	$\begin{array}{l} KFe_3(SO_4)_2(OH)_6\\ NaFe_3(SO_4)_2(OH)_6\\ (H_3O)Fe_3(SO_4)_2(OH)_6\\ (NH)_4Fe_3(SO_4)_2(OH)_6\\ AgFe_3(SO_4)_2(OH)_6\\ Pb[Fe_3(SO_4)_2(OH)_6]_2\\ PbCu(Fe,Al_2)(SO_4)_2(OH)_6\\ Tl_{0.8}K_{0.2}Fe_3(SO_4)_2(OH)_6 \end{array}$
Beudantite Group AI>Fe hidalgoite hinsdalite kemmlitzite svanbergite woodhouseite weilerite gallobeudantite	$\begin{array}{l} PbAI_3[(As,S)O_4]_2(OH,H_2O)_6\\ PbAI_3[(P,S)O_4]_2(OH)_6\\ (Sr,Ce)AI_3[(As,S)O_4]_2(OH,H_2O)_6\\ SrAI_3[(P,S)O_4]_2(OH,H_2O)_6\\ CaAI_3[(P,S)O_4]_2(OH,H_2O)_6\\ BaAI_3[(As,S)O_4](OH)_6\\ PbGa_3[(As,S)O_4]_2(OH,H_2O)_6\\ \end{array}$	Beudantite Group Fe>AI beaudantite corkite	$PbFe_{3}[(As,S)O_{4}]_{2}(OH,H_{2}O)_{6}$ $PbFe_{3}[(P,S)O_{4}]_{2}(OH,H_{2}O)_{6}$

Crandallite

Group AI>re
crandallite
plumbogummite
goyazite
gorceixite
arsenocrandallite
phillipsbornite
arsenogoyazite
arsenogorceixite
lusungite
florencite-(Ce)
florencite-(La)
florencite-(Nd)
arsenoflorencite-
(Ce)
arsenoflorencite-
(La)
arsenoflorencite-
(Nd
waylandite
eyelettersite
arsenowaylandite

 $CaAl_3(PO_4)_2(OH, H_2O)_6$ $PbAl_3(PO_4)_2(OH, H_2O)_6$ SrAl₃(PO₄)₂(OH,H₂O)₆ $BaAl_3(PO_4)_2(OH,H_2O)_6$ $CaAl_3[(As,P)O_4]_2(OH,H_2O)_6$ $PbAI_3(AsO_4)_2(OH,H_2O)_6$ (Sr,Ca,Ba)Al₃[(As,P)O₄]₂(OH,H₂O BaAl₃(AsO₄)₂(AsO₃•OH)(OH)₆ (Sr,Pb)Fe₃(PO₄)₂(OH,H₂O)₆ $CeAl_3(PO_4)_2(OH)_6$ LaAl₃(PO₄)₂(OH)₆ NdAl₃(PO₄)₂(OH)₆ CeAl₃(AsO₅)(OH)₆ LaAl₃(AsO₄)(OH) NdAl₃(AsO₄)(OH) $(Bi,Ca)Al_3(PO_4,SiO_4)_2(OH)_6$ (Th,Pb,¹)Al₃(PO₄,SiO₄)₂(OH)₆

(Bi,Ca)Al₃(AsO₄)₂(OH)₆

Crandallite Group

16241	
benauite	
kintoreite	
zairite	
dussertite	
segnitite	

 $\begin{array}{l} SrFe_{3}(PO_{4})_{2}(OH,H_{2}O)_{6}\\ PbFe_{3}(PO_{4})_{2}(OH,H_{2}O)_{6}\\ BiFe_{3}(PO_{4})_{2}(OH)_{6}\\ BaFe_{3}(AsO_{4})_{2}(OH)_{5}\\ PbFe_{3}(AsO_{4})_{2}(OH,H_{2}O)_{6} \end{array}$



General Reaction: $\text{FeS}_2 + 3.5\text{O}_2 + \text{H}_2\text{O}$ $\text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+$

Steps: (1.1) $FeS_2 + 3.5O_2 + H_2O$ $Fe^{2+} + 2SO_4^{2-} + 2H^+$ (1.2) $Fe^{2+} + 0.25O_2 + H^+$ $Fe^{3+} 0.5H_2O$ (1.3) $FeS_2 + 14Fe^{3+} + 8H_2O$ 15 $Fe^{2+} + 2SO_4^{2-} + 16H^+$ (1.4) $Fe^{3+} + 3H_2O$ $Fe(OH)_3 + 3H^+$ (1.41) $Fe^{3+} + 2H_2O$ $FeOOH + 3H^+$ $(1.42) 4Fe^{3+} + Fe^{2+} + 6SO_4^{2-} + 22H_2O$ $Fe^{2+}Fe^{3+}(SO_4)_6(OH)_220H_2O + 6H^{+}$ (1.43) 3Fe³⁺ + K⁺ +2SO₄²⁻ +6H₂O KFe3³⁺(SO₄)₂(OH)₆ + 6H⁺ $(1.44) 8 \text{Fe}^{3+} \text{SO}_{4}^{2-} + 14 \text{H}_2 \text{O} \qquad \text{Fe}_8 \text{O}_8 (\text{OH})_6 (\text{SO}_4) + 22 \text{H}^+$

Figure 1.1. Schematic diagram showing the "steps" in pyrite oxidation and possible secondary Fe minerals that may form as weathering products (modified from Bigham and Nordstrom 2000).



Figure 1.2. Stability relations for some less soluble secondary minerals in the Fe- S - K-O - H system at 25°C. (Nordsrom and Alpers 1999a, modified from Alpers et al. 1989). Note: the relationship between Eh and pe at 25°C is Eh+0.059 pe.



Figure 1.3. Polyhedral drawing of the general structure of the jarosite group. Potassium jarosite is shown. Iron octahedra are shown in light grey, sulfate tetrahedra are dark grey. The A site is shown as dark grey spheres; H1 are small white spheres.



Figure 1.4. Equipment used for the synthesis of jarosite group minerals. The starting solution is in a polypropylene bottle, which is placed in a stainless steel bomb that is partially filled with water. The bomb is sealed with a silicone plug. The polypropylene bottle is 125 ml.

Chapter 2: Jarosite – hydronium jarosite solid-solution series with full iron site occupancy: Mineralogy and crystal chemistry.

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Abstract

Structural changes within the jarosite – hydronium jarosite solid-solution series, (K, H₃O)Fe₃(SO₄)₂(OH)₆, were investigated by X-ray Rietveld analysis of powder diffraction data from synthetic samples. All previous studies of jarosite solid-solution consisted of samples that were non-stoichiometric with respect to iron. In this study, stoichiometric samples in the series were synthesized under hydrothermal conditions at 140°C using starting materials of $Fe_2(SO_4)_3 \cdot 5H_2O + K_2SO_4 + H_2O$ in hydrothermal conditions. End-member potassium jarosite was also synthesized under similar conditions from a stoichiometric mixture of $FeCl_3 + KCl + LiCl + Fe(SO_4)_3 \cdot 5H_2O +$ H₂O. Crystals were initially zoned with potassium-rich cores and hydronium-rich rims. Samples were homogenized by grinding and re-heating in the reactant solution. One iron deficient sample was synthesized to determine the effect of non-stoichiometry. Substitution of H₃O by K changes the unit cell parameters in a linear fashion; c increases significantly and *a* decreases to a lesser degree. Unit cell parameters from stoichiometric samples determined in this study are larger than synthetic samples analyzed in previous studies as a result of full iron occupancy. Potassium substitution in the alkali site (A site) mainly affects the A – O2 bond length which causes the Fe – O2 and Fe – O3 bonds to

lengthen and shorten respectively. As potassium substitutes into the structure, there is an overall increase in the *c* axis. Iron deficiency leads to a significant decrease in unit cell volume (large in *c*, minor in *a*), which is caused by bond length Fe - O3 which is markedly shorter than stoichiometric samples with similar potassium occupancy. The synthetic samples are compared with natural samples of jarosite and hydronium jarosite collected from mine waste deposits in Rio Tinto, Huelva, Spain. The natural samples have close to full iron occupancy, resulting from high iron content in solution and correlate well to the synthetic samples. Samples were also analyzed using short-wave infrared spectroscopy (SWIR). It was found that there is a subtle difference in spectra between end-members hydronium jarosite and potassium jarosite that can be tracked across the solid-solution series.

Keywords: jarosite – hydronium jarosite solid-solution series, crystal synthesis, IR spectroscopy, SWIR, crystal structure, XRD data, Rietveld refinement

Introduction

The jarosite group of minerals is part of the alunite supergroup, which consists of 40 mineral species that have the general formula $AB_3(TO_4)_2(OH)_6$. There is extensive solid-solution in the A, B and T sites within the alunite supergroup, where A is H_3O^+ , Na^+ , K^+ , Rb^+ , Ag^+ , TI^+ , NH^{4+} , $\frac{1}{2}$ Ca²⁺ or $\frac{1}{2}$ Pb²⁺, B is Fe³⁺ or Al³⁺ and TO₄ is SO₄²⁻, PO₄³⁻ or AsO₄³⁻ (Scott 1987; Stoffregen and Alpers 1987). The jarosite group is characterized by B = Fe³⁺ and T = S. Jarosite (A = potassium) and natrojarosite (A = sodium) are the most prevalent naturally occurring jarosite group minerals and hydronium jarosite is quite rare, though most jarosite group minerals contain some hydronium in the A site (Ripmeester et al. 1986; Drouet and Natrotsky 2003; and Majzlan et al. 2004). Hydronium jarosite will only form from alkali-deficient solutions, as alkali-rich jarosite forms preferentially. For the sake of clarity, jarosite, *sensu stricto*, will be referred to as potassium jarosite throughout this paper.

The jarosite group of minerals has been extensively studied as a result of its importance as a by-product of the metal-processing industry as well as being very common in acid-mine waste. Minerals within the jarosite group are commonly found in acidic, high-sulfate environments associated with mine tailings. Metal-rich acidic sulfate containing waters originate from the oxidation of sulfide minerals, such as pyrite (FeS₂). This natural process is amplified by human activities relating to mining and mineral processing, which exposes these minerals to water and air. Oxidation of sulfide minerals leads to the formation of soluble and insoluble metal-bearing sulfates, hydroxysulfates and hydrous oxides. The formation of these secondary phases typically leads to the generation of acidic solutions. The mineral group jarosite commonly forms after ferrous iron in the acidic sulfate waters oxidizes to ferric iron. As jarosite is a sink for iron, it is used in the zinc industry as a means of eliminating iron that is commonly present in Zn-Fe solution concentrates. One hundred and twenty-five thousand tonnes of jarosite containing 25-36 wt% Fe is produced annually (Dutrizac and Jambor 2000).

Jarosite has been identified as a possible mineral on Mars (Klingelhöfer et al. 2004) based on Mössbauer spectra. Jarosite on Mars may form through similar processes as it does on Earth, such as oxidation of sulfide minerals (Burns 1987, 1988, Papike et al. 2006). Jarosite is a hydrous mineral with approximately 10 weight % H₂O in the form of OH⁻ groups. The presence of jarosite on Mars would be important mineralogical evidence for water being on Mars at some time.

Natural and synthetic jarosite group minerals commonly have significant quantities of hydronium in the alkali (A) site and minor to major deficiencies in the iron site (B). Most jarosite group minerals synthesized in previous studies and many natural jarosite group minerals have B site occupancies as low as 86%. Studies that address the iron and/or aluminum deficiency are: Hendricks (1937), Kubisz (1970), Ripmeester et al. (1986), Drouet and Navrotsky (2003) and Drouet et al. (2004). The iron nonstoichiometry and hydronium substitution has led to discrepancies in the literature about the unit cell parameters of potassium jarosite. It is thought that charge neutrality for the iron deficient samples is maintained by protonation of the hydroxyl groups in the structure, creating water molecules (Ripmeester et al. 1986).

Ripmeester et al. (1986) confirmed the presence of hydronium ions in the alunite structure using NMR (nuclear magnetic resonance) and Wills and Harrison (1996)

proposed a model for the H₃O group in hydronium jarosite based on neutron-diffraction data. The structure of hydronium jarosite was refined by Majzlan et al. (2004) based on X-ray data. A number of studies exist in the literature which address hydronium in the jarosite structure, including Drouet and Navrotsky (2003), Kubisz (1970), Dutrizac and Kaiman (1976) and Ripmeester et al. (1986).

Stoichiometric alunite group minerals have been synthesized previously by Rudolph et al. (2003). The potassium-hydronium alunite solid-solution series was synthesized under hydrothermal conditions, with stoichiometric end-members. These experiments were done at 180-200°C, which is not possible for jarosite, as Fe₂O₃ and Fe(OH)SO₄ form above 160°C (Kubisz 1970). Natrojarosite with full sodium occupancy was synthesized by a two-step method described by Stoffregen (1993). The method involved synthesizing non-stoichiometric natrojarosite with 67% alkali site occupancy and then heating the natrojarosite in a 1.0 mH_2SO_4 -0.5Na₂SO₄ solution at 200°C for 8 days, which yielded an A site occupancy of 98%.

The purpose of this work is to study the crystal chemical effect hydronium substitution and iron deficiency has on the crystal structure of potassium jarosite. The $(H_3O)_{1-x}K_xFe_3(SO_4)_2(OH)_6$ solid-solution series, with x = 0.0, 0.10, 0.20, 0.35, 0.51, 0.60, 0.70, 0.86, and 0.95, with full iron occupancy, has been synthesized by hydrothermal methods. Rietveld refinements of powder diffraction patterns show the structural changes caused by the replacement of K⁺ by H₃O⁺. In addition, structural changes as a result of non-stoichiometry of Fe³⁺ are examined.

Natural samples in the hydronium – potassium jarosite solid-solution series were collected from mine waste associated with Rio Tinto mine and surrounding smaller mines

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in Huelva Province, SW Spain, to study in conjunction with the synthetic samples. The Rio Tinto mining district is part of the Iberian Pyrite Belt (IPB). The area is underlain by the Lower Carboniferous Volcanic-Sedimentary Complex, which host massive and stockwork pyrite ore bodies containing base and precious metals such as Cu, Pb, Zn, Au and Ag. The IPB has been mined using both opencast and underground mining methods, from approximately 2500 BC to the present day (Hudson-Edwards et al. 1999). During this time approximately 300 million tonnes of ore have been extracted (García García 1996) producing extensive tailing deposits and other mining wastes, creating acid-mine waste rich alluvium in the Rio Tinto and Odiel rivers. One of the collected natural samples has close to full iron occupancy, which is probably due to the extremely high iron content of the acidic waters as well as slow equilibrium growth in a natural setting. In addition, the samples have low sodium content, making them ideal as natural representatives for the synthetic analogues grown in this study.

Short wave infrared (SWIR) spectra were collected from the synthetic samples to determine the changes due to H₃O content. SWIR is often used in the field to evaluate minerals associated with acid-mine waste. The method is based on detecting the presence of molecular water, OH and other hydroxyl radicals in the mineral structure, which can be used for mineral identification. Remote sensing has been used to identify alunite group minerals near mining sites, and to map acidic mine waste (Clark et al. 2003, King et al. 1995, Kruse et al. 1989 and Swayze et al. 2000).

Experimental Methods

Sample synthesis
The solid-solution series $(H_3O)_{1-x}K_xFe_3(SO_4)_3(OH)_6$ was synthesized hydrothermally in stainless steel bombs at 140°C for 48 hours. Synthesis conditions are summarized in Table 2.1. To precipitate enough sample for Rietveld analysis the volume of starting liquid was 100 ml. The sample container consisted of polypropylene bottles (125 ml), which were placed in stainless steel bombs. The bombs were fabricated from stainless steel threaded pipe and two lids. One lid is welded on and the other is open and closed with pipe wrenches. To ensure a tight seal, a silicone plug is used in the lid. The stainless steel bombs were partially filled with water. The pressure inside the bombs and polypropylene bottles was approximately the vapor pressure of water at 140°C, 3.58 atm. Samples were synthesized by using a variation of the method described by Wills and Harrison (1996) for synthesizing hydronium jarosite. Forty grams of ACROS brand $Fe_2(SO_4)_3 \cdot 5H_2O$ and varying amounts of Fisher Scientific K₂SO₄ (0 - 2.0 g) were mixed with deionized water to a volume of 100 ml at room temperature. These conditions were used to ensure a high concentration of Fe^{3+} ions in solution. It was noted by Kubisz (1970) that low relative concentration of Fe^{3+} ions in the starting solutions resulted in deficiency of iron in synthesized jarosites. During the H₃O – K jarosite solidsolution synthesis, potassium-rich jarosite precipitated out of solution first in all samples, followed by hydronium-rich jarosite. This was noted on preliminary XRD patterns and confirmed by SEM analysis. XRD scans show a number of the peaks are broadened and in some extreme cases, split forming two separate peaks. The peak broadening was most evident for peak (006) where there is a large difference in peak position between potassium-rich and potassium-poor phases in the mixture. To produce a single

homogeneous phase, samples were finely ground in a McCrone Micronizing Mill after the initial synthesis and heated at 140°C in the reactant solution. Samples were analyzed every 3 days using XRD to determine sample homogeneity. Samples with compositions close to hydronium jarosite were more difficult to homogenize and had to be exchanged for a longer period of time (sample B – 20 days, sample H – 3 days). The samples were deemed to be homogeneous when the 006 peak was sharp and the full width at half maximum (FWHM) did not decrease with further annealing. Figure 2.1 shows part of an XRD scan (peak 006) of sample B before exchange compared to hydronium jarosite and potassium jarosite to show the peak splitting/broadening.

End-member potassium jarosite could not be grown using the above method as hydronium remains in the structure with high initial potassium content in the starting solution. Close to fully occupied potassium jarosite was grown in a chloride-rich medium using a similar method to Frost et al. (2005). Five ml of 1.23 M FeCl₃ and 0.5g KCl were dissolved in 12 ml concentrated LiCl solution. Six g of Fe(SO₄)₃ • 5H₂O was dissolved in 25 ml deionized water and slowly added to the chloride solution. The final solution was heated for 48 hours in a stainless steel pressure bomb at 140°C. It was found that the high chloride concentration reduced the amount of hydronium entering the structure. This procedure yielded potassium jarosite with 95.3% K, as determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). All samples were rinsed thoroughly with de-ionized water, filtered and dried at 120°C to eliminate any excess water. Drying at this temperature did not influence the X-ray diffraction pattern of the samples. All samples consisted of intergrown rhombohedral (pseudocubic) crystals ranging from <10 µm (initial growth, beside jar wall) to 100 µm (final growth). One sample was synthesized using a method similar to that of Drouet and Navrotsky (2003) in order to obtain a sample that is non-stoichiometric with respect to iron. This sample was used as a comparison to the rest of the solid-solution series grown during this study. The sample was precipitated from 5 g $Fe_2(SO_4)_3 \cdot 5H_2O$, 12.5 g K_2SO_4 and 250 ml deionized water, which was stirred for two hours at 95°C.

X-ray diffraction and Rietveld refinement

Powder-diffraction data were collected from 15° -100° 2 θ (Fe filtered CoK α radiation) from a back-packed sample using a Panalytical X'Pert theta-theta diffractometer and an X'celerator position-sensitive detector equipped with incident- and diffracted-beam soller slits, and $1/2^{\circ}$ divergence and 1° anti-scatter slits. The normalfocus Co X-ray tube was operated at 40 kV and 45 mA. Profiles were taken with a step interval of 0.008 2θ , counting time per step 30 s. To eliminate preferred orientation, samples were ground for 2 minutes in a McCrone Micronizing Mill, mixed with Fisher Scientific Al_2O_3 (ground for 5 minutes) and then backpacked on 320 grit sandpaper. The alumina is used to influence the packing geometry of the jarosite powder, helping to randomly orient the grains. Approximately 30% of the final sample is alumina. The data were refined with the Rietveld refinement program Topas Academic (Coelho 2004). Starting atomic parameters were taken from Majzlan et al. 2004. The instrument parameters were modeled using a full axial divergence model defined by Cheary and Coelho (1998b). CoKa source emission profiles were taken from Hölzer et al. (1997). Broadening due to crystallite size was refined using the Double-Voigt approach (Balzar

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1999). The oxygen of the H_3O group was located at (0, 0, 0) similar to Majzlan et al.

(2004). The model put forth by Wills and Harrison (1996) was not followed, who moved the oxygen of the H_3O group to (0, 0, z) and invoked disorder at the hydronium site. The occupancy of potassium in the A site was fixed to the occupancy determined with ICP-OES and the T site is assumed to be fully occupied by S. The occupancy of oxygen in the A site for the end-member hydronium jarosite was found to 0.92(1), determined by Rietveld refinement, which is similar to results found by Majzlan et al. 2004 (discussed below). Based on the hydronium jarosite results, the occupancy of the hydronium in the A site was refined independently for samples containing potassium. It was found that for samples A and B the occupancy $K + H_3O$ was less than 1, with the combined occupancy increasing with increasing potassium content. The occupancy of the A site was refined to 1.02 for sample C, which is within error of 1. The alkali site occupancy for the samples in the remaining solid-solution series was constrained so that $K + H_3O = 1$. When the occupancy of the site was not restrained in these samples many of the refinements became unstable, with the occupancy of the alkali site exceeding 1 and bond lengths becoming unreasonable. Starting hydrogen positions (OH group) were taken from the single-crystal study of hydronium jarosite by Majzlan et al. (2004). Without a restraint the O3 – H bond length was significantly shorter than typical values. As hydrogen is not easily detected by X-rays, the positions are not as accurate as heavier atoms. The O - Hbond length was restrained at 0.8 Å instead of 0.98 Å, which is the average O – H bond length in crystalline solids refined by X-ray diffraction (Baur 1972), because observed O - H distances in X-ray determinations tend to be on average 0.2 Å shorter than in neutron diffraction (Baur 1972). The displacement parameters of the H atoms were fixed at 2 and

not refined. Rietveld quality data were also collected and analyzed for two natural samples from Rio Tinto, Spain. The samples consist of jarosite and quartz. Both phases were included in the refinement. No alumina was added to these samples and they were ground using a mortar and pestle. The refinements were done in the same manner as the synthetic samples. The data collection and structure refinement details are given in Table 2.2. A final plot of observed and calculated intensities for a representative Rietveld refinement is shown in Figure 2.2.

Short-wave Infrared Reflectance Spectroscopy (SWIR)

Short-wave infrared reflectance spectra of the synthetic K-H₃O jarosite solidsolution series were collected using a Portable Infrared Mineral Analyzer, Integrated Spectronics PIMA SP instrument, which measures in the 1200 - 2600 nm range. The samples were analyzed as finely ground dry powders.

Chemical analysis

The iron, potassium and sulfur content of the solid jarosite samples and reactant solutions were determined using a Varian vista CCD Simultaneous ICP-OES at Analytical Services Unit, Queen's University. The solid samples were digested in aqua regia and both the digested samples and reactant solutions were diluted for analysis. The average analytical error for each element is: Fe $\pm 1\%$; K $\pm 5\%$ and S $\pm 2\%$. From these data the stoichiometry of the alkali and iron sites were determined in the solid samples

based on the ratio of alkali and iron to sulfur. The potassium and iron in these sites were normalized to 2 S per chemical formula based on the ideal chemical formula. The mol % potassium and iron in the reactant solutions were also normalized to sulfur for the sake of comparison. The chemical compositions of synthetic and natural samples are given in Table 2.1 and chemical compositions of the reactant solutions are shown in Figure 2.3.

Natural Samples

Hydronium – potassium jarosite samples were collected in the current study from mine waste in the immediate vicinity of abandoned mines in the Rio Tinto mining area and alluvium along the Rio Tinto River. Only two samples were analyzed by Rietveld methods as most of the samples were mixed with a number of other minerals. The two samples analyzed were mixed only with quartz. Potassium-rich jarosite was collected from a small creek at the base of a tailings impoundment associated with Rio Tinto Mine (GPS coordinates: N 37°44'14.6" W 6°36'44.2"). The tailings consisted predominantly of sulfides, quartz and clay minerals. A sample of hydronium jarosite was collected from the bank of the Rio Tinto River, approximately 16 km from the mine, south of Berrocal where highway HV5137 crosses the river. The samples were very fine-grained yellow powders, which were washed in de-ionized water, filtered and air dried before X-ray analysis.

Results and Discussion

Synthesis Experiments

As noted previously, potassium-rich jarosite precipitated out of solution first, followed by hydronium-rich jarosite. Even when a very low amount of potassium is added to the solution, the first jarosite precipitate has a very high potassium content. Sample D was examined before exchange using XRD and SEM analysis. After exchange, the double (006) peaks merge and move to higher 20 (higher hydronium content) (Figure 2.1). The jarosite precipitate forms a crust on the polypropylene jar walls, which was cross-sectioned and analyzed with an SEM to confirm that potassiumrich jarosite was precipitating out of solution first. As can be seen in Figure 2.4 the jarosite that precipitates out of solution first, closer to the polypropylene jar, is much higher in potassium than the jarosite in contact with the solution.

Figure 2.3 shows the partitioning of potassium and iron between the solution and precipitated crystals. As noted in previous studies (Brophy and Sheridan 1965, Brown 1970, Dutrizac 1983), potassium is preferentially taken into the jarosite structure over sodium and hydronium. Potassium jarosite is more thermodynamically stable than both sodium jarosite and hydronium jarosite (Drouet and Navrotsky 2003). The same results were also found in this study for potassium and hydronium. Nearly all the potassium that is added to the system is taken up in the jarosite crystals. Only in samples where the iron has become depleted, and therefore jarosite no longer precipitates, will appreciable amounts of potassium remain in solution (when potassium >> iron in the starting solution). The iron in the precipitate remains relatively constant at 100% occupancy for all of the samples except for J. When the system is saturated with iron, the precipitating jarosite will have full iron occupancy. In sample J there was less iron in the starting

solution; jarosite still precipitated but iron occupancy was less than one. As expected, the iron remaining in the reactant solution reduces as larger amounts of potassium are added. This trend is associated with yield volume of the samples. As the potassium in the reactant solution increases, the jarosite yield increases dramatically, therefore reducing the amount of iron remaining in solution. The increase in yield correlating with potassium content of the starting solution has also been discussed by Dutrizac (1983).

Relationship between structural parameters and potassium content

The XRD patterns of the $(H_3O)_{1-x}K_xFe_3(SO_4)_3(OH)_6$ solid-solution series show a progressive change in unit cell parameters as a result of hydronium substitution. As determined by Rietveld refinement and ICP-OES, all samples have close to full or full iron occupancy and the end-member potassium jarosite has 95.3% potassium occupancy. The reliability factors, positional parameters, site occupancies, and selected interatomic distances and angles obtained are given in Tables 2.2, 2.3, and 2.4.

A structural drawing of potassium jarosite is shown in Figure 2.5. The jarosite group crystallizes in space group $R\bar{3}m$, with Z = 3 (in the hexagonal unit cell). The basic structure of the jarosite group consists of SO₄ tetrahedra and Fe-cation octahedra, where the octahedra corner-share to form sheets perpendicular to the *c* axis. The SO₄ tetrahedra occur as two crystallographically independent sites within a layer; one set of SO₄ points towards +*c*, which alternate with another set pointing toward -*c*. The oxygen and hydroxyl group form an icosahedron, in which the alkali cation or hydronium group is located. The univalent cations (K⁺, H₃O⁺, Na⁺, etc) are surrounded by twelve anions,

consisting of six oxygen atoms (O2), and six OH groups (O3).

The unit cell parameters *a* vs. *c* from the current study and previously synthesized members of the hydronium – potassium jarosite solid-solution series are plotted in Figure 2.6. Natural samples from previous studies are not included as many contain sodium as well, or chemical data are not available. The data from this study fall close to a straight line (correlation coefficient $r^2 = 0.97$) connecting hydronium jarosite and potassium jarosite, therefore following Vegard's Law, confirming ideal solid-solution. Unit cell parameters vs. potassium content for synthetic samples from the current study are given in Figure 2.7. Substitution of H₃O by K increases unit cell parameter *c* significantly and decreases *a* to a lesser degree. All data points for *a* and *c* fall close to a straight line: correlation coefficients for *a* are $r^2 = 0.98$ and *c* are $r^2 = 0.96$. All the jarosite samples from this study, which have full iron occupancy, have larger unit cell parameters than most of the samples grown in previous studies. Jarosite group minerals grown in previous studies are non-stoichiometric with respect to iron, which reduces the unit cell parameters and causes the scatter of data points.

Polyhedra bond lengths A – O2 and O3 and Fe – O2 and O3 are shown in Figures 2.8 and 2.9. With increasing K substitution bond lengths A – O3 remain approximately the same and A – O2 decreases. An ideal hydronium ion has on average O – H bond length of ~0.98 Å and H – O – H bond angle of ~111° (Begemann and Saykally 1985). Chiari and Ferraris (1982) show that the minimum, maximum and average O – H … O bond distances are 2.617, 3.085 and 2.835 Å, respectively for water molecules in crystalline substances. Since the position of H was not determined for the H₃O⁺, possible orientations for the H₃O group in the A polyhedra are based on hydronium geometry and

bond length trends through the solid-solution series. The oxygen of the hydronium group is located in the center of the polyhedra and it is likely that the hydrogen atoms are hydrogen bonded to the O2 atoms located roughly around the horizontal of the A polyhedra (Figure 2.10). There are six O2 atoms in the polyhedra, three slightly above the horizontal and three slightly below (Figure 2.5). The average bond angle between O2 atoms and the A site in hydronium jarosite is 110.4° and the bond distance between the A site and the O2 atoms is 3.026 Å. This angle is ideal for hydronium geometry and the bond length is within the range of $O - H \cdots O$ distances commonly found for water molecules in crystalline substances (Begemann and Saykally 1985, Chiari and Ferraris 1982). Another possible orientation of the hydronium group was proposed by Grohol et al. (2003) and Kubisz (1970), in which the protons from H_3O^+ in the A site transfer to neighboring $OH^{-}(O3)$ forming H₂O. This is based on infrared data and ²H NMR spectroscopy showing evidence of H_3O^+ , H_2O and OH^- in hydronium jarosite. The average bond angle between O3 atoms and the A site in hydronium jarosite is 59.6° , which significantly smaller than the average hydronium bond angle of $\sim 111^{\circ}$. Based solely on bond angles between O2 and O3 atoms, this scenario is not as likely as the hydronium group hydrogen bonding to the O2 atoms. As the A site in hydronium jarosite is not fully occupied with hydronium (found to be 92% occupied in the current study and 91% occupied by Majzlan et al. 2004), it is probable that charge neutrality is maintained by protonation of OH^- to form H_2O (Majzlan et al. 2004). This protonation would give evidence of H₃O⁺, H₂O and OH⁻ in spectroscopic studies of hydronium jarosite, as seen by Grohol et al. (2003) and Kubisz (1970).

It is commonly thought that the hydronium ion is disordered with two orientations

with equal probability (Figure 2.10). The A polyhedra are face sharing with the iron octahedra, which are corner sharing with sulfate tetrahedra. Additionally, O3 is a hydroxyl group, which is hydrogen bonded to O1 of the sulfate group. This bonding environment reduces the amount that A - O3 bond length can change with substitutions in the A site. Therefore, substitution in the A site mainly effects the A - O2 distances. As a result of the A - O2 bond shortening with K substitution, the Fe – O2 and Fe – O3 bonds lengthen and shorten respectively. At low potassium content the A polyhedra is quite distorted and becomes more regular at higher potassium contents, though still distorted. In contrast, the iron (B) octahedra are increasingly distorted at higher potassium content and are very regular at low potassium concentration. As potassium substitutes into the structure, the distance between the A site and B site increase, therefore causing an increase in the length of the *c* axis.

Non-stoichiometry of the A and B sites

One sample was grown that was not fully stoichiometric with respect to iron. Sample J, which has 86.3% iron and 87.3% potassium occupancy (as determined by ICP-OES), has significantly different unit cell parameters than the fully stoichiometric sample with similar potassium occupancy (sample H, 85.7% K). Unit cell parameter *a* is very similar for both sample J and H. Unit cell parameter *a* for sample J falls very close to the regression line for the stoichiometric solid-solution series. Unit cell dimension *c* is 0.16 Å smaller for J than sample H and falls far below the regression line (Figure 2.7). The Fe – O3 bond length is the same as stoichiometric samples but the Fe – O2 bond length is markedly shorter than in sample H, which has similar potassium occupancy. The Fe – O2 and O3 bond lengths of sample H are 2.042(3) and 1.9794(8) Å, respectively, and the average bond lengths of sample J are 2.002(6) and 1.982(1) Å, respectively. Correspondingly, the A – O2 bond length for sample J is longer than for sample H.

Samples A and B are non-stoichiometric with respect to the alkali site, with the occupancy of $K + H_3O < 1$. This was only found in samples with very high hydronium content. This is similar to results found by Majzlan et al. (2004) for end-member hydronium jarosite. The A – O2 bond length is smaller than expected in sample A (hydronium jarosite) and B as a result of the lower occupancy, while A – O3 bond length is unaffected. As bond length A – O2 is smaller, Fe – O2 is approximately the same amount longer (Table 2.4).

When the B site is not fully occupied by Fe^{3+} , it is thought that charge neutrality is maintained by protonation of OH⁻ to form H₂O (Kubisz, 1970; Wills and Harrison, 1996). Majzlan et al. (2004) state that charge neutrality could be maintained in similar manner for partial occupancy of hydronium giving a general formula for the hydronium jarosite synthesized in this study (H₃O_{0.92})Fe₃(SO₄)₂[(OH)_{5.92}(H₂O)_{0.16}]. From Rietveld refinement, it appears that the A site is fully occupied with hydronium and potassium at higher potassium contents, but not for samples with lower potassium content.

Crystal chemistry of natural samples

The two natural samples from Rio Tinto, Spain (7-13-2-1 and 7-11-3-8) are close to fully occupied with respect to iron. Sample 7-13-2-1 has 1.9% K and 1.9% Na

occupancy and therefore, can be described as a hydronium jarosite. Sample 7-11-3-8 is closer to stoichiometric (potassium) jarosite with 84.3% K and 1.1% Na occupancy. Both natural jarosite samples are structurally very close to the synthetic jarosite samples grown with full iron occupancy. ICP-OES results confirm that the samples do have close to full iron occupancy as well. The unit cell parameters and bond lengths of the natural samples are plotted with the synthetic samples in Figures 2.6 and 2.7.

Waters associated with Rio Tinto are characterized by low pH values (1.5-2.7) and extremely high metal and sulfate concentrations (Hudson-Edwards et al. 1999). As determined by Hudson-Edwards et al. (1999), the concentration of iron is very high in the Rio Tinto River downstream of the mining area and decreases sharply near the estuary. Iron concentrations can be as high as 28,989 mg/L (Fernández-Remolar et al. 2005) and range from 2000-4300 mg/L before the estuary. Potassium-rich jarosite formed when there was potassium available (from the dissolution of feldspar and clay minerals), which is similar to results found in the current synthetic studies. Further down stream the Rio Tinto River hydronium jarosite forms, as all potassium has been removed from solution by jarosite (and other associated minerals) precipitating closer to the mining areas.

A natural jarosite sample structurally analyzed by Kato and Miuri (1977) has very similar unit cell parameters and bond lengths as the end-member potassium jarosite synthesized in this study. Based on their results and the results from natural samples analyzed in this study, it is probable that many natural jarosite samples are close to full Fe occupancy of the B site and are more closely correlated with the results of this study than previous structural studies done on synthetic non-stoichiometric samples.

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SWIR

The short-wave infrared (SWIR) spectra, shown in Figure 2.11, are typical of the jarosite structure and the transmittance bands have been assigned based on the assignments by Bishop and Murad (2005). As can be seen from the spectra there are subtle difference between end-members hydronium jarosite and potassium jarosite that can be tracked across the solid-solution series. Specific bands could not be attributed to hydronium specifically but it can be seen that detail is lost from the spectra with increasing hydronium content. Specifically, bands that are dampened or lost are shoulders B (1514 nm), E (2214 nm), G (2296 nm) and area H (2380 – 2500 nm). Detailed assignments of the absorption bands are given in Figure 2.11. Velasco et al. (2005) found similar results from SWIR spectra collected on natural hydronium jarosite from San Miguel mine, SW Spain. Swayze et al. (2006) noted that OH-related vibrational absorptions became narrow and more well defined in high temperature synthetic jarosite and alunite samples which are fully hydroxylated. They postulated that replacement by H_2O of the hydroxyl groups in low-temperature samples due to a B site deficiency, disrupts strong vibrational coupling, weakening the spectral absorptions. As it is probable that there is protonation of OH⁻ groups in hydronium jarosite due to an A site deficiency, this same circumstance is likely. As there is a difference between spectra for hydronium-rich jarosite and potassium-rich jarosite, SWIR spectroscopy could be a useful field based method in determining a rough estimate of the hydronium content of the jarosite. As discussed in Fernández-Remolar et al. (2005), jarosite formation at Rio

Tinto is probably similar to jarosite formation on Mars. Therefore, SWIR spectroscopy may be a useful method in determining the hydronium content of the Martian jarosites.

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	Starting solut	ion compositions(g)	Analytical re	sults (ICP-OE	S) (% occup	ancy) ar	nd Formula
Synthetic samples	$K_2(SO_4)$	Fe(SO ₄) ₃ •xH ₂ O	Fe%	K%	Na%	S%	Formula
A	0.00	40	102.050	0.374	na	100	$(K_0H_3O_1)Fe_{3.06}(SO_4)_2(OH)_6$
В	0.08	40	102.818	10.156	na	100	(K _{0.102} H ₃ O _{0.898})Fe _{3.08} (SO ₄) ₂ (OH) ₆
С	0.16	40	103.554	19.973	na	100	(K _{0.200} H ₃ O _{0.800})Fe _{3.11} (SO ₄) ₂ (OH) ₆
D	0.24	40	97.686	34.976	na	100	$(K_{0.350}H_3O_{0.650})Fe_{2.93}(SO_4)_2(OH)_6$
E	0.50	40	98.085	51.291	na	100	$(K_{0.512}H_3O_{0.488})Fe_{2.94}(SO_4)_2(OH)_6$
F	1.00	40	97.405	60.506	na	100	$(K_{0.605}H_3O_{0.395})Fe_{2.92}(SO_4)_2(OH)_6$
G	1.50	40	100.546	70.367	na	100	$(K_{0.704}H_3O_{0.296})Fe_{3.02}(SO_4)_2(OH)_6$
Н	2.00	40	98.830	85.693	na	100	$(K_{0.857}H_3O_{0.143})Fe_{2.96}(SO_4)_2(OH)_6$
*	na	na	95.727	95.291	na	100	(K _{0.953} H ₃ O _{0.047})Fe _{2.87} (SO ₄) ₂ (OH) ₆
J ^ψ	12.50	5	86.345	87.321	na	100	(K _{0.873} H ₃ O _{0.127})Fe _{2.59} (SO ₄) ₂ (OH) ₆
Natural samples							
7-13-2-1	na	na	99.731	1.858	1.918	100	$(K_{0.019}H_3O_{0.981}Na_{0.019})Fe_{2.99}(SO_4)_2(OH)_6$
7-11-3-8	na	na	91.088	84.304	1.080	100	(K _{0.843} H ₃ O _{0.146} Na _{0.011})Fe _{2.73} (SO ₄) ₂ (OH) ₆
* synthesized in chlo	ride media simi	ilar to Frost et al. 200	5, see text for	details			

Table 2.1: Synthesis conditions and chemical compositions of synthetic and natural jarosite samples

 $^{\Psi}$ synthesized using method from Drouet and Navrotsky, 2003, see text for

details

	А	В	С	D	E	F	G	Н	I	J	7-13-2-1	7-11-3-8
х	0.00	0.10	0.20	0.35	0.51	0.60	0.70	0.86	0.95	0.87	0.02	0.84
a(Å)	7.3552(2)	7.3521(1)	7.3428(2)	7.3373(1)	7.33009(8)	7.32070(6)	7.3112(1)	7.3070(1)	7.30293(8)	7.3063(1)	7.3478(1)	7.3128(1)
c(Å)	16.9945(4)	17.0108(3)	17.0316(5)	17.1030(3)	17.1374(2)	17.1517(3)	17.1792(2)	17.1916(3)	17.2043(2)	17.0341(4)	17.0280(2)	17.1973(4)
V(Å)	796.21(4)	796.31(3)	795.26(5)	797.40(3)	797.43(2)	796.05(2)	795.27(3)	794.93(3)	794.62(2)	787.50(3)	796.18(2)	796.44(3)
R_p	3.571	4.236	5.321	3.408	2.903	4.111	3.378	3.668	3.289	4.137	3.013	3.589
R_{wp}	4.773	5.849	8.020	5.052	3.994	5.707	4.415	4.788	4.288	5.441	3.976	4.988
R_{exp}	3.882	3.923	4.098	2.726	2.787	3.513	3.621	4.204	3.570	4.479	3.078	3.467
S	1.230	1.491	1.957	1.854	1.433	1.624	1.219	1.139	1.201	1.215	1.291	1.439
D-W	0.691	0.498	0.300	0.336	0.567	0.483	0.726	0.825	0.745	0.731	0.645	0.523

Table 2.2: Data collection and structure refinement details: hydronium jarosite – jarosite R3m

Step interval (°20) 15-100°, step 0.008.

 $R_{p}: R\text{-pattern}, R_{wp}: weighted\text{-pattern}, R_{exp}: R\text{-expected}, S(=R_{wp}/R_{exp}): Goodness of fit (Young 1993)$

D-W: Durbin-Watson *d*-statistic (Hill and Flack 1987).

Site	W	Х	у	Z	В	Ν
Sample A	, K occ =	0				
H₃O	3a	0	0	0	3.4(5)	0.92(1)
Fe	9d	0.166667	-0.166667	-0.16667	1.99(8)	1
S	6c	0	0	0.3095(2)	0.9(1)	1
01	6c	0	0	0.3946(3)	2.6(3)	1
02	18h	0.2253(3)	-0.2253(3)	-0.0565(2)	1.5(2)	1
O3	18h	0.1279(2)	-0.1279(2)	0.1368(1)	0.5(1)	1
Н	18h	0.163(1)	-0.163(1)	0.100(1)	2	1
Sample B	, K occ =	0.10				
K	3a	0	0	0	4.1(6)	0.10
H₃O	3a	0	0	0	4.1(6)	0.86(1)
Fe	9d	0.166667	-0.166667	-0.16667	2.55(8)	1
S	6c	0	0	0.3098(2)	2.0(1)	1
01	6c	0	0	0.3955(4)	7.0(4)	1
02	18h	0.2255(3)	-0.2255(3)	-0.0574(2)	2.5(2)	1
O3	18h	0.1265(2)	-0.1265(2)	0.1350(2)	0.19(1)	1
Н	18h	0.186(2)	-0.186(2)	0.125(1)	2	1
Sample C	, K occ =	0.20				
K	3a	0	0	0	2.8(6)	0.20
H₃O	3a	0	0	0	2.8(6)	0.81(2)
Fe	9d	0.166667	-0.166667	-0.16667	3.0(1)	1
S	6c	0	0	0.3109(2)	2.2(2)	1
01	6c	0	0	0.3962(3)	6.3(5)	1
02	18h	0.2264(3)	-0.2264(3)	-0.0589(3)	2.4(2)	1
O3	18h	0.1309(3)	-0.1309(3)	0.1334(2)	1.9(2)	1
Н	18h	0.155(2)	-0.155(2)	0.092(1)	2	1
Sample D	, K occ =	0.35				
K	3a	0	0	0	1.4(2)	0.35
H₃O	3a	0	0	0	1.4(2)	0.65
Fe	9d	0.166667	-0.166667	-0.16667	2.48(7)	1
S	6c	0	0	0.3100(1)	1.27(9)	1
01	6c	0	0	0.3961(2)	3.8(2)	1
02	18h	0.2242(2)	-0.2242(2)	-0.0569(2)	2.3(1)	1
O3	18h	0.1284(2)	-0.1284(2)	0.1365(1)	1.2(1)	1
Н	18h	0.160(1)	-0.160(1)	0.097(1)	2	1
Sample E	, K occ =	0.51				
K	3a	0	0	0	1.1(1)	0.51
H₃O	3a	0	0	0	1.1(1)	0.49
Fe	9d	0.166667	-0.166667	-0.16667	1.98(5)	1
S	6c	0	0	0.3089(1)	1.39(7)	1
01	6c	0	0	0.3940(3)	3.2(2)	1
02	18h	0.2224(2)	-0.2224(2)	-0.0557(1)	2.5(1)	1
O3	18h	0.1266(1)	-0.1266(1)	0.1358(1)	0.93(9)	1

Table 2.3: Refined atomic positions, displacement parameters and occupancies of synthetic and natural jarosite samples

Н	18h	0.177(1)	-0.177(1)	0.1105(8)	2	1
Sample F	K occ = (0.60				
K	3a	0	0	0	1.1(2)	0.60
H₃O	3a	0	0	0	1.1(2)	0.40
Fe	9d	0.166667	-0.166667	-0.16667	2.3(1)	1
S	6c	0	0	0.3096(3)	1.9(2)	1
01	6c	0	0	0.3953(5)	4.6(4)	1
02	18h	0.2213(3)	-0.2213(3)	-0.0556(3)	2.7(2)	1
O3	18h	0.1270(2)	-0.1270(2)	0.1360(2)	2.0(2)	1
Н	18h	0.177(2)	-0.177(2)	0.111(1)	2	1
Sample G	, K occ = (0.70				
К	3a	0	0	0	0.3(1)	0.70
H₃O	3a	0	0	0	0.3(1)	0.30
Fe	9d	0.166667	-0.166667	-0.16667	1.26(6)	1
S	6c	0	0	0.3092(2)	1.2(1)	1
01	6c	0	0	0.3958(3)	2.3(2)	1
02	18h	0.2213(2)	-0.2213(2)	-0.0553(2)	2.5(2)	1
O3	18h	0.1267(1)	-0.1267(1)	0.1350(1)	0.4(1)	1
Н	18h	0.173(1)	-0.173(1)	0.107(1)	2	1
Sample H	, K occ = (D.86		()		
ĸ	3a	0	0	0	1.4(1)	0.86
H₂O	3a	0	0	0	1 4(1)	0 14
Fe	9d	0 166667	-0 166667	-0 16667	1.3(1)	1
S	60 60	0	0	0.3082(2)	1.8(1)	1
01	60 60	0	0	0.3953(2)	3 9(2)	1
02	18h	02214(2)	-0 2214(2)	-0.0549(1)	21(1)	1
03	18h	0.1254(1)	-0.1254(1)	0.1350(1)	0.7(1)	1
Н	18h	0.1201(1)	-0 185(1)	0 125(1)	2	1
Sample I.	K occ = 0	.95	01100(1)	01120(1)	-	
K	3a	0	0	0	1.04(8)	0.95
H.O	39	0	0	0	1 04(8)	0.05
Fo	0d	0 166667	0 -0 166667	0 ₋0 16667	1.04(0)	1
\$	50 60	0.100007	0.100007	0.3088(1)	1.0(3) 1 15(7)	1
01	60 60	0	0	0.3030(7)	1.13(7) 1.8(2)	1
02	18h	0 2211(1)	0 ₋0 2211(1)	-0.0544(1)	1.52(0)	1
02	18h	0.2211(1) 0.1252(1)	-0.2211(1)	-0.03++(1) 0.1344(1)	0.80(8)	1
н	18h	0.1262(1)	-0.1202(1)	0.1289(8)	2	1
Sample I	K occ = 0	187 Fe occ = 0	-0.1000(0) 86	0.1200(0)	L	1
K	3a	0	0	0	2 4(2)	0 87
	20	0	0	0	-1.1(-)	0.42
П ₃ U Го	29 04	0 166667	0 166667	0 16667	2.4(2)	0.13
ге С	90 60	0.100007	-0.100007	-0.10007	2.7(1) 1.7(2)	0.00
01	60	0	0	0.3111(3)	1.1(Z) 3.5(A)	1
02	18h	0 2227(4)	0 _0.2227(4)	-0.0568(4)	2.5(4) 2.5(2)	1
02	18h	0.2221(4)	-0.2221(4) _0.1278(2)	-0.0000(4) 0.1360(2)	2.J(2) 2.1(2)	1
н	18h	0.1270(2) 0.168(2)	-0.1210(2)	0.100(2)	2.1(Z) 2	1
Sample 7	13_2_1 ⊮	0.100(2)	-0.100(2)	0.102(2)	۲	I
K	3a	$0.02, 1^{-}0$	0	0	1 4(A)	0
H ₂ O	3a	0	0	0	1 4(4)	1
	54	-	-	-		•

Fe	9d	0.166667	-0.166667	-0.16667	1.95(7)	1
S	6c	0	0	0.3095(2)	1.1(1)	1
01	6c	0	0	0.3949(3)	2.6(2)	1
02	18h	0.2243(3)	-0.2243(3)	-0.0566(2)	2.2(1)	1
O3	18h	0.1267(1)	-0.1267(1)	0.1356(1)	0.9(1)	1
Н	18h	0.165(1)	-0.165(1)	0.1000(8)	2	1
Sample 7	-11-3-8, K	occ = 0.84, Fe	occ = 0.91			
К	3a	0	0	0	1.4(1)	0.84
H₃O	3a	0	0	0	1.4(1)	0.16
Fe	9d	0.166667	-0.166667	-0.16667	1.62(7)	0.91
S	6c	0	0	0.3090(2)	1.5(1)	1
01	6c	0	0	0.3935(4)	1.4(2)	1
02	18h	0.2215(2)	-0.2215(2)	-0.0565(2)	2.8(2)	1
O3	18h	0.1274(2)	-0.1274(2)	0.1367(2)	1.0(1)	1
Н	18h	0.166(1)	-0.166(1)	0.102(1)	2	1
Note: nun	nbers in pa	arentheses in th	is and subsequ	ient tables are	estimated	
standard	deviations					

	A	В	С	D	E	F	G	Н	Ι	J	7-13-2-1	7-11-3-8
	0.000	0.102	0.200	0.350	0.512	0.605	0.704	0.857	0.953	0.873	0.011	0.843
K, H3O - O3 x 6	2.839(2)	2.806(3)	2.817(4)	2.848(2)	2.829(2)	2.835(3)	2.821(2)	2.811(2)	2.802(2)	2.826(4)	2.817(2)	2.832(3)
K, H3O - O2 x 6	3.026(4)	3.033(3)	3.049(4)	3.010(3)	2.981(2)	2.964(4)	2.959(3)	2.957(2)	2.949(2)	2.980(5)	3.013(3)	2.972(3)
Average	2.9325	2.9195	2.933	2.929	2.905	2.8995	2.89	2.884	2.8755	2.903	2.915	2.902
Fe - O3 x 4	1.9904(9)	1.992(1)	1.986(5)	1.9898(9)	1.9847(7)	1.983(1)	1.9845(9)	1.9794(8)	1.9806(7)	1.982(1)	1.9899(7)	1.985(1)
Fe - O2 x 2	2.015(4)	2.005(3)	2.014(2)	2.014(3)	2.029(2)	2.027(5)	2.034(3)	2.042(3)	2.050(2)	2.002(6)	2.012(3)	2.011(3)
Average	1.999	1.996	1.995	1.998	1.999	1.998	2.001	2.000	2.004	1.989	1.997	1.994
S - 01	1.447(7)	1.459(7)	1.453(7)	1.474(4)	1.458(5)	1.470(9)	1.487(7)	1.497(6)	1.463(5)	1.456(9)	1.455(6)	1.437(6)
S - O2 x 3	1.485(4)	1.489(3)	1.496(5)	1.501(3)	1.507(2)	1.522(4)	1.517(3)	1.507(3)	1.510(2)	1.518(5)	1.496(3)	1.525(3)
Average	1.476	1.482	1.485	1.494	1.495	1.509	1.510	1.505	1.498	1.503	1.486	1.503
O2 - Fe - O3 x 4	89.6(1)	89.8(1)	89.13(8)	89.8(8)	88.92(7)	88.7(1)	88.08(9)	88.08(9)	87.65(7)	89.2(1)	89.61(9)	88.48(9)
O2 - Fe - O3 x 4	90.4(1)	90.2(1)	90.87(8)	90.3(8)	91.08(7)	91.3(1)	91.92(9)	91.92(9)	92.35(7)	90.8(1)	90.39(9)	91.52(9)
O3 - Fe - O3 x 2	89.7(1)	88.9(1)	88.59(2)	89.5(1)	89.06(9)	89.4(1)	88.9(1)	87.98(9)	87.67(8)	90.0(2)	89.18(9)	89.4(1)
O3 - Fe - O3 x 2	90.3(1)	91.1(1)	91.41(2)	90.5(1)	90.95(9)	90.7(2)	91.1(1)	92.02(9)	92.33(8)	90.0(2)	90.82(9)	90.6(1)
01 - S - O2 x 3	112.0(1)	112.7(4)	114.6(1)	112.47(8)	110.86(9)	111.07(4)	110.7(1)	109.9(1)	109.93(8)	112.8(2)	111.90(9)	111.85(4)
O2 - S - O2 x 3	106.9(2)	106.0(1)	103.9(3)	106.3(2)	108.1(1)	107.8(2)	108.2(2)	109.0(2)	109.01(8)	105.9(3)	106.9(2)	107.0(1)
Average	109.5	109.4	109.3	109.4	109.5	109.4	109.5	109.5	109.5	109.4	109.4	109.4
O3 – H	0.767(2)	0.77(2)	0.77(2)	0.780(2)	0.773(2)	0.775(3)	0.762(2)	0.774(2)	0.779(1)	0.77(3)	0.774(2)	0.793(2)
O3 – H … O1	2.914(3)	2.910(3)	2.841(4)	2.893(1)	2.924(2)	2.909(4)	2.898(2)	2.915(2)	2.923(2)	2.881(3)	2.916(2)	2.918(4)

Table 2.4: Selected interatomic distances (Å) and angles ($\sp{\circ}$)



Figure 2.1. XRD plot showing the 006 peak from hydronium jarosite (long dashes, right), potassium jarosite (medium dashes, left), sample B before exchange (solid line) and sample B after exchange (dotted line). Sample B before exchange had not been ground and re-equilibrated with the reactant solution and shows peak splitting/broadening.



Figure 2.2. Rietveld refinement plot of sample D, (K0.350H3O0.650)Fe2.93(SO4)2(OH)6. The sample was refined with two phases (jarosite + alumina). The grey line is the observed data and the solid line is the calculated pattern. The vertical bars mark all possible Bragg reflections (CoKa1 and Ka2), where upper and lower bar marks are jarosite and alumina, respectively. The difference between the observed and calculated patterns is shown at the bottom.



Figure 2.3. Yield and partitioning of potassium and iron between the solution and precipitated crystals as a function of K in the starting solution. Hydronium-rich jarosite is plotted on the left and potassium-rich jarosite is plotted on the right. The triangles in the lower two plots represent sample J, which was grown with significantly more potassium in the starting solution than the rest of the solid solution series, resulting in lower iron occupancy. The potassium and iron in the solution and precipitating crystals were normalized to sulfur for the sake of comparison.



Figure 2.4. Secondary electron micrograph showing a cross-section through synthetic jarosite. The bottom of the cross-section was the first to grow and was found adhered to the bottle wall. The top of the section was the last to grow and was in contact with the reactant solution. Potassium was preferentially taken into the earlier jarosite crystals.



Figure 2.5. Polyhedral representation of the jarosite structure. Potassium polyhedra are light grey, iron octahedra are dark grey and sulfate tetrahedra are mid-range grey.



- \triangle Present Study 87% Fe occupancy
- Majzlan et al. (2004)

Figure 2.6. Unit cell parameters c vs a of synthetic samples containing only K and H₃O in the A site. All samples from the current synthetic study are shown as white circles. Note that the unit cell dimensions fall close to a straight line, and are larger than most of the previous studies as they have full iron occupancy in the B site.



Figure 2.7. Unit cell dimensions a and c vs. potassium occupancy in the alkali site. Black circles are from samples that are fully stoichiometric with respect to iron, the grey triangle is sample J, with 86.34% Fe occupancy, and the grey squares are natural samples 7-13-2-1 and 7-11-3-8, collected from Rio Tinto Mines, Spain. Error bars are smaller than the symbols.



Figure 2.8. A - O polyhedra bond lengths vs. potassium occupancy in the alkali (A) site. Samples that are fully stoichiometric with respect to iron are represented by black and grey circles and sample J (86.34% Fe occupancy) is represented by black and grey triangles.



Figure 2.9. Fe - O octahedral bond lengths vs. potassium occupancy in the alkali site. Samples that are close to fully stoichiometric with respect to are iron are represented by black and grey circles and sample J (86.34% Fe occupancy) is represented by black and grey triangles.


Figure 2.10. Hydronium polyhedra showing possible orientations of H_3O^+ . The hydrogen are thought to be disordered and the two orientations of the hydronium group are shown. The oxygen is represented by white and the hydronium group can be pointed upwards (dark grey H) or downwards (mid grey H). Hydrogen bonding to O2 atoms is represented by dashed lines.



Figure 2.11. Short-wave infrared (SWIR) spectra of the hydronium - potassium jarosite solid solution series. End-member hydronium jarosite is at the top, potassium jarosite is at the bottom, with intermediate stages of the solid solution series in between. The bands have been assigned to the following: A - OH vibration and H₂O absorption, B - Fe-OH vibration, C - Fe-OH vibration, D - H₂O absorption, E - Fe-OH vibration, F - Fe-OH vibration, G - Fe - OH vibration , and H - (SO₄)₂ stretching and OH vibration. Band assignments were taken from Bishop and Murad, 2005. Spectra have been offset for comparison.

Chapter 3: Crystal chemistry of the natrojarosite – jarosite and natrojarosite - hydronium jarosite solid-solution series: a synthetic study with full iron site occupancy

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Abstract

Members of the natrojarosite – hydronium jarosite (Na, H_3O)Fe₃(SO₄)₂(OH)₆ and jarosite – natrojarosite (Na, K)Fe₃(SO₄)₂(OH)₆ solid-solution series were synthesized and investigated by Rietveld analysis of X-ray powder diffraction data. The synthesized samples have full iron occupancy, where in many previous studies there was significant vacancies in the B site. Well-defined trends can be seen in the unit cell parameters across the solid-solution series in the synthetic samples. The majority of the samples in this study were directly synthesized under hydrothermal conditions at 140°C. End-member natrojarosite was synthesized using a two-step method, where the initial sample was heated in a $1.0mH_2SO_4 - 0.5Na_2SO_4$ solution at 200°C for 3 days, yielding a sample with 100% Na occupancy. Many of the samples were initially zoned and required grinding and re-heating in the reactant solution for homogenization. Substitution of H₃O and K into natrojarosite changes unit cell parameters in a linear fashion. The unit cell parameters presented here are significantly different than the majority of previous studies on synthetic samples, as samples in the current study have full iron occupancy and the Na - K jarosite series has no H₃O substitution in the A site. Substitution in the A site mainly affects unit cell parameter c with little change in a. As Na occupancy increases there is a

decrease in A – O2 and O3 distances and a subsequent increase in Fe – O2 and O3 distance leading to an overall decrease in unit cell parameter *c* in both the Na – H₃O and Na – K jarosite series. The synthetic samples are compared to natural samples from mine waste deposits in Rio Tinto, Huelva, Spain, Ely Mine, Vermont and a mineral collecting locality near Sharbot Lake, Ontario as well as natural and synthetic samples documented in the literature. Based on unit cell parameters many of the natural samples appear to have full iron occupancy and correlate well with the synthetic samples from this study. The infrared spectra of the samples were analyzed and there is a gradual change in the spectral features across the solid-solution series between end-members. The results from this study will aid in the interpretation of the possible chemical compositions of natural jarosite group minerals in mine waste and on Mars.

Introduction

The jarosite group of minerals is part of the alunite supergroup, which consists of 40 mineral species that have the general formula $AB_3(TO_4)_2(OH)_6$. There is extensive solid-solution in the A, B and T sites within the alunite supergroup, where A may be occupied by H_3O^+ , Na^+ , K^+ , Rb^+ , Ag^+ , Tl^+ , NH^{4+} , $\frac{1}{2}Ca^{2+}$ or $\frac{1}{2}Pb^{2+}$, B may be occupied by Fe³⁺ or Al³⁺ and TO₄ may be SO₄²⁻, PO₄³⁻ or AsO₄³⁻ (Scott 1987; Stoffregen and Alpers 1987). The jarosite group is characterized by B = Fe³⁺ and T = S. Jarosite (A = potassium) and natrojarosite (A = sodium) are the most prevalent naturally occurring jarosite group minerals and hydronium jarosite is quite rare, though most jarosite group minerals contain some hydronium in the A site (Ripmeester et al. 1986; Drouet and Natrotsky 2003; Majzlan et al. 2004). Hydronium jarosite will only form in alkalideficient solutions, as alkali-rich jarosite forms preferentially. For the sake of clarity, jarosite, *sensu stricto*, will be referred to as potassium jarosite throughout this paper.

The jarosite group of minerals has been extensively studied as a result of its importance as a by-product of the metal-processing industry as well as being a common supergene mineral in ore deposits, and its association with acid-mine waste. Minerals within the jarosite group are commonly found in acidic, high sulfate environments. In mine waste, metal-rich, acidic waters originate from the oxidation of sulfide minerals, such as pyrite (FeS₂). Jarosite is thought to exist on Mars and its presence suggests that water existed on Mars in the past (Klingelhöfer et al. 2004; Madden et al. 2004; Papike et al. 2006a; Papike et al. 2006b). The position of Fe³⁺ ions in the jarosite structure may be described by a Kagomé lattice and the magnetic properties have led to additional research

in this area (Wills and Harrison 1996; Greedan 2001; Grohol et al. 2003; Harrison 2004; Nocera et al. 2004; Bartlett and Nocera 2005). The jarosite group is thought to be the principle model for studying spin frustration. The Kagomé layers are formed from the corner sharing Fe^{3+}_{3} -(μ -OH)₃ triangles, and is the most highly geometrically frustrated two-dimensional lattice (Bartlett and Nocera, 2005).

Synthetic and natural members of the jarosite group often have vacancies in the B site with Fe site occupancies as low as 86%. Non-stoichiometry in the B site has been studied by Hendricks (1937), Kubisz (1970), Ripmeester et al. (1986), Drouet and Navrotsky (2003), Grohol et al. (2003), Drouet et al. (2004) and Basciano and Peterson (2007). Additionally, there is often substantial substitution by hydronium for Na or K in the A site. Iron deficiency in the B site leads to a decrease in unit cell parameter c and hydronium substitution increases unit cell a. Many synthetic samples in the literature exhibit the effects of iron deficiency and hydronium substitution. Jarosite with fully occupied B sites have been synthesized by Grohol and Nocera (2002), Grohol et al. (2003), and Basciano and Peterson (2007). The presence or absence of H_3O^+ in alunite and jarosite group structures has been extensively discussed in the literature (Nielson et al. 2007; Drouet and Navrotsky 2003; Kubisz 1970; Dutrizac and Kaiman 1976 and Ripmeester et al. 1986). The orientation of the hydronium group has not been determined reliably in either X-ray diffraction or neutron diffraction studies (Lager et al. 2001, Majzlan et al. 2004, Nielson et al. 2007) as the molecule is dynamically disordered. As the A site is not fully occupied by a cation in most cases, it has been assumed in the majority of studies to be the result of hydronium substitution. Majzlan et al. (2004) and Basciano and Peterson (2007) found that the A site is not fully occupied in end-member

hydronium jarosite with the occupancy of oxygen in the A site to be 91% and 92%, respectively. In these cases, it is probable that charge neutrality is maintained by protonation of OH⁻ to form OH₂ (Majzlan et al. 2004). Recently, Nielson et al. (2007) reinvestigated structural defects in the alunite structure of natural and synthetic alunites with multi-nuclear solid-state NMR spectroscopy, including B site deficiencies and hydronium substitution in the A site. They found that the hydronium ion (H₃O⁺) is observed in hydronium alunite but was not detected in the spectra of alunite and natroalunite that had less than 100% A site occupancy of K or Na. They suggest that an Al vacancy at the B site is compensated by the addition of 4 H⁺. The resulting H₂O in the A site is then not necessary for charge balance resulting in the A site vacancy that is commonly seen.

The solid-solution series between Na – K – H₃O jarosite has been studied previously by Brophy and Sheridon (1965), Brown (1970), Kubisz (1970, 1972), Dutrizac (1983), and Drouet and Navrotsky (2003). The B sites in the synthesized jarosite members in these previous studies were not fully occupied with iron resulting in smaller unit cell parameters. Unit cell parameters of members of the Na – K jarosite solid-solution series were plotted in Stoffregen et al. (2000) from unpublished data. The crystal structure of natrojarosite has not been studied in detail previously. Grohol et al. (2003) reported the structure of stoichiometric natrojarosite in a study relating to the magnetic properties of jarosite. There are differences between the unit cell parameters reported in that study and those reported here.

Experimental Methods

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Sample Synthesis

The solid-solution series $(H_3O)_{1-x}Na_xFe_3(SO_4)_3(OH)_6$ was synthesized using the same method as in Basciano and Peterson (2007). Samples were synthesized hydrothermally in stainless steel bombs at 140°C for 48 hours. Synthesis conditions are summarized in Table 3.1. Forty grams of ACROS brand $Fe_2(SO_4)_3 \cdot 5H_2O$ and varying amounts of Fisher Scientific Na₂SO₄ (0 - 1.0 g) were mixed with deionized water to a volume of 100 ml at room temperature. These conditions were used to ensure a high concentration of Fe^{3+} ions in solution. Low relative concentration of Fe^{3+} ions in the starting solutions resulted in deficiency of iron in synthesized jarosites (Kubisz, 1970). During the H₃O – Na jarosite solid-solution synthesis, it was noted that below approximately 50% Na in the final product there was some peak broadening, indicating non-homogeneity of the samples similar to results found in Basciano and Peterson (2007) for the potassium jarosite – hydronium jarosite solid-solution series. In samples where there was peak broadening, samples were finely ground in a McCrone Micronizing Mill with deionized water after the initial synthesis and re-heated at 140°C in the reactant solution. Samples were analyzed after 3 days of heating using XRD to determine sample homogeneity. All samples were homogenized after 2 cycles of annealing, based on achieving sharp peaks in XRD spectra of the annealed samples.

The solid-solution series $(Na)_{1-x}K_xFe_3(SO_4)_3(OH)_6$ was synthesized in a chloriderich medium using a similar method to Frost et al. (2005). It was found that the high chloride concentration reduced the amount of hydronium entering the structure. Five ml of 1.23 M FeCl₃ solution and a 0.5 g mixture of NaCl and KCl were dissolved in 12 ml concentrated LiCl solution. Six grams of Fe(SO₄)₃ • 5H₂O was dissolved in 25 ml deionized water and slowly added to the chloride solution. The final solution was heated for 48 hours in a stainless steel pressure bomb at 140°C. All samples had varying amounts of peak widening during preliminary X-ray analysis. As in the potassium – hydronium jarosite solid-solution series (Basciano and Peterson, 2007), potassium jarosite precipitated out of solution first, followed by natrojarosite. The samples were ground in a McCrone Micronising Mill and annealed in the reactant solution until the sample was homogeneous based on XRD spectra.

End-member natrojarosite with the A site fully occupied with Na was not grown using the two above methods as some hydronium remains in the structure. Fully occupied natrojarosite was grown using a two-step method similar to Stoffregen (1993). Natrojarosite with approximately 87% Na occupancy was first grown using the same method outlined above for the Na – H₃O jarosite series and then ground in a McCrone Micronising Mill. The sample was then heated in a $1.0mH_2SO_4 - 0.5Na_2SO_4$ solution at $200^{\circ}C$ for 3 days in a Parr pressure bomb, which yielded an A site occupancy of 100% Na as determined by ICP-OES and normalized to 2 S per formula unit.

Atomic structural parameters for end-members potassium jarosite and hydronium jarosite were taken from Basciano and Peterson (2007).

X-ray powder diffraction and Rietveld refinement

Powder-diffraction data were collected from $15^{\circ}-100^{\circ} 2\theta$ (Fe filtered CoK α radiation) from a back-packed sample using a Panalytical X'Pert theta-theta

diffractometer and an X'celerator position-sensitive detector equipped with incident- and diffracted-beam soller slits, and 1/2° divergence and 1° anti-scatter slits. The normalfocus Co X-ray tube was operated at 40 kV and 45 mA. Profiles were taken with a step interval of 0.008° 2 θ , and an effective counting time per step of 30 seconds. To eliminate preferred orientation, samples were ground for 2 minutes in a McCrone Micronizing Mill in water and backpacked against a 320 grit sandpaper surface. The data were refined with the Rietveld refinement program Topas Academic (Coelho, 2004). Starting atomic parameters were taken from Majzlan et al. (2004). The instrument parameters were modeled using a full axial divergence model defined by Cheary and Coelho (1998). CoK α source emission profiles were taken from Hölzer et al. (1997). Broadening due to crystallite size was refined using the Double-Voigt approach (Balzar 1999). Sodium and potassium occupancy in the A position were set to the occupancy determined with ICP-OES and the T site is assumed to be fully occupied by S. Starting hydrogen positions (OH group) were taken from the single-crystal study of hydronium jarosite by Majzlan et al. (2004) and were restrained at 0.8 Å. The O – H bond length was restrained at 0.8 Å. instead of 0.98 Å, which is the average O - H bond length in crystalline solids refined by X-ray diffraction (Baur, 1972), because observed O – H distances in X-ray determinations tend to be on average 0.2 Å shorter than in neutron diffraction (Baur, 1972). The displacement parameters of the H atoms were fixed at 2 and not refined.

The data collection and structure refinement details are given in Table 3.2. A final Rietveld refinement plot of observed and calculated intensities for end-member ammoniojarosite is shown in Figure 3.1.

Short-Wave Infrared Reflectance Spectroscopy (SWIR) and Mid-Infrared Analysis (MIR)

Short-wave infrared reflectance spectra of the synthetic Na $-H_3O$ and Na -K jarosite solid-solution series were collected using a Portable Infrared Mineral Analyzer (PIMA), Integrated Spectronics SP instrument, which measures in the 1200 - 2600 nm range. Mid-infrared-absorption spectra of the synthetic samples were collected using a Nicolet Avatar 320 Fourier Transform Infrared Spectrometer and a Golden Gate diamond ATR. Spectra were measured from 400 - 4000 cm⁻¹. Spectral measurements were obtained from finely ground powders created for X-ray powder diffraction and Rietveld refinement.

Chemical Analysis

The iron, potassium, sodium and sulfur content of the solid jarosite samples were determined using a Varian Vista CCD Simultaneous ICP-OES at Analytical Services Unit, Queen's University. The samples were digested in aqua regia and diluted for analysis. The average analytical accuracy and precision for each element is: Fe $\pm 2\%$, 4.1%; Na $\pm 6\%$, 5.2%; K $\pm 5\%$, 4.7% and S $\pm 2\%$, 5.3%. From these data the occupancy of the alkali and iron sites were determined in the solid samples based on the ratio of alkali and iron to sulfur. The mol % potassium, sodium and iron in these sites were normalized to two sulfur atoms per chemical formula based on the ideal jarosite chemical

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formula where the sulfate tetrahedral is fully occupied by S. The chemical compositions of synthetic samples are given in Table 3.1.

Natural Samples

Natural supergene samples were collected from the San Miguel mine in the Rio Tinto mining area in Spain, Ely Mine in Vermont and from near Sharbot Lake, Ontario. Only a small number of samples from each area were analyzed using Rietveld refinement as the others were a mixture of many minerals. The Rio Tinto mining district is part of the Iberian Pyrite Belt (IPB), which is host to massive and stockwork pyrite ore bodies containing base and precious metals such as Cu, Pb, Zn, Au and Ag. The IPB has been mined using both opencast and underground mining methods, from approximately 2500 BC to the present day (Hudson-Edwards et al., 1999). Ely mine is part of the Vermont copper belt, which has been mined from 1793 to 1958. Ely and associated mines are Besshi-type massive sulfide deposits that are enriched in copper as well as Zn, Ag and Au. The sample from Sharbot Lake was collected from a cut of an abandoned railroad in the southern part of the town of Sharbot Lake, Ontario. The sample was found in a 5 mm vug in a silicicious rock sample taken from the railroad cut. The sample location was a dravite mineral collection locality. All of the samples were very fine-grained yellow powders, which were washed in de-ionized water, filtered and air dried prior to X-ray analysis.

Data were collected and unit cell parameters were determined for a number of the natural samples. Dry, ground samples were sieved through a 210 micron mesh on to a

zero-background silicon plate to reduce preferred orientation. The Topaz Academic software package was used to determine unit cell parameters. Starting parameters were taken from Majzlan et al. (2004) and the unit cell parameters were refined. Starting parameters from hydronium jarosite were chosen as unit cell parameter *c* is approximately mid way between jarosite and natrojarosite. Atomic coordinates and site occupancies were not refined.

The samples were analyzed using an Amray 1830 scanning electron microscope (SEM) and Link ISIS Oxford Systems energy dispersive spectrometer (EDS). Results confirmed the presence or absence of elemental substitutions in the A or B sites, which aided in the interpretation of the unit cell parameters.

Analyses of natural samples reported in the literature were reviewed and unit cell parameters were plotted along with data from synthetic samples produced in this study. Chemical analyses were not available for the majority of the samples, so samples that were labeled as jarosite, hydronium jarosite or natrojarosite that have unit cell dimension a less than 7.29Å were not studied further as they most likely contained substantial aluminum substitution in the B site. Aluminum in the B site causes a reduction in unit cell parameter a (Brophy et al. 1962).

Results and Discussion

Sample synthesis and homogeneity

It was found in the synthesis experiments that samples produced in the $Na - H_3O$ jarosite solid-solution series differed in sample homogeneity through the series. Samples

that had below 50% Na occupancy in the A site were homogeneous with no peak splitting (samples S, T and U, where starting solutions contained 1.0 g, 0.6 g and 0.2 g of Na₂SO₄). Starting solutions with above 1.0 g of Na₂SO₄ resulted in spectra with peak broadening of peak (006). Peak broadening is most evident for peak (006) where there is a large difference in peak position between sodium-rich and sodium-poor phases in the mixture (see Figure 2.1). When annealed, these samples did become homogeneous with >85% Na occupancies when more than 1.0g of Na₂SO₄ was used in the starting solution. To complete the solid-solution series, samples with 0.7 and 0.85g of Na₂SO₄ in the starting solution produced samples with 68.6% and 87.5% Na occupancy in the final product after annealing. Samples below 50% Na occupancy in the final product did not require annealing as they were homogeneous. It was found that when samples with below 50% Na were annealed at 140°C in the original solution the resulting jarosite product increased in sodium content.

End-member natrojarosite with A site fully occupied with Na could not be grown using the chloride method even though the other compositions in the $(Na)_{1-x}K_xFe_3(SO_4)_3(OH)_6$ solid-solution series could be grown. The resulting product when using the chloride method had approximately 90% Na occupancy. This may occur because natrojarosite and hydronium jarosite have similar solubilities (Glynn 2000). In systems where there is a large difference in the solubilities of end-members, the first phase to precipitate out of solution is the less soluble end-member component. In the jarosite – natrojarosite series, jarosite is the first to precipitate and dominates. In the natrojarosite – hydronium jarosite series, neither end-member is overly dominant. Endmember solubility products from PHREEQC (Parkhurst and Appelo 2000) are: $10^{-5.28}$ for natrojarosite, $10^{-5.39}$ for hydronium jarosite and $10^{-9.21}$ for jarosite.

As in the K – H₃O jarosite solid-solution series (Basciano and Peterson 2007) potassium rich jarosite precipitated out of solution first in the Na – K series, followed by Na rich jarosite. During initial X-ray scans the (006) peak was often split indicating two jarosite samples with intermediate compositions between sodium and potassium jarosite. After annealing at 140°C for up to 6 days the samples became one homogeneous phase, as determined by peak widths. From these experiments it was found that a single phase is stable at 140°C for any composition in the K – H₃O and K – Na series.

The zoning seen in the synthetic samples is common in nature. Oscillatory zoning was found by Papike et al. (2007) in a number of natural samples. The zoning is probably caused by a similar mechanism that is seen in the current experiments, where potassium in the solution is taken up in the jarosite structure before sodium. The variation in the composition of natural samples discussed by Papike et al. (2007) probably reflects a change in fluid composition during crystallization.

Solid-solution and structural parameters

Synthetic samples

There is a progressive change in unit cell parameters for both solid-solution series $(Na)_{1-x}H_3O_xFe_3(SO_4)_3(OH)_6$ and $(Na)_{1-x}K_xFe_3(SO_4)_3(OH)_6$ with increasing sodium content. From chemical analysis and unit cell dimensions determined by Rietveld refinement, all samples have full iron occupancy and the A site in the $(Na)_{1-x}$

 $_{x}K_{x}Fe_{3}(SO_{4})_{3}(OH)_{6}$ solid-solution series is completely occupied by Na and/or K. The reliability factors, positional parameters, site occupancies, and selected interatomic distances and angles obtained are given in Tables 3.2, 3.3 and 3.4.

A structural drawing of natrojarosite is shown in Figure 3.2. The jarosite group crystallizes in space group $R\overline{3}m$, with Z = 3 (in the hexagonal unit cell). The basic structure of the jarosite group consists of SO₄ tetrahedra and Fe-cation octahedra, where the octahedra corner-share to form sheets perpendicular to the *c* axis. The SO₄ tetrahedra have two orientations within a layer; one set of SO₄ points towards +*c*, which alternate with another set pointing toward -*c*. Twelve anions, consisting of six oxygen atoms (O2) and six OH groups (O3) form an icosahedron, in which the alkali cation (K⁺, H₃O⁺, Na⁺, etc) is located.

Natrojarosite has a much smaller unit cell volume than potassium jarosite and hydronium jarosite as a result of the smaller diameter of Na⁺, 1.39Å, than K⁺, 1.64Å and H₃O⁺, 1.52Å (Shannon, 1976; Dutrizac and Jambor, 2000). Substitution of sodium into potassium jarosite decreases unit cell parameter *c* significantly (0.617 Å) and increases *a* to a minor degree (0.012 Å). Substitution of sodium into hydronium jarosite decreases unit cell parameter *c* significantly (0.408 Å) and decreases *a* (0.040 Å).

The unit cell parameters *a* vs *c* for solid-solution series $(Na)_1$. _xH₃O_xFe₃(SO₄)₃(OH)₆ and $(Na)_{1-x}K_x$ Fe₃(SO₄)₃(OH)₆ from the current study and solidsolution series $(K)_{1-x}H_3O_x$ Fe₃(SO₄)₃(OH)₆ from Basciano and Peterson (2007) are plotted in Figure 3.3. Data from previous studies of sodium – hydronium jarosite and sodium – potassium jarosite solid-solution series are also included on the graph. Data from previous synthetic studies of the K – H₃O jarosite solid-solution series, other than those from Basciano and Peterson (2007), are not included on the graph for clarity. The majority of synthetic K – H₃O samples plot below those from Basciano and Peterson (2007) due to iron deficiency. The data from this study fall close to straight lines for both the sodium – hydronium jarosite series (correlation coefficient $r^2 = 0.99$) and the sodium – potassium jarosite series ($r^2 = 0.97$), following Vegard's law of ideal solid-solution. Variation of the unit cell parameters vs. sodium content for the sodium – hydronium jarosite series and sodium – potassium series are presented in Figure 3.4.

It was found in Basciano and Peterson (2007) that an iron deficiency in the B site causes a significant reduction in unit cell parameter c. The majority of synthetic jarosite group minerals grown in previous studies do have iron deficiencies in the B site, causing a reduction in c. As a result of full iron occupancy in the synthetic samples grown in the current study, unit cell parameter c of the Na – H₃O and Na – K jarosite solid-solution series are larger than most previous work with comparable A site occupancies. Additionally, there is no substitution in the A site by H₃O⁺ in the Na – K jarosite series. Well defined trends can be seen in the unit cell parameters across the solid-solution series in the synthetic samples from this study and Basciano and Peterson (2007).

End-member potassium jarosite with full iron occupancy was grown by Grohol et al. (2003) (labeled 5 in Figure 3.3) and the unit cell parameters closely match endmember potassium jarosite grown in Basciano and Peterson (2007). Natrojarosite grown by Grohol et al. (2003) was reported to be stoichiometric with respect to iron and with full sodium occupancy, but the unit cell parameters are not similar to the natrojarosite grown in this study and do not follow the trend of the solid-solution series. Unit cell parameter c is similar for both samples but a is significantly larger than the sample grown in this study. The unit cell parameters for natrojarosite grown by Grohol et al. (2003) are similar to a sample grown by Kubisz (1970), which has a formula of $Na_{0.67}(H_3O)_{0.33}Fe_{2.83}(SO_4)_2(OH)_{5.49}(H_2O)_{0.51}$.

Previous samples grown in the Na – K jarosite solid-solution series by Drouet and Navrotsky (2003) (labeled 4 on Figure 3.3) contain approximately 30% H₃O in the A site and are iron deficient by 11 - 14% in the B site. Hydronium substitution causes a unit cell parameter shift towards end – member hydronium jarosite and the iron deficiency causes a decrease in unit cell parameter c. In Figure 3.3, the Drouet and Navrotsky (2003) samples plot to the right of the K – Na jarosite samples synthesized in this study as they are a solid-solution between jarosite, natrojarosite and hydronium jarosite. The samples do not have a uniform level of iron deficiency; iron occupancy of the samples ranges from 2.57 to 2.67. If the samples had full iron occupancy, they should plot on tie lines from the Na – K solid-solution line to hydronium jarosite. As there is a difference in the iron occupancy of the samples, there is considerable scatter and correlation between sodium and potassium content in the A site and unit cell parameters is lost as unit cell parameter c is affected by both A site content and iron deficiency in the B site. Samples from previous studies in the $Na - H_3O$ jarosite solid-solution series that are iron deficient (Kubisz, 1970; Dutrizac and Kaiman, 1976; and Drouet and Navrotsky, 2003) plot below the samples grown in this study in Figure 3.3.

Polyhedral bond lengths A – O2 and O3 and Fe – O2 and O3 for Na – H₃O jarosite, Na – K jarosite and K – H₃O (Basciano and Peterson, 2007) solid-solution series are shown in Figure 3.5. Data were included for the K – H₃O jarosite solid-solution series for completeness. Polyhedral bond lengths of the A and B site vary linearly

according to occupancy. With sodium substitution into potassium jarosite, A - O3 decreases and A - O2 decreases to a very minor degree. Correspondingly, Fe - O3 increases and Fe - O2 increases to a minor degree.

Similarly in the Na – H_3O jarosite solid-solution series, bond lengths A – O3 and A - O2 decrease with sodium substitution, and Fe - O3 and Fe - O2 increase. As proposed in Basciano and Peterson (2007), it is assumed that the hydrogens of the H₃O groups are hydrogen bonded to the O2 atoms in the A polyhedra based on hydronium geometry. The A - O3 bond length is affected more significantly in the Na - H₃O series than in K – H₃O series. This is likely caused by the much smaller ionic diameter of Na^+ than H_3O^+ . Both A – O2 and A – O3 decrease by a similar degree (0.09 and 0.16 Å, respectively) while Fe - O2 increases by 0.035Å and Fe - O3 increases by only 0.0076Å. A similar trend is seen in the Na - K solid-solution series for the Fe polyhedra. As the A polyhedra are face sharing with the iron octahedra and O3 is a hydroxyl group that is hydrogen bonded to O1 of the sulfate group, there is less possible flexibility in the Fe-O3 bond length. Substitutions in the A site mainly effect the Fe - O2 bond length. As determined by the differences in maximum and minimum bond lengths, the A polyhedra in the $Na - H_3O$ series remains distorted though as Na content increases, while the Fe octahedra becomes increasingly distorted as Na increases. In the Na – K series the A polyhedra becomes increasingly distorted as Na increases and the distortion of the Fe octahedra remains relatively constant across the series.

Natural samples

Unit cell parameters of three natural samples were measured in this study and are plotted in Figure 3.3. The Sharbot Lake sample appears to be a stoichiometric K jarosite and has very similar unit cell parameters to synthetic stoichiometric K jarosite with unit cell parameters a 7.304(1) c 17.206(4) Å. No aluminum or sodium was found during EDS analysis. The sample analyzed from Ely Mine, Vermont contains both Na and K in roughly similar proportions. The sample plots approximately half way between Na jarosite and K jarosite to the left of the synthetic samples. The *a* parameter is approximately 0.01 Å less than the synthetic samples. These results suggest that there is a minor amount of aluminum in the sample as this would cause a reduction in the a parameter. The presence of Al was confirmed with SEM - EDS analysis. Sample 7-10 1-5 from Rio Tinto, Spain has unit cell parameters a 7.333(2) c 16.856(4) Å and plots approximately half way between hydronium jarosite and natrojarosite. The sample plots above the synthetic samples indicating that either there is potassium substituting into the A site or aluminum substituting into the B site. SEM - EDS analysis indicates a minor amount of aluminum in the sample and no potassium. Aluminum substitution would cause a decrease in unit cell parameter a and no change in c (Brophy et al., 1962). Potassium substitution would have caused a decrease in unit cell parameter a and an increase in c.

Unit cell parameters from natural samples reported in the literature were also plotted on Figure 3.3. No chemical analyses were reported for the majority of the samples. The samples that plot to the left of the synthetic K – Na jarosite samples probably have Al substitution in the B site causing a reduction in unit cell parameter a or the unit cell parameters are not as accurate due to the older methods of unit cell parameter determination. Three of the samples analyzed by Abbaticchio et al. (1977) do have minor amounts of Al, which cause the small reduction in *a* relative to our synthetic samples. In Figure 3.3 it can been seen that a number of the natural samples plot close to the synthetic samples grown in this study and Basciano and Peterson (2007), indicating near to full iron occupancy in the B site. From these results and natural samples analyzed in Basciano and Peterson (2007) and Papike et al.(2007) it is probable that many natural jarosite samples have close to full occupancy of the B site. The jarosite group members synthesized in this study are probably more similar to many natural samples than jarosites synthesized in earlier studies, which likely have Fe-deficiencies.

Hydronium in the jarosite group

The presence of hydronium in jarosite and alunite has been investigated in a number of studies. The most recent study done by Nielson et al. (2007) found that H_3O^+ is not found in alunite or natroalunite in solid state NMR studies that have both A and B site deficiencies. They did see evidence for H_3O^+ in hydronium alunite. Nielson et al. (2007) postulated that vacancies in the B site are compensated by the addition of 4 H⁺ ions, resulting in 4 Al-OH₂ bonds per vacancy. This substitution is accompanied by deprotonation of H_3O^+ in the A site, forming H_2O , which is then unnecessary for charge balance resulting in an A site vacancy. As the complete solid-solution series between K – H_3O jarosite and Na – H_3O jarosite in this study and Basciano and Peterson (2007) have been synthesized with no B site vacancies, it is probable that hydronium exists through the series in the A site. In samples that contain B site vacancies it is possible that an

addition of H^+ , creating 4 Fe-OH₂ groups per B site vacancy and subsequent vacancy in the A site would occur for only a number of the A sites. As all of the B site vacancies are compensated there would be no additional vacancies created in the A site, the remaining A sites are likely filled with H_3O^+ . It is common to see as much as 13% vacancy in the B site of jarosite in synthetic studies and it is probable that a similar percentage of A sites are vacant and the remaining occupancy of the A site that is not Na^+ or K^+ is H_3O^+ .

SWIR and MIR

Short-wave infrared (SWIR) reflectance spectra and infrared (IR) spectra are shown in Figures 3.6 and 3.7. SWIR region data were collected for both the Na – H₃O and Na – K jarosite solid-solution series. The SWIR data for the Na – H₃O jarosite solidsolution series is shown in entirety, including the spectrum for hydronium jarosite taken from Basciano and Peterson (2007), for completeness. Only one spectrum from the Na – K solid-solution series is shown in Figure 3.6 as the differences in band shape and position in the spectra are subtle. The spectra are typical of the jarosite structure and the vibrational features have been labeled with assignments from Bishop and Murad (2005). In the Na – H₃O jarosite solid-solution series there is a change in spectra that can be tracked across the series. Similar to the SWIR spectra for the K – H₃O jarosite solidsolution series analyzed in Basciano and Peterson (2007), detail is lost from the spectra across the series with increasing hydronium content. Bands that are dampened or lost are shoulders at 1514 nm, 2214 nm, 2296 nm and the area between 2380 and 2500 nm. Detailed assignments of the bands are given in Figure 3.6.

Mid-infrared absorbance data were collected for samples in the $K - H_3O$, Na – H_3O and Na - K jarosite solid-solution series. Samples in the $K - H_3O$ series are from the previous study Basciano and Peterson (2007). For clarity, only spectra for endmembers and two samples within each series are included in Figure 3.7. Infrared spectra for jarosite group members have been reported and discussed elsewhere as well (Kubisz, 1972; Powers et al., 1975; Baron and Palmer, 1996; Drouet and Navrotsky, 2003; Drouet et al., 2004; Bishop and Murad, 2005; Frost et al., 2006). The absorbance spectra shown here are similar to those presented in the literature. What can be seen in these spectra is the change that occurs across the solid-solution series, especially changes due to the effect of H₃O. Spectral detail is lost with substitution of H₃O when H₃O transfers a proton to make OH₂. The OH₂ disrupts vibrational coupling causing some absorption features to disappear (Swayze et al., 2006). As many of the samples synthesized in this study have little to no H₃O the differences are apparent in the spectra. Band assignments for vibrational features are given in Table 3.5. There is some evidence of minor H₃O in the K jarosite spectrum, which was expected as the K jarosite analyzed has 95% K and 5 % H₃O occupancy in the A site. There is no evidence for H₃O in the Na jarosite spectrum. There are minor changes between the Na and K jarosite spectra with minor peak shifts as a result of the difference in energies caused by the degree of interpenetration controlled by A site cation size (Drouet and Navrotsky, 2003). Hydronium in the A site causes peak shifts as well as peak widening (464 cm^{-1}) or elimination of peaks (466, 577 shoulder, and 665 cm⁻¹ in K jarosite). H₃O jarosite does have one peak and shoulder that both K jarosite and Na jarosite are missing or are very weak in (1639 and 1576 cm-1) that are assigned to the water band (δH_2O).

Conclusions

The complete solid-solution series between the most common jarosite group members, potassium jarosite, natrojarosite and hydronium jarosite, have been synthesized and analyzed by X-ray diffraction, Rietveld analysis, chemical analysis, SWIR and MIR spectroscopy. As the jarosite group samples in the current study and those from Basciano and Peterson (2007) have full iron occupancy and the samples in the Na – K jarosite series have no hydronium substitution, the unit cell parameters are significantly different than those reported in the majority of previous studies of synthetic samples. It appears that many natural samples are stoichiometric with respect to iron and correlate well with the samples from this study. The data from these solid-solution studies can be used as a guide in future studies of natural jarosite samples to determine the composition of the sample.

These data as well as other recent advances in the knowledge of the jarosite group of minerals (Glynn, 2000; Papike et al., 2007; Nielson et al., 2007) will aid in the interpretation of jarosite group minerals analyzed in future Mars missions where the combined XRD/XRF (CheMin) instrument will be used. In order for such an instrument to be successful at discriminating different jarosite compositions, it must have a resolution sufficient to employ Figure 3.3 in this study. As discussed in Papike et al. (2007) the X-ray patterns of Martian jarosite may show two patterns and the unit cell analyses done in this study and Basciano and Peterson (2007) will help in the interpretation of the possible chemical compositions of the jarosite species encountered.

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Starting solution	compositions(g)	Analytical results (ICP-OES) (% occupancy) and For				d Formula
Na ₂ (SO ₄)	$K_2(SO_4)$	Fe%	K%	Na%	S%	Formula
0.05	0.45	100.2	77.6	25.6	100	(K _{0.78} Na _{0.26})Fe _{3.01} (SO ₄) ₂ (OH) ₆
0.10	0.40	104.7	60.9	41.5	100	(K _{0.61} Na _{0.41})Fe _{3.14} (SO ₄) ₂ (OH) ₆
0.25	0.25	102.5	52.2	46.1	100	(K _{0.52} Na _{0.46})Fe _{3.08} (SO ₄) ₂ (OH) ₆
0.40	0.10	98.5	28.8	69.5	100	(K _{0.29} Na _{0.69})Fe _{2.95} (SO ₄) ₂ (OH) ₆
0.45	0.05	98.8	11.1	85.0	100	(K _{0.11} Na _{0.85})Fe _{2.96} (SO ₄) ₂ (OH) ₆
na	na	102.0		97.7	100	(Na _{1.0} H ₃ O _{0.0})Fe _{3.06} (SO ₄) ₂ (OH) ₆
0.85		98.8		87.5	100	(Na _{0.87} H ₃ O _{0.13})Fe _{2.96} (SO ₄) ₂ (OH) ₆
0.70		98.3		68.6	100	(Na _{0.67} H ₃ O _{0.33})Fe _{2.95} (SO ₄) ₂ (OH) ₆
1.0		103.8		49.4	100	(Na _{0.49} H ₃ O _{0.51})Fe _{3.11} (SO ₄) ₂ (OH) ₆
0.6		99.8		35.0	100	(Na _{0.35} H ₃ O _{0.65})Fe _{2.99} (SO ₄) ₂ (OH) ₆
0.2		99.4		23.8	100	$(Na_{0.24}H_{3}O_{0.76})Fe_{2.98}(SO_{4})_{2}(OH)_{6}$
	Starting solution (Na ₂ (SO ₄) 0.05 0.10 0.25 0.40 0.45 na 0.85 0.70 1.0 0.6 0.2	Starting solution compositions(g) Na2(SO4) K2(SO4) 0.05 0.45 0.10 0.40 0.25 0.25 0.40 0.10 0.45 0.05 0.40 0.10 0.45 0.05 0.45 0.05 0.45 0.05 0.85 0.70 1.0 0.6 0.2 0.2	Starting solution compositions(g)Analytical res $Na_2(SO_4)$ $K_2(SO_4)$ Fe%0.050.45100.20.100.40104.70.250.25102.50.400.1098.50.450.0598.8nana102.00.8598.80.7098.31.0103.80.699.80.299.4	Starting solution compositions(g)Analytical results (ICP-OES $Na_2(SO_4)$ $K_2(SO_4)$ Fe%K%0.050.45100.277.60.100.40104.760.90.250.25102.552.20.400.1098.528.80.450.0598.811.1nana102.00.8598.80.7098.31.0103.80.699.80.299.4	Starting solution compositions(g)Analytical results (ICP-OES) (% occup Na2(SO4))K2(SO4)Fe%K%Na%0.050.45100.277.625.60.100.40104.760.941.50.250.25102.552.246.10.400.1098.528.869.50.450.0598.811.185.0nana102.097.70.8598.887.50.7098.368.61.099.835.00.2599.835.00.7099.423.8	Starting solution compositions(g)Analytical results (ICP-OES) (% occupancy) an Na2(SO4)Na2(SO4) $K_2(SO4)$ Fe%K%Na%S%0.050.45100.277.625.61000.100.40104.760.941.51000.250.25102.552.246.11000.400.1098.528.869.51000.450.0598.811.185.01000.450.0598.811.185.01000.8598.887.51000.7098.368.61001.0103.849.41000.699.835.01000.299.423.8100

Table 3.1. Chemical compositions of starting solutions and synthetic jarosite samples

* synthesized in chloride media similar to Frost et al.(2005), see text for details
 ^ψ samples were not annealed as there was no evidence of peak broadening.
 note: chemical analyses are based on 2 S per formula unit

potassium jarosite –natrojarosite R3 m							
Sample	*	К	L	Μ	Ν	0	Р
(Na,K)	(0.0,0.95)	(0.26,0.78)	(0.41,0.61)	(0.46,0.52)	(0.69,0.29)	(0.85,0.11)	(1.0,0.0)
a(Å)	7.30293(8)	7.3045(1)	7.3052(2)	7.3079(2)	7.3101(1)	7.3144(1)	7.31525(6)
c(Å)	17.2043(2)	17.0875(3)	16.9706(6)	16.9028(4)	16.7658(4)	16.6491(2)	16.5868(2)
V(Å ³)	794.62(2)	789.57(3)	784.32(5)	781.76(4)	775.90(3)	771.40(3)	768.69(1)
R_{p}	3.289	3.932	4.179	7.037	6.431	3.561	4.498
R_{wp}	4.288	6.124	6.525	10.754	9.861	5.190	5.896
R_{exp}	3.570	3.394	3.376	4.631	4.545	3.200	4.946
S	1.201	1.805	1.933	2.322	2.170	1.622	1.192
D-W	0.745	0.346	0.293	0.209	0.241	0.430	0.754

Table 3.2. Data collection and structure refinement details.

natrojarosite – hydronium jarosite **R3**m

Sample	Q	R	S	Т	U	A*
Na	0.87	0.67	0.49	0.35	0.24	0.00
a(Å)	7.31984(9)	7.3254(1)	7.33876(9)	7.3420(2)	7.34742(9)	7.3552(2)
c(Å)	16.6474(2)	16.7209(3)	16.8105(2)	16.8574(4)	16.9253(2)	16.9945(4)
V(Å)	772.47(2)	777.07(3)	784.07(2)	786.95(4)	791.29(2)	796.21(4)
R _p	3.077	4.943	5.040	3.131	3.549	3.571
R _{wp}	4.188	7.099	6.801	4.356	4.651	4.773
R _{exp}	3.166	4.405	4.902	3.124	3.904	3.882
S	1.323	1.612	1.387	1.395	1.191	1.230
D-W	0.623	0.424	0.554	0.547	0.740	0.691

Step range (°20) 15-100°, step interval 0.008.

 R_p : R-pattern, R_{wp} : weighted-pattern, R_{exp} : R-expected, S(= R_{wp}/R_{exp}):Goodness of fit (Young, 1993) D-W: Durbin-Watson *d*-statistic (Hill and Flack, 1987).

* (potassium) jarosite from Basciano and Peterson (2007)

note: A site occupancy determined with ICP-OES

Cito				-	D	0.00
Site	VV	X	у	Z	Б	UCC
Sample	θĸ					
Na	3a	0	0	0	0.7(1)	0.26
К	3a	0	0	0	0.7(1)	0.78
Fe	9d	0.166667	-0.166667	-0.16667	2.27(9)	1
S	6c	0	0	0.3091(2)	1.6(1)	1
01	6c	0	0	0.3947(4)	2.4(3)	1
02	18h	0.2226(3)	-0.2226(3)	-0.0542(3)	1.9(2)	1
O3	18h	0.1275(2)	-0.1275(2)	0.1325(2)	0.6(1)	1
Н	18h	0.165(1)	-0.165(1)	0.168(2)	2	1
Sample	e L					o. ()
Na	3a	0	0	0	1.0(2)	0.41
K	3a	0	0	0	1.0(2)	0.61
Fe	9d	0.166667	-0.166667	-0.16667	2.6(1)	1
S	6c	0	0	0.3096(3)	1.5(1)	1
01	6c	0	0	0.3952(5)	2.4(3)	1
02	18h	0.2236(3)	-0.2236(3)	-0.0541(3)	2.2(2)	1
03	18h	0.1275(3)	-0.1275(3)	0.1333(2)	0.3(1)	1
H	18h	0.161(1)	-0.161(1)	0.172(2)	2	1
Sample	e M	0	0	0	4.0(0)	0.40
Na	3a	U	U	U	1.9(2)	0.46
К	3a	0	0	0	1.9(2)	0.52
Fe	9d	0.166667	-0.166667	-0.16667	2.14(9)	1
S	6c	0	0	0.3102(3)	1.2(2)	1
01	6c	0	0	0.3945(5)	2.0(3)	1
02	18h	0.2246(3)	-0.2246(3)	-0.0540(3)	1.9(2)	1
O3	18h	0.1271(2)	-0.1271(2)	0.1325(2)	0.4(2)	1
Н	18h	0.157(2)	-0.157(2)	0.173(2)	2	1
Sample	e N	-	-	-		• • •
Na	3a	0	0	0	2.5(2)	0.69
К	3a	0	0	0	2.5(2)	0.29
Fe	9d	0.166667	-0.166667	-0.16667	2.02(7)	1
S	6c	0	0	0.3112(2)	0.7(1)	1
01	6c	0	0	0.3972(4)	1.9(3)	1
O2	18h	0.2252(3)	-0.2252(3)	-0.0528(3)	1.1(2)	1
O3	18h	0.1267(2)	-0.1267(2)	0.1315(2)	0.2(2)	1
Н	18h	0.162(2)	-0.162(2)	0.170(2)	2	1
Sample	e O					
Na	3a	0	0	0	3.4(2)	0.85
К	3a	0	0	0	3.4(2)	0.11
Fe	9d	0.166667	-0.166667	-0.16667	1.62(6)	1
S	6c	0	0	0.3121(2)	1.2(1)	1
01	6c	0	0	0.4008(3)	1.4(2)	1
O2	18h	0.2229(2)	-0.2229(2)	-0.0510(2)	1.5(1)	1
O3	18h	0.1257(1)	-0.1257(1)	0.1305(1)	0.4(1)	1

Table 3.3. Refined atomic positions, displacement parameters and occupancies of synthetic and natural jarosite samples

Н	18h	0.162(1)	-0.162*1)	0.169	2	1
Sample P						
Na	3a	0	0	0	3.0(1)	1.0
К	3a	0	0	0	3.0(1)	0.0
Fe	9d	0.166667	-0.166667	-0.16667	1.09(4)	1
S	6c	0	0	0.3123(1)	0.91(6)	1
01	6c	0	0	0.4020(2)	0.8(1)	1
02	18h	0.2220(2)	-0.2220(2)	-0.0505(1)	0.85(8)	1
O3	18h	0.1252(1)	-0.1252(1)	0.13018(9)	0.33(8)	1
Н	18h	0.1583(9)	-0.1583(9)	0.1697(9)	2	1
Sample Q						
Na	3a	0	0	0	3.0(1)	0.87
H₃O	3a	0	0	0	3.0(1)	0.13
Fe	9d	0.166667	-0.166667	-0.16667	1.43(5)	1
S	6c	0	0	0.3117(1)	1.16(9)	1
01	6c	0	0	0.4012(2)	1.0(2)	1
02	18h	0.2222(2)	-0.2222(2)	-0.0510(1)	1.3(1)	1
O3	18h	0.1252(1)	-0.1252(1)	0.1304(1)	0.64(9)	1
Н	18h	0.1671(9)	-0.1671(9)	0.164(1)	2	1
Sample R						
Na	3a	0	0	0	3.5(2)	0.67
H ₃ O	3a	0	0	0	3.5(2)	0.33
Fe	9d	0.166667	-0.166667	-0.16667	1.70(5)	1
S	6c	0	0	0.3111(1)	0.99(9)	1
01	6c	0	0	0.3995(3)	1.0(2)	1
02	18h	0.2235(3)	-0.2235(3)	-0.0522(2)	1.4(1)	1
O3	18h	0.1255(1)	-0.1255(1)	0.1308(1)	0.68(9)	1
Н	18h	0.166(1)	-0.166(1)	0.166(1)	2	1
Sample S						
Na	3a	0	0	0	5.4(2)	0.49
H₃O	3a	0	0	0	5.4(2)	0.51
Fe	9d	0.166667	-0.166667	-0.16667	1.66(4)	1
S	6c	0	0	0.3099(1)	1.44(7)	1
01	6c	0	0	0.3990(3)	1.4(2)	1
02	18h	0.2235(2)	-0.2235(2))	-0.0535(2)	1.9(1)	1
O3	18h	0.1255(1)	-0.1255(1)	0.1320(1)	0.42(9)	1
Н	18h	0.166(1)	-0.166(1)	0.166(1)	2	1
Sample T						
Na	3a	0	0	0	8.0(3)	0.35
H₃O	3a	0	0	0	8.0(3)	0.65
Fe	9d	0.166667	-0.166667	-0.16667	1.84(5)	1
S	6c	0	0	0.3089(2)	1.81(9)	1
01	6c	0	0	0.3979(3)	0.5(2)	1
O2	18h	0.2229(2)	-0.2229(2)	-0.0538(2)	2.6(1)	1
O3	18h	0.1257(1)	-0.1257(1)	0.1326(2)	0.5(1)	1
Н	18h	0.171(1)	-0.171(1)	0.163(1)	2	1
Sample U						
Na	3a	0	0	0	7.1(3)	0.24
H ₃ O	3a	0	0	0	7.1(3)	0.76
Fe	9d	0.166667	-0.166667	-0.16667	2.11(6)	1
----	-----	-----------	------------	------------	---------	---
S	6c	0	0	0.3094(2)	1.9(1)	1
01	6c	0	0	0.3998(3)	2.2(2)	1
02	18h	0.2242(2)	-0.2242(2)	-0.0548(2)	2.8(1)	1
O3	18h	0.1266(1)	-0.1266(1)	0.1338(1)	0.3(1)	1
Н	18h	0.169(1)	-0.169(1)	0.167(1)	2	1

Note: numbers in parentheses in this and subsequent tables are estimated standard deviations, A site occupancies determined with ICP-OES

	К	L	М	Ν	0	Р	Q	R	S	Т	U
A site occ (%)	Na 26 K 78	Na 41 K 61	Na 46 K 52	Na 69 K 29	Na 85 K 11	Na 100 K 0	Na 87 H₃O 13	Na 67 H₃O 33	Na 49 H₃O 51	Na 35 H₃O 65	Na 24 H₃O 76
K,Na - O3 x 6	2.780(3)	2.778(3)	2.757(3)	2.727(3)	2.694(2)	2.679(1)	2.689(2)	2.706(2)	2.734(2)	2.748(2)	2.780(2)
K, Na - O2 x 6	2.965(4)	2.974(4)	2.985(5)	2.986(4)	2.949(3)	2.935(2)	2.942(2)	2.968(3)	2.980(2)	2.976(2)	3.000(3)
Average	2.873	2.876	2.871	2.857	2.822	2.807	2.816	2.837	2.857	2.862	2.890
Fe - O3 x 4	1.997(1)	1.992(1)	1.995(1)	1.997(1)	1.9983(8)	1.9980(2)	1.9985(7)	1.9999(3)	1.9982(7)	1.9971(8)	1.9963(8)
Fe - O2 x 2	2.048(4)	2.042(5)	2.040(6)	2.049(4)	2.053(2)	2.050(2)	2.049(3)	2.045(3)	2.035(2)	2.032(3)	2.030(3)
Average	2.023	2.017	2.018	2.023	2.026	2.024	2.024	2.022	2.017	2.015	2.013
S - 01	1.462(8)	1.454(8)	1.425(2)	1.441(7)	1.477(6)	1.489(4)	1.489(4)	1.478(4)	1.498(5)	1.489(3)	1.484(3)
S - O2 x 3	1.491(4)	1.481(4)	1.473(5)	1.462(4)	1.484(3)	1.492(2)	1.492(3)	1.480(2)	1.485(2)	1.502(4)	1.531(6)
Average	1.477	1.468	1.449	1.452	1.481	1.491	1.491	1.479	1.492	1.496	1.508
O2 - Fe - O3 x 4	87.2 (1)	88.0(1)	88.0(1)	87.9(1)	86.93(8)	86.63(6)	86.75 (5)	87.25(7)	87.84(7)	87.90(7)	88.75(7)
O2 - Fe - O3 x 4	92.8 (1)	92.0(1)	92.0 (1)	92.2(1)	93.07 (8)	93.37 (6)	93.25(5)	92.75(7)	92.16(7)	92.10(7)	91.25(7)
O3 - Fe - O3 x 2	88.8(1)	89.1(1)	88.6(2)	88.2(1)	87.3(1)	86.87(8)	86.89(8)	87.20(9)	87.52(9)	87.73(9)	88.6(1)
O3 - Fe - O3 x 2	91.2 (1)	90.9 (1)	91.4(2)	91.9(1)	92.7(1)	93.13(8)	93.11(8)	92.80(9)	92.48(9)	92.27(9)	91.4(1)
01 - S - 02 x 3	110 1(2)	110 3(2)	110 8(2)	110 5(2)	109 5(1)	109 10(6)	109 2(1)	109 8(1)	109 9(1)	109 4(1)	110 6(2)
$O_{1}^{2} = O_{2}^{2} \times 3$	108.8(2)	108.6(2)	108 1(3)	108 3(2)	109.0(1)	100.10(0)	109.2(1)	109.0(1)	109.0(1)	100.4(1)	108 3(2)
02 - 3 - 02 X 3	100.0(2)	100.0(2)	100.1(3)	100.3(2)	109.4(2)	109.8(1)	109.7(1)	109.2(1)	109.0(1)	109.5(1)	100.5(2)
Average	109.5	109.5	109.5	109.4	109.5	109.5	109.5	109.5	109.5	109.5	109.5
O3 – H	0.77(3)	0.78(3)	0.79(3)	0.78(3)	0.79(2)	0.78(2)	0.78(2)	0.775(2)	0.77(2)	0.775(2)	0.775(2)
O3 – H … O1	2.874(4)	2.872(3)	2.875(4)	2.852(3)	2.833(2)	2.828(1)	2.837(1)	2.850(2)	2.867(2)	2.880(2)	2.868(3)

Table 3.4. Selected interatomic distances (Å) and angles (°)

	5		, <i>j</i> =
<u>K jarosite</u>	<u>H₃O jarosite</u>	<u>Na jarosite</u>	Assignment
445	464 b	445	$v_2(SO_4)^{2-}$
466	-	474	Fe-O
503	503	503	Fe – O
577 sh	-	584 sh	$\gamma(OH)$
627	623	627	$v_4(SO_4)^{2-}$
665	-	682	$v_4(SO_4)^{2-}$
999	1004	1006	δ(OH)
~1022 sh	-	~1014 sh	δ(OH)
1083	1089	1091	$v_3(SO_4)^{2-}$
1184	1195	1172	$v_3(SO_4)^{2-}$
-	1576 sh	-	$\delta(H_2O)$
1639 vw	1639	-	$\delta(H_2O)$
3384	3367 b	3353	v(OH)

Table 3.5. Band assignments for vibrational features in synthetic K, H₃O and Na jarosite

Notes: sh = shoulder, b = wide, vw = very weak. Band assignments are from Bishop and Murad (2005).



Figure 3.1. Rietveld refinement plot of sample P, natrojarosite. The grey line is the observed data and the solid line is the calculated pattern. The vertical bars mark all possible Bragg reflections ($CoK\alpha_1$ and $K\alpha_2$). The difference between the observed and calculated patterns is shown at the bottom.



Figure 3.2. Polyhedral representation of the natrojarosite structure. Sodium polyhedra (A site) are light grey, iron octahedra are dark grey (B site) and sulfate tetrahedra are medium grey.



Figure 3.3. Unit cell parameters *a* vs *c* of synthetic Na – H₃O and Na – K jarosite series from the current study, synthetic samples from previous studies that contain Na, K and H₃O or Na and H₃O in the A site and natural jarosite samples that contain varying amounts of Na, K and H₃O. All samples from the current synthetic study are shown as black squares or triangles. Note that the unit cell dimensions fall close to a straight line, and unit cell parameter *c* is larger than most of the previous synthetic studies as the B site is fully occupied. Data from previous synthetic studies are shown as numbers and natural samples are shown as grey symbols. Samples labeled 4 contain Na and K in the A site and have iron deficiencies in the B site causing a shift down and to the right of the Na – K solid solution line. Samples below the Na – H₃O solid solution line have iron deficiencies in the B site causing a reduction in unit cell parameter *c*.



Figure 3.4. Unit cell dimensions *a* and *c* vs. sodium occupancy in the A site for synthetic samples in this study. Black circles represent samples from the Na – K series and white squares represent samples from the Na – H₃O series. Error bars reported by Rietveld refinement are smaller than the symbols.



Figure 3.5. A – O polyhedra bond lengths and Fe – O octahedral bond lengths vs. A site occupancy in the Na – H₃O, Na – K and K – H₃O series. Data from the K – H₃O jarosite solid solution series is taken from Basciano and Peterson (2007).



Figure 3.6. Short-wave infrared reflectance spectra of samples from the Na - H₃O jarosite solid solution series and sample M from the Na – K jarosite solid solution series. The bands have been assigned to the following: 1 - OH vibrations; 1,2 – OH stretch overtones; 3 – OH stretch and Fe – OH bend; 4 - H₂O and H₃O combination band absorption; 5, 6, 7 – Fe – OH combination bands (out of plane) and Fe – OH combination bands (in plane); and 8 - (SO₄)₂ stretching and OH vibration. Band assignments are from Bishop and Murad (2005) and Swayze (written comm.). Spectra have been offset vertically for comparison.





Figure 3.7. Mid infrared absorbance spectra of samples from the Na – H₃O and Na – K jarosite solid solution series. Endmembers Na, K and H₃O jarosite are shown in bold with intermediate compositions between. Spectra have been offset vertically for clarity. Plot A shows 400 – 1200 cm⁻¹ and plot B shows around 3300 cm⁻¹ (OH stretch region).

Chapter 4: The crystal structure of ammoniojarosite, $(NH_4)Fe_3(SO_4)_2(OH)_6$, and the crystal chemistry of the ammoniojarosite – hydronium jarosite solid-solution series

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Abstract

The atomic structure of ammoniojarosite $[(NH_4)Fe_3(SO_4)_2(OH)_6]$, a = 7.3177(3) Å, c = 17.534(1) Å, space group $R\overline{3}m$, Z = 3 has been solved using single-crystal X-ray diffraction to wR 3.64% and R 1.4%. The atomic coordinates of the hydrogen atoms of the NH₄ group have been located and it was found that the ammonium group has two different orientations with equal probability. Hydronium commonly substitutes into jarosite group mineral structures and samples in the ammoniojarosite – hydronium jarosite solid-solution series were synthesized and analyzed using powder X-ray diffraction and Rietveld refinement. Changes in unit cell dimensions and bond lengths are noted across the solid-solution series. The end-member ammoniojarosite synthesized in this study has no hydronium substitution in the A site and the unit cell dimensions determined have a smaller *a* dimension and larger *c* dimension than previous studies of ammoniojarosite. Two natural ammoniojarosite samples were analyzed and have similar unit cell dimensions to the synthetic samples. Short-wave infrared and Fourier transform infrared spectra were collected for samples from the $NH_4 - H_3O$ jarosite solid-solution series and difference between end-members are notable. Both are useful tools for determining NH₄ content in jarosite group minerals.

Introduction

Ammoniojarosite has been extensively studied as it is a by-product of the zinc industry (Salinas et al. 2001). The jarosite method is used to precipitate dissolved iron from the hot acid-leach solutions prior to subsequent zinc recovery. One hundred and twenty-five thousand tonnes of jarosite containing 25-36 wt% Fe is produced annually (Dutrizac and Jambor 2000). Ammoniojarosite and sodium jarosite are commonly used instead of the other jarosite group minerals due to the lower costs required. Natural ammoniojarosite is quite rare as concentrated ammonium-containing solutions are not common. The ammonium must come from the decomposition of organic substances or biologic activity associated with organic matter (Frost et al. 2006). Natural ammoniojarosite is most often found in lignitic shale associated with other ammoniumbearing minerals. Natural ammoniojarosite has been reported in samples from Buffalo, Wyoming (Odem et al. 1982) and southern Utah (Shannon 1927, 1929).

Ammonioalunite (NH₄)Al₃(SO₄)₂(OH)₆ was first described by Altaner et al. (1988) in a sample from the hot-springs at The Geysers (Sonoma County), California. The ammonioalunite was intermixed with ammoniojarosite. In that same study, ammonioalunites with intermediate NH_4^+ substitution were described from the Ivanhoe Deposit (Elko County), California. The ammonioalunite from The Geysers, California forms in NH₄-rich fluids and the ammonioalunite samples from the Ivanhoe deposit form in hydrothermally altered basalt (Altaner et al. 1988). The rarity of ammonioalunite is attributed to the fact that aqueous NH_4^+ is most abundant in reducing and acidic fluids while alunite group minerals form in oxidizing and acidic environments. Similar to ammoniojarosite, ammonioalunite requires fluids with low K content as K will readily substitute into the structure in preference to NH₄.

The jarosite group of minerals is part of the alunite supergroup, which consists of 40 mineral species that have the general formula $AB_3(TO_4)_2(OH)_6$. There is extensive solid-solution in the A, B and T sites within the alunite supergroup, where A is H_3O^+ , Na^+ , K^+ , Rb^+ , Ag^+ , TI^+ , NH^{4+} , $\frac{1}{2}$ Ca²⁺ or $\frac{1}{2}$ Pb²⁺, B is Fe³⁺ or Al³⁺ and TO₄ is SO₄²⁻, PO₄³⁻ or AsO₄³⁻ (Scott, 1987; Stoffregen and Alpers, 1987). The jarosite group is characterized by B = Fe³⁺ and T = S. Jarosite (A = potassium) and natrojarosite (A = sodium) are the most prevalent naturally occurring jarosite group minerals. End-member hydronium jarosite is quite rare, though most jarosite group minerals contain some hydronium in the A site (Ripmeester et al. 1986; Drouet and Natrotsky 2003; Majzlan et al. 2004; Basciano and Peterson 2007).

The unit cell dimensions were determined for synthetic ammoniojarosite samples by Smith and Lampert (1973) and Dutrizac and Kaiman (1976). Both samples were not end-member ammoniojarosite, and exhibited significant H₃O substitution in the A site.

Natural and synthetic jarosite group minerals commonly have significant quantities of hydronium in the alkali (A) site and minor to major deficiencies in the iron site (B). Most jarosite group minerals synthesized in previous studies and many natural jarosite group minerals have B site occupancies as low as 86%. Studies that address the iron and/or aluminum deficiency are: Hendricks (1937), Kubisz (1970), Ripmeester et al. (1986), Drouet and Navrotsky (2003) and Drouet et al. (2004).

The crystal structure, including hydrogen positions of the OH and NH₄ groups, was determined in this study using single-crystal X-ray diffraction. Additionally,

structures were refined using Rietveld refinement of ammoniojarosite and 3 samples in the ammoniojarosite – hydronium jarosite solid-solution series. Two natural samples of ammoniojarosite were analyzed and compared to the synthetic samples. Short-wave infrared (SWIR) spectra Fourier transform infrared (FTIR) spectra were collected for the synthetic samples to determine the changes in the IR spectra due to H₃O content.

Natural Samples

Two natural samples were obtained from the Royal Ontario Museum in Toronto, Canada for analysis. Sample M38446 is from Buffalo, Johnson County, Wyoming. The sample locality was originally described by Odem et al. (1982). The sample is finegrained yellow, and occurs as aggregates. The ammoniojarosite was from a lignitic black to brown shale (Odem et al. 1982). Sample M16514 is from the west side of the Kaibab Fault, southern Utah. The location and sample were originally described by Shannon (1927, 1929). Shannon (1927) described the sample as small lumps and hard irregular flattened nodules up to 4 centimeters broad by 5 millimeters thick embedded in blackishbrown lignitic material. The ammoniojarosite is closely associated with tschermigite ($NH_4Al(SO_4)_2 \cdot 12H_2O$). The two natural samples were analyzed using powder X-ray diffraction to determine unit cell dimensions and with SEM-EDS to determine if there are any chemical substitutions in the A or B sites, which would affect the unit cell dimensions.

Sample synthesis

The solid-solution series $(H_3O, NH_4)Fe_3(SO_4)_2(OH)_6$ was synthesized using conditions outlined in Basciano and Peterson (2007) to ensure full iron occupancy in the samples. Forty grams of reagent-grade $Fe_2(SO_4)_3 \cdot 5H_2O$ and varying amounts of reagent-grade $(NH_4)_2SO_4$ (0.2, 0.4 and 1.0 g) were mixed with de-ionized water to a volume of 100 ml at room temperature and heated in sealed stainless-steel bombs at 140°C for 48 hours. During the H₃O – NH₄ jarosite solid-solution synthesis, ammoniumrich jarosite precipitated out of solution first in all samples, followed by hydronium-rich jarosite. Ammoniojarosite may have a lower solubility than hydronium jarosite, causing it to precipitate out of solution first as in the case with sodium and potassium jarosite (Glynn 2000). Chemical compositions of the starting solutions and analytical results of the resulting ammoniojarosite – hydronium jarosite samples are given in Table 4.1. Xray diffraction scans of samples B, C and D show that a number of the peaks are broadened due to non-homogeneity of the samples. As ammoniojarosite preferentially precipitates out of solution before hydronium rich jarosite, samples are composed of a number of different chemistries along the solid-solution series. The peak broadening was most evident for peak (006) where there is a large difference in peak position between ammonium-rich and ammonium-poor phases in the mixture. Similar findings are discussed in Basciano and Peterson (2007) for the potassium-hydronium jarosite solidsolution series. To produce a single homogeneous phase, samples were finely ground in a McCrone Micronizing Mill after the initial synthesis and re-heated at 140°C in the reactant solution. Samples were analyzed every 3 days using XRD to determine sample homogeneity. The samples were deemed to be homogeneous when the full width at half

maximum (FWHM) of peak (006) did not decrease with further annealing. All samples were rinsed thoroughly with de-ionized water, filtered and dried at 120°C to eliminate any excess water. Drying at this temperature did not influence the X-ray diffraction pattern of the samples. All samples consisted of intergrown rhombohedral (pseudocubic) crystals varying in size from <10 μ m (initial growth) to 100 μ m (final growth). Data for end-member hydronium jarosite were taken from Basciano and Peterson (2007). Endmember ammoniojarosite could not be grown using the above method as there was hydronium substitution in the A site in all samples as determined by Rietveld refinement and analysis of unit cell dimensions.

End-member ammoniojarosite was grown using a two-step method similar to Stoffregen (1993). Ammoniojarosite with approximately 80% NH₄ occupancy was grown using the same method outlined above. To produce single-crystals and a powder for Rietveld refinement, the resulting sample was heated in a $1.0 \ mH_2SO_4$ -0.5NH₄SO₄ solution at 200°C for 3 days in a Parr pressure bomb. This procedure yielded a sample with A site occupancy of 100% NH₄ as determined by ICP-OES and ICP-MS. Singlecrystals were hand-picked from the bulk for single-crystal analysis and the remainder of the sample was ground in a McCrone Micronising Mill for powder X-ray diffraction and Rietveld refinement.

Diffraction experiments

Single-crystal X-ray diffraction

A single crystal of end-member ammoniojarosite (amber coloured, cubic shaped,

size 0.10 x 0.08 x 0.06 mm) was mounted on a glass fiber for X-ray diffraction. Data collection was performed on a Bruker SMART CCD 1000 X-ray diffractometer with a graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å), operating at 50 kV and 35 mA at 180 K over a θ range of 3.42 to 28.08° (Department of Chemistry, Queen's University). Data were processed using the Bruker AXS Crystal Structure Analysis Package. The single-crystal unit cell dimensions were obtained using APEX2 software and refined with SAINT software, using all the observed reflections. The raw intensity data were converted (including corrections for background, Lorentz and polarization effects) to structure amplitudes and their esd values using the program SAINT. Structure solution was done with XPREP and SHELXTL (Bruker 2000), the structure refinement was done with SHELXTL. The X-ray single-crystal data set includes 2978 reflections, which sorted to 276 unique reflections with an agreement factor of R = 0.014 in space group $R\bar{3}m$. Scattering curves for neutral atoms were taken from *International Tables for* X-ray Crystallography, Vol. C. Least-squares refinement including anisotropic temperature factors and site-occupancy factors, with H atoms disordered, resulted in a wR of 0.04. Hydrogen atoms that are part of the NH₄ group were soft constrained so that bond distances N-H2 and H3 are approximately equal and the atomic displacement parameters of H1, H2 and H3 were restrained to be equal. The data collection and structure refinement details are given in Table 4.2, atomic coordinates and temperature factors are given in Table 4.3, and bond lengths and angles in Table 4.4.

X-ray powder diffraction and Rietveld refinement

Powder-diffraction data were collected from 15° - 100° 2 θ (Fe filtered CoK α

radiation) from a back-packed sample using a Panalytical X'Pert theta-theta diffractometer and an X'celerator position-sensitive detector equipped with incident- and diffracted-beam soller slits, and $1/2^{\circ}$ divergence and 1° anti-scatter slits. The normalfocus Co X-ray tube was operated at 40 kV and 45 mA. Profiles were taken with a step interval of 0.008 2 θ and an equivalent counting time per step of 30 s. To eliminate preferred orientation, samples were ground for 2 minutes in a McCrone Micronizing Mill and backpacked on 320 grit sandpaper. The data were refined with the Rietveld refinement program Topas Academic (Coelho 2004). Starting atom positions were taken from single-crystal results from this study. The instrument dimensions were modeled using a full axial-divergence model defined by Cheary and Coelho (1998). CoK α source emission profiles were taken from Hölzer et al. (1997). Broadening due to crystallite size was refined using the Double-Voigt approach (Balzar 1999).

The nitrogen of the NH₄ group was located at (0, 0, 0) similar to the oxygen of the hydronium jarosite (Majzlan et al. 2004; Basciano and Peterson 2007). The occupancy of ammonium in the A site was fixed to the occupancy determined with ICP-OES and ICP-MS and the T site is assumed to be fully occupied by S. Starting hydrogen positions (OH group) were taken from the single-crystal study of hydronium jarosite by Majzlan et al. (2004) and starting hydrogen positions (NH₄ group) were taken from single-crystal results (this study). Without a restraint, the O – H1 bond lengths for the OH group were significantly shorter than typical values. The O – H1 bond length were restrained to 0.8 Å, which is the average O – H bond length in crystalline solids refined by X-ray diffraction (Baur 1972). Observed O – H distances in X-ray determinations tend to be on average 0.2 Å shorter than in neutron diffraction (Baur 1972). The atomic displacement

parameters of the H atoms were fixed at 2 and not refined. The atomic position of H2 and H3 (NH₄ group) were not refined due to the two possible orientations of the NH4 group and low scatter of H with occupancy of H₃O in the A site. Isotropic displacement parameters (B) for N, Fe, S and O were refined with no restrictions and were found to be low for O3. The z coordinate for H1 for samples B, C and D (samples intermediate between hydronium jarosite and ammoniojarosite) are probably inaccurate and indicate a systematic error in the refinement. A final Rietveld refinement plot of observed and calculated intensities for end-member ammoniojarosite is shown in Figure 4.1.

Chemical analysis

The iron and sulfur content of the solid jarosite samples were determined using a Varian vista CCD Simultaneous ICP-OES at Analytical Services Unit, Queen's University. The solid samples were digested in aqua regia and both the digested samples and reactant solutions were diluted for analysis. The average analytical error for each element is: $Fe \pm 1\%$ and $S \pm 2\%$. The nitrogen content of the solid jarosite phases were determined using a Costech Elemental Analyser coupled to a Thermo Finnigan Delta plus XP using continuous flow technology at the Queen's ICP/MS lab. The average analytical error for N is $\pm 2\%$. From these data the stoichiometry of the ammonium group and iron site were determined in the solid samples based on the ratio of nitrogen and iron to sulfur. The percent nitrogen and iron in these sites were normalized to 2 S per chemical formula based on the ideal chemical formula. The chemical compositions of synthetic samples are given in Table 4.1. The A site is assumed to be full and contain H₃O.

Short-wave Infrared Reflectance Spectroscopy (SWIR) and Fourier Transform Infrared Analysis (FTIR)

Short-wave infrared reflectance spectra of the synthetic samples were collected using a Portable Infrared Mineral Analyzer, Integrated Spectronics PIMA SP instrument, which measures in the 1200 - 2600 nm range. Infrared spectra of the synthetic samples were collected using a Nicolet Avatar 320 Fourier Transform Infrared Spectrometer and a Golden Gate diamond ATR. Spectra were measured from 400 - 4000 cm⁻¹. The samples were analyzed by SWIR and IR as finely ground powders after being micronized for Rietveld refinement.

Discussion

Description of the structure of ammoniojarosite

The structure of ammoniojarosite was determined using single-crystal X-ray diffraction at 180 K. A structural drawing of ammoniojarosite is shown in Figure 4.2 (one orientation of NH₄ shown). Members of the jarosite group crystallize in space group $R\overline{3}m$, with Z = 3 (in the hexagonal unit cell). The basic structure of the jarosite group consists of SO₄ tetrahedra and Fe-cation octahedra, where the octahedra corner-share to form sheets perpendicular to the *c* axis. There are two different orientations of SO₄ tetrahedra occur within a layer; one set of SO₄ points towards +*c*, which alternate with

another set pointing toward -*c*. The oxygen and hydroxyl groups form an icosahedron, in which the alkali cation, hydronium or ammonium group is located. The univalent cations $(K^+, H_3O^+, NH_4^+, etc)$ are surrounded by twelve anions, consisting of six oxygen atoms (O2), and six OH groups (O3).

The ammonium group is disordered with two orientations with equal probability. The hydrogen bonding scheme of one orientation of the NH₄ group is shown in Figure 4.3. Nitrogen is located at special position 3a (0, 0, 0) and is coordinated by four hydrogen atoms forming a tetrahedron. The N - H2 and N - H3 distances are 0.82Å, and the H2 – N - H3 angle is 113°. The average N – H bond length, based on neutron diffraction studies of many compounds is 1.01 Å, with a range of 0.94 – 1.10 Å and the average H – N – H angle is 110° with a range of 104 - 122° (Baur 1972). The observed N – H bond length is shorter than the average determined with neutron diffraction because hydrogen bond lengths tend to be shorter in structures determined using X-ray diffraction. It was found by Baur (1972) that observed O – H distances in X-ray determinations tend to be on average 0.2Å shorter than neutron diffraction. The H2 – N – H3 angle of 113° is very close to the average H – N – H angle (°). The N – H....O3 distance is 2.898Å and H...O3 distance is 2.26. The remainder of the structure is similar to the other members of the jarosite group.

As part of the ammoniojarosite – hydronium jarosite solid-solution study, the structure of end-member ammoniojarosite was refined using powder X-ray diffraction data collected at room temperature with Rietveld refinement. Unit cell dimension a of both sets of data are very similar (single-crystal a: 7.3177 Å, powder a: 7.3178 Å). Unit cell dimension c of the powder data is 0.074 Å larger than the single-crystal data (single-

crystal *c*: 17.534 Å, powder *c*: 17.609 Å). The difference can be attributed to the temperature difference during data collection, with the single data collected at liquid nitrogen temperature and the powder data collected at room temperature. From this it can be seen that at these temperatures an increase in temperature mainly effects cell dimension *c* and not *a*. The increase in temperature causes an increase in bond lengths N – H ...O2 and N – H ...O3 of 0.010 and 0.014 Å, respectively. The N – H ...O3 bond is largely along the *c* axis and N – H ...O2 has a component along the *c* axis. As the unit cell dimension of ammoniojarosite is much larger along *c* than *a*, a change in bond length parameters effects the *c* dimension to a larger degree. Additionally, the ammoniojarosite structure is more weakly bonded in the *c* dimension because the linking along the *c* axis is related to hydrogen bonding of O1...H1-O3, and the bifurcated hydrogen bond with H in the disordered NH⁴⁺ groups with O2 and O3 anions. These bonds produce a larger allowance in the *c* direction than rotation of the Fe octahedra or dilation of the Fe-O bonds along *a*.

The calculated intensities and positions of diffraction peaks for synthetic ammoniojarosite are listed in Table 4.5. It is improved from previous published diffraction patterns (Dutrizac and Kaiman 1976; Smith and Lampert 1973) as a result of the full occupancy of NH₄ in the A site, with no H₃O substitution. In reference pattern 026-1014 (Smith and Lampert 1973) of the ICDD data base (PDF – 2, 2001) there are a number of peaks that are shifted due to the hydronium content and others that were measured as one peak, where in the current study, two or more exist.

Solid-solution and structural dimensions

As hydronium is very common in the jarosite group of minerals and readily substitutes in the A site of natural and synthetic ammoniojarosite, the ammoniojarosite – hydronium jarosite series was examined with powder X-ray diffraction and Rietveld refinement. The data refinement details and unit cell dimensions are given in Table 4.6. The atomic coordinates and site occupancies are given in Table 4.7 and selected interatomic distances and angles are given in Table 4.8. Data for end-member hydronium jarosite is taken from Basciano and Peterson 2007.

There is a progressive change in unit cell dimensions for the $(NH_4)_1$. $_{x}H_{3}O_{x}Fe_{3}(SO_{4})_{2}(OH)_{6}$ solid-solution with increasing ammonium content. The unit cell dimensions a vs c are plotted in Figure 4.4. Data fall close to a straight line with a correlation coefficient of $r^2 = 0.98$. There is no H_3O^+ substitution in the A site of endmember ammoniojarosite, causing the unit cell dimension a to be smaller and c to be larger than synthetic ammoniojarosite samples grown by Dutrizac and Kaiman (1976) and Smith and Lampert (1973). The samples synthesized in these previous studies contain appreciable amounts of hydronium (9 and 20%, respectively) and plot between sample C and D from the current study. Unit cell dimensions vs. ammonium content for the synthetic ammonium - hydronium jarosite series is shown in Figure 4.5. With increasing ammonium content unit cell dimension a is reduced by a minor amount and unit cell dimension c increases to a larger degree. As in other jarosite group members, substitution in the A site mainly effects unit cell dimension c. End-member hydronium jarosite is non-stoichiometric with respect to hydronium with A site occupancy of 92% (Basciano and Peterson 2007). Unit cell parameter c is smaller than expected as a result of the A site deficiency.

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Unit cell dimensions of two natural ammoniojarosite samples are included in Figure 4.4. Sample M16514 from Utah has similar unit cell dimensions as the synthetic end-member ammoniojarosite. Sample M38446 plots to the left of the synthetic samples from this study. It was determined with SEM-EDS analysis that the sample contains a minor amount of Al in the B site, which causes a reduction in unit cell dimension a (Brophy et al. 1962). The sample has a similar *c* dimension to end-member ammoniojarosite, indicating that the A site is predominantly filled with ammonium with minor hydronium substitution. No other cations were found with SEM-EDS analysis in either sample that would substitute into either the A site or B site. Similar to findings in Basciano and Peterson (2007), natural samples of jarosite are often not B-site deficient due to slower growth conditions. Additionally, natural samples usually are close to endmember compositions or are zoned. Based on unit cell dimensions, both natural samples in this study are end-member ammoniojarosite with little hydronium substitution in the A site. Unit cell dimensions can be used quite reliably to determine substitution in the A and B sites of jarosite samples (Basciano and Peterson, in press).

Polyhedral bond lengths A – O2 and O3 and Fe – O2 and O3 of the synthetic samples are shown in Figure 4.6. Polyhedral bond lengths of the A and B site linearly vary according to occupancy. With ammonium substitution into hydronium jarosite, A – O3 increases and A – O2 decreases. Correspondingly, Fe – O3 remains relatively constant and Fe – O2 increases. The A – O2 bond distance for hydronium jarosite is smaller than the trend would indicate as a result of non-stoichiometry of the A site with 92% H₃O occupancy (Basciano and Peterson 2007). The difference in bond length between sample B (26% NH₄ occupancy) and sample E (100% NH₄ occupancy) is 0.046 Å. This is similar to the difference in the Fe – O2 bond lengths between sample B and E (0.049 Å). Substitutions in the A site mainly effect the Fe – O2 bond length. Substitution of NH₄ in the A site increases bond length A – O3 by 0.052 Å. The ionic diameter of H₃O⁺ is 1.52 Å (Dutrizac and Jambor 2000) and NH₄⁺ is 1.69 Å in 9-fold coordination (Khan and Baur 1972). In 12-fold coordination the diameter of NH₄⁺ is probably >1.69 Å (Altaner et al. 1988). Bond distances A – O3 and Fe – O2 are directed predominantly along the *c* axis. As NH⁴⁺ occupancy of the A site increases, its bonding contribution to O3 grows, which is compensated by slightly increasing the Fe – O2 distances. As the O2...H2 - N bond (A - O2) shortens, the H bonding contribution to O2 increases and is compensated by enlargement of the Fe - O2 and A – O3 bonds.

SWIR and FTIR

Short-wave infrared (SWIR) spectra for the synthetic $NH_4 - H_3O$ jarosite solidsolution series is shown in Figure 4.7. Data for hydronium jarosite taken from Basciano and Peterson (2007) is included for completeness. The spectra are typical of the jarosite structure and the transmittance bands have been assigned based on the assignments by Bishop and Murad (2005). In the $NH_4 - H_3O$ jarosite solid-solution series there is a change in spectra that can be tracked across the series. The distinct SWIR patterns for ammoniojarosite, hydronium jarosite and sodium/potassium jarosite (Basciano and Peterson 2007) can enable quick identification of the type of jarosite while in the field.

Fourier-transform infrared spectra for ammoniojarosite have been previously discussed by Frost et al. (2006), Ristić et al. (2005) and Musić et al. (1993). The spectra

obtained here are similar to those in the literature. The FTIR spectra for the ammoniojarosite – hydronium jarosite solid-solution series are shown in Figure 4.8. Band assignments for vibrational features are given in Table 4.9. Hydronium in the A site causes peak shifts as well as peak widening (3407 cm⁻¹) or elimination of peaks. Most notably, a sharp peak at 1423 cm⁻¹ is seen in ammoniojarosite and not hydronium jarosite. This peak is evident in sample B, which has 26% NH₄ and would probably be noted in samples with much less ammonium substitution, making it characteristic of ammonium-containing jarosite samples.

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	Starting solution compositions(g)		Analytical results - ICP-OES and ICP- MS		
Synthetic samples	(NH ₄) ₂ (SO ₄)	Fe ₂ (SO ₄) ₂ •xH ₂ O	Formula		
A*	0.0	40	(H ₃ O)Fe _{3.06} (SO ₄) ₂ (OH) ₆		
В	0.2	40	[(NH ₄) _{0.32} (H ₃ O) _{0.68}]Fe _{3.04} (SO ₄) ₂ (OH) ₆		
С	0.4	40	[(NH ₄) _{0.59} (H ₃ O) _{0.41}]Fe _{3.03} (SO ₄) ₂ (OH) ₆		
D	1.0	40	[(NH ₄) _{0.93} (H ₃ O) _{0.07}]Fe _{3.05} (SO ₄) ₂ (OH) ₆		
E ^ψ			(NH ₄) _{1.08} Fe _{3.10} (SO ₄) ₂ (OH) ₆		
* from Basciano and Peterson (2007)					
$^{\Psi}$ see text for sample synthesis					

Table 4.1. Chemical compositions of starting solutions and synthetic jarosite samples

IGG identification code	
Wavelength (Å)	0.71073
Crystal system	Hexagonal
Space group	<i>R</i> 3m
Unit-cell dimensions (Å)	a = 7.3177(3)
	c = 17.534(1)
Volume (Å ³)	813.15(8) `´
Z	3
Absorption coefficient (mm ⁻¹)	4.433
θ range for data collection (°)	3.42 to 28.08
Index ranges	-9 ≤ h ≤ 9
	-9 ≤ k ≤ 9
	-22 ≤ ≤ 22
Reflections collected	2978
Independent reflections	276
R(int)	0.0141
Completeness to $\theta = 28.08^{\circ}$	98.6%
Data/restraints/dimensions	276/1/32
Goodness-of-fit on F ²	1.242
Final R indices [I>20(I)	R1 = 0.0140
	wR2 = 0.0364
R indices (all data)	R1 = 0.0145
	WR2 = 0.068

Table 4.2.Ammoniojarosite: data collection andstructure refinement information for single-crystal data

Atom	Position	Х	у	Z	U_{eq}	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Fe	9d	0.1667	-0.1667	-0.1667	6(1)	5(1)	5(1)	8(1)	0(1)	0(1)	3(1)
S	6c	0	0	0.3059(1)	6(1)	6(1)	6(1)	6(1)	0	0	3(1)
01	6c	0	0	0.3891(1)	9(1)	11(1)	11(1)	7(1)	0	0	5(1)
02	18h	0.2231(1)	-0.2231(1)	-0.0564(1)	9(1)	11(1)	11(1)	9(1)	0(1)	0(1)	8(1)
O3	18h	0.1277(1)	-0.1277(1)	0.1371(1)	8(1)	6(1)	6(1)	11(1)	-1(1)	1(1)	3(1)
Ν	3a	0	0	0	10(1)	12(1)	12(1)	7(2)	0	0	6(1)
H1	18h	0.176(2)	-0.176(2)	0.118(2)	27(8)						
H2	18h	0.059(3)	0.119(6)	0.018(3)	27(8)						
H3	6c	0	0	-0.047(2)	27(8)						
Note: t	Note: the anisotropic displacement factor takes the form: $-2\pi^2[h^2a^{*2}U^{11}++2hka^{*}b^{*}U^{12}]$										

Table 4.3. Atom coordinates and anisotropic-displacement dimensions ($Å^2 \times 10^3$) for ammoniojarosite, determined by single-crystal refinement.

Fe - O3 x 4	1.9832(6)	O3 – H1	0.70(2)
Fe - O2 x 2	2.062(1)	H2O3	2.25(4)
Average	2.009		
-		O2 - Fe - O3 x 4	89.00(5)
S - 01	1.459(2)	O2 - Fe - O3 x 4	91.00(̀5)́
S - O2 x 3	1.486(1)	O3 - Fe - O3 x 2	89.98(8)
Average	1.479 ໌	O3 - Fe - O3 x 2	90.02(8)
N – 03	2 898(1)	01 - S - 02 x 3	109 97(6)
N – O2	2.9957(8)	O2 - S - O2 x 3	108.97(6)
		Average	109.47 `´
N – H2	0.82(3)	0	
N – H3	0.82(4)	H2 – N – H3	113(4)
Symmetry trans	formations used	to generate equivalent	atoms:
#1 x-y,x,-z #2	y,-x+y,-z #3 -x-	+y+1/3,-x-1/3,z-1/3	
#4 -y+1/3,x-y-1	/3,z-1/3 #5 -x+1	/3,-y-1/3,-z-1/3	
#6 -y-1/3,x-y-2/	3,z+1/3 #7 -x+y	+2/3,-x+1/3,z+1/3	
#8 x-1/3,y+1/3,z	z+1/3 #9 x+1/3,	y-1/3,z-1/3 #10 x,x-y,z	<u>,</u>

Table 4.4. Selected interatomic distances (Å) and angles (°) for ammoniojarosite, as determined by single-crystal diffraction

l/l _o	2θ(°)	$d_{(calc)}(Å)$	no.*	h	k	1
13.5	17.25	5.963	6	1	0	1
30.5	17.53	5.870	2	0	0	3
100.0	20.03	5.144	6	0	1	2
9.3	28.30	3.659	6	1	1	0
3.9	28.65	3.616	6	1	0	4
74.5	33.34	3.119	6	0	2	1
95.0	33.49	3.105	12	1	1	3
5.5	33.78	3.078	6	0	1	5
3.4	34.92	2.982	6	2	0	2
16.1	35.49	2.935	2	0	0	6
12.9	40.71	2.572	6	0	2	4
32.5	44.99	2.338	6	1	0	7
28.9	53.49	1.988	6	0	3	3
9.2	54.00	1.970	6	0	2	7
9.3	54.41	1.957	2	0	0	9
26.5	58.54	1.829	6	2	2	0
5.3	61.61	1.747	12	2	2	3
6.1	62.52	1.724	12	3	1	2
4.9	66.46	1.632	12	1	3	4
6.2	66.99	1.621	12	1	2	8
3.8	69.06	1.578	6	4	0	1
3.5	70.01	1.559	6	0	4	2
11.8	70.36	1.553	12	2	2	6
21.0	71.06	1.539	6	0	2	10
3.7	73.74	1.491	6	4	0	4
3.3	76.50	1.445	6	0	4	5
4.8	77.15	1.434	12	2	3	2
3.9	83.29	1.346	12	4	1	3
4.6	84.04	1.336	12	2	2	9
6.4	90.57	1.259	12	3	2	7
3.1	94.35	1.220	6	3	3	0
3.2	96.94	1.195	12	2	4	1
4.8	98.69	1.179	12	2	1	13
3.0	98.83	1.178	6	4	0	10

Table 4.5. Calculated powder - diffraction pattern of synthetic ammoniojarosite ($I/I_o \ge 3$; the ten strongest reflections are in bold)
ammonioja	arosite – hydro	onium jarosite i	R 3 m		
sample	Е	D	С	В	А
$NH_4\%$	100	93	59	32	0*
a(Å)	7.31780(8)	7.3226(1)	7.3293(2)	7.3431(1)	7.3552(2)
c(Å)	17.6094(2)	17.4990(3)	17.3584(4)	17.1595(4)	16.9945(4)
V(Å ³)	816.65(2)	812.60(2)	807.54(4)	801.30(4)	796.21(4)
R _p	2.744	5.689	6.104	7.165	3.571
R_{wp}	3.500	8.025	9.348	11.427	4.773
R _{exp}	3.104	4.811	4.349	4.457	3.882
S	1.128	1.668	2.150	2.564	1.230
D-W	0.848	0.383	0.238	0.174	0.691
R. R-natte	ern R weigt	nted-pattern R		$d S(=R_{m}/R_{m})$).Goodness

Table 4.6. Data collection and structure refinement details: Rietveld refinement of powder data

R_p: R-pattern, R_{wp}: weighted-pattern, R_{exp}: R-expected, S(=R_{wp}/R_{exp}):Goodness of fit (Young, 1993) D-W: Durbin-Watson *d*-statistic (Hill and Flack, 1987). * from Basciano and Peterson (2007)

Site	W	Х	у	Z	B (Å ²)	Occ.
Sample	e A*		*		· · ·	
H₃O	3a	0	0	0	3.4(5)	0.92(1)
Fe	9d	0.16667	-0.16667	-0.16667	1.99(8)	1
S	6c	0	0	0.3095(2)	0.9(1)	1
01	6c	0	0	0.3946(3)	2.6(3)	1
02	18h	0.2253(3)	-0.2253(3)	-0.0565(2)	1.5(2)	1
O3	18h	0.1279(2)	-0.1279(2)	0.1368(1)	0.5(1)	1
H1	18h	0.163(1)	-0.163(1)	0.100(1)	2	1
Sample	B					
Ν	3a	0	0	0	7.4(5)	0.32
H₃O	3a	0	0	0	7.4(5)	0.68
Fe	9d	0.16667	-0.16667	-0.16667	3.12(9)	1
S	6c	0	0	0.3088(3)	1.6(1)	1
01	6c	0	0	0.3969(6)	5.8(4)	1
02	18h	0.2268(3)	-0.2268(3)	-0.0582(3)	2.3(2)	1
O3	18h	0.1283(2)	-0.1283(2)	0.1363(2)	0.3(2)	1
H1	18h	0.170(2)	-0.170(2)	0.168(2)	2	1
H2 [™]	6c	0.059	0.119	0.018	2	0.16
H3 '	60	U	0	-0.047	2	0.16
Sample	2 C	0	0	0	2 2/4	0.50
IN	3a	U	U	U	3.3(4)	0.59
H₃O	3a	0	0	0	3.3(4)	0.41
Fe	9d	0.16667	-0.16667	-0.16667	2.19(6)	1
S	6c	0	0	0.3065(2)	1.12(9)	1
01	60	0	0	0.3923(4)	3.2(3)	1
02	18h	0.2259(2)	-0.2259(2)	-0.0577(2)	1.4(1)	1
03	18h	0.1291(2)	-0.1291(2)	0.1355(2)	0.2(2)	1
H1 μο ^Ψ	18h	0.152(1)	-0.152(1)	0.176(2)	2	1
H2 μ2Ψ	6C	0.059	0.119	0.018	2	0.30
H3 Semala	6C	U	U	-0.047	2	0.30
Sample	30	0	0	0	1 5/2)	0.02
	Sd	0	0	0	1.5(3)	0.93
H₃O F	3a	0	0	0	1.5(3)	0.07
Fe	9d	0.16667	-0.1667		1.65(5)	1
5	6C	U	U	0.3070(2)	0.96(8)	1
01	0C	U 0.0044(0)	0 2244(2)	0.3920(3)	1.2(2)	1
02		0.2244(2)	-0.2244(2)	-0.0573(2)	0.7(1)	1
U3	105	0.1309(2)	-0.1309(2)	0.1349(2)	0.3(1)	1
пι ⊔о ^Ψ	IQU	0.130(2)	-0.130(2)	0.178(1)	2	1
⊓∠ ⊔₂ ^Ψ	00 60	0.059	0.119	0.010	∠ 2	0.47
H3 ⁻	6c	0	0	-0.047	2	0.47

Table 4.7. Refined atomic positions, displacement parameters and occupancies of synthetic ammoniojarosite – hydronium jarosite samples as determined by powder X-ray diffraction and Rietveld refinement.

Sample	E					
Ν	3a	0	0	0	4.2(3)	1
H₃O	3a	0	0	0	4.2(3)	0
Fe	9d	0.16667	-0.16667	-0.16667	1.40(4)	1
S	6c	0	0	0.3051(1)	0.34(8)	1
01	6c	0	0	0.3897(2)	0.5(1)	1
02	18h	0.2235(2)	-0.2235(2)	-0.0571(1)	0.1(1)	1
O3	18h	0.12743(9)	-0.12743(9)	0.1376(1)	0.07(9)	1
H1	18h	0.1899(9)	-0.1899(9)	0.129(1)	2	1
$H2^{\Psi}$	6c	0.059	0.119	0.018	2	0.5
Η3 ^Ψ	6c	0	0	-0.047	2	0.5

* Data taken from Basciano and Peterson (2007)
^Ψ Atomic positions taken from single-crystal results, current study.
Note: numbers in parentheses in this and subsequent tables are estimated

standard deviations, A site occupancies determined with ICP-OES and ICP-MS

	E	D	С	В	A*
A site occ (%NH ₄)	100	93	59	32	0
A - O3 x 6	2.912(2)	2.886(2)	2.868(3)	2.852(3)	2.839(2)
A - O2 x 6	3.006(2)	3.017(2)	3.038(3)	3.052(4)	3.026(4)
Average	2.959	2.951	2.953	2.952	2.932
	4 000 4 (0)	o o o o o (o)	4 00=(4)	4 000(4)	
Fe - O3 x 4	1.9804(6)	2.0062(9)) 1.997(1)	1.992(1)	1.9904(9)
Fe - O2 x 2	2.060(2)	2.049(3)	2.035(4)	2.013(5)	2.015(4)
Average	2.007	2.020	2.010	1.999	1.999
S 01	4 400(4)	1 400(0)	1 404(0)	4 54(4)	4 4 4 7 (7)
5-01	1.490(4)	1.486(6)	1.491(8)	1.51(1)	1.447(7)
S - O2 x 3	1.482(2)	1.484(3)	1.465(3)	1.473(4)	1.485(4)
Average	1.484	1.484	1.471	1.482	1.476
02 - Fe - 03 x 4	89 32(7)	88 28(7)	89 35(9)	89 6(1)	89 6(1)
	00.02(7)	00.20(7)	00.00(0)	00.0(1)	00.0(1)
02 - Fe - 03 x 4	90.68(7)	91.72(7)	90.65(9)	90.4(1)	90.4(1)
O3 - Fe - O3 x 2	89.87(7)	88.4(1)	89.4(1)	89.6(2)	89.7(1)
O3 - Fe - O3 x 2	90.13(7)	91.6(1)	90.6(1)	90.4(2)	90.3(1)
	110 02/0)	111 1(2)	111 5/2)	112 1/2)	112 0/1)
01-3-02 x 3	110.03(9)	111.4(2)	111.5(2)	113.1(2)	112.0(1)
O2 - S - O2 x 3	108.91(9)	107.4(2)	107.4(2)	105.6(2)	106.9(2)
Average	109.47	109.4	109.4	109.3	109.5
03 – H	0.805(1)	0 754(2)	0 762(3)	0 758(3)	0 767(2)
03 H 01	2.000(1)	2 202(2)	2012(4)	2,901(4)	2.014(2)
05-1101	2.970(2)	2.095(2)	2.913(4)	2.091(4)	2.914(3)

Table 4.8. Selected interatomic distances (Å) and angles (°) of ammoniojarosite – hydronium jarosite solid-solution samples as determined by powder X-ray diffraction and Rietveld refinement.

* from Basciano and Peterson (2007)

NH ₄ jarosite	<u>H₃O jarosite</u>	Assignment
449	464 b	$v_2(SO_4)^{2-}$
464	-	Fe – O
495	503	Fe – O
573 sh	-	γ(OH)
624	623	V ₄ (SO ₄) ²⁻
871 sh	-	δ(OH)
987	1004	δ(OH)
~1012 sh vw	-	δ(OH)
1070	1089	$v_3(SO_4)^{2}$
1184	1195	$v_3(SO_4)^{2-}$
1423	-	$V_4(NH_4)$
-	1576 sh	δ(H ₂ O)
1647 vw	1639	$\delta(H_2O)$
1743	-	?
3207	-	v ₃ (NH ₄)
3320	-	$v_3(NH_4)$
3412	3367 b	v(OH)

Table 4.9. Band assignments for vibrational features in synthetic ammoniojarosite and hydronium jarosite

Notes: sh = shoulder, b = wide, vw = very weak. Band assignments are based on Altaner *et al.*, 1988, Bishop and Murad (2005) and Frost *et al.* (2005).



Figure 4.1. Rietveld refinement plot of sample E, ammoniojarosite. The grey line is the observed data and the solid line is the calculated pattern. The vertical bars mark all possible Bragg reflections ($CoK\alpha_1$ and $K\alpha_2$). The difference between the observed and calculated patterns is shown at the bottom.



Figure 4.2. Polyhedral representation of the ammoniojarosite structure (*ATOMS* 6.0, Dowty 2003). Sulfate tetrahedra are dark grey, iron octahedra are light grey, nitrogen atoms are dark grey spheres and positionally disordered hydrogen atoms are white spheres.



Figure 4.3. Polyhedral drawing showing the hydrogen bonding scheme of the ammonium groups in the A site of ammoniojarosite (*ATOMS* 6.0, Dowty 2003). Only one orientation of the ammonium group is shown for clarity. Iron octahedra are shown in light grey, sulfate tetrahedra are dark grey. The nitrogen atom is shown in dark grey; H1 are small dark grey spheres; H2 and H3 atoms are small white spheres (bonded to N). Hydrogen bonding is shown as thin lines.



- □ ROM M16514 Utah
- LI ROM M16514 Utah
- Figure 4.4. Unit cell parameters c vs a of synthetic NH₄ H₃O solid-solution series from the current study, synthetic samples from previous studies and natural ammoniojarosite samples. Samples from the current synthetic powder diffraction study are shown as black circles, samples from previous studies are shown in grey and natural samples are shown in white. Note that the unit cell dimension of ammoniojarosite from this study (far left sample, black circle) has a smaller a dimension and a larger c dimension than previously synthesized ammoniojarosite. This is due to no hydronium substitution in the A site. If any of the samples had iron deficiencies in the B site, the cell dimensions would have lower c cell parameters the samples synthesized in this study.



Figure 4.5. Unit cell dimensions a and c vs. ammonium occupancy in the A site. Increased NH₄ content leads to a larger c unit cell parameter. Error bars reported by Rietveld refinement are smaller than the symbols.



Figure 4.6. A – O polyhedra bond lengths and Fe – O octahedral bond lengths vs. A site occupancy the ammoniojarosite – hydronium jarosite solid-solution series. Polyhedra bond lengths of the A and B sites vary linearly with NH₄ occupancy in the A site. The A – O2 bond length for hydronium jarosite is smaller than the trend would indicate due to non-stoichiometry of the A site with 92% H₃O occupancy (Basciano and Peterson 2007).



Figure 4.7. Short-wave infrared (SWIR) spectra of samples from the NH₄ - H₃O jarosite solid-solution series. The bands have been assigned to the following: 1 (1460 nm) - OH vibration and H₂O absorption, 2 (1504 nm) - Fe-OH vibration, 4 (1854 nm) - Fe-OH vibration, 8 (2260 nm) – Fe-OH vibration, 9 (2288 nm) – Fe – OH vibration , and 10 (2396-2488 nm) - (SO₄)₂ stretching and OH vibration. Bands labeled 3 (1634 nm), 5 (1990 nm), 6 (2112 nm) and 7 (2186 nm) are attributed to NH₄ (Altaner et al. 1988). Band assignments for 1, 2, 4, 8, 9 and 10 were taken from Bishop and Murad (2005). Spectra have been offset for comparison.



Figure 4.8. Fourier transform infrared spectra of samples from the $NH_4 - H_3O$ jarosite solidsolution series. Band assignments are given in Table 4.9. Note the band at 1423 cm⁻¹, attributed to $v_4(NH_4)$, which can be useful method of determining the approximate amount of ammonium substituting into the jarosite structure.

Chapter 5: Crystallographic study of the incomplete solid-solution between plumbojarosite and jarosite

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Abstract

An incomplete solid-solution series exists between jarosite, $KFe_3(SO_4)_2(OH)_6$ and plumbojarosite, $Pb[Fe_3(SO_4)_2(OH)_6]_2$, based on experimental and mineralogical data. Samples were synthesized in a chloride-rich solution at 140°C and 110°C and analyzed using X-ray powder diffraction and Rietveld analysis. Under these conditions plumbojarosite will only precipitate with large amounts of Pb in the starting solution. The jarosite structure forms preferentially from solutions with up to 79 mol% Pb. Both the jarosite and plumbojarosite structure form from a solution with 85 mol% Pb. A single plumbojarosite phase formed in the solution containing 99 mol% Pb. At the studied synthesis conditions, Pb substitution in jarosite is extremely limited with occupancy of 2% in the K site. Increased Pb in the starting solution resulted in no increased substitution of Pb into jarosite, but an increased substitution of H_3O^+ . Substitution of Pb^{2+} is limited in the jarosite structure due to the difference in charge and size. An increase in charge in the A site causes a charge imbalance in the structure. Potassium substitution in plumbojarosite is more extensive. From Rietveld refinement, potassium substitution preferentially occurs in one of the two A sites. The majority of lead is located in A2, with much less in A1 and all of the potassium is located in A1. Both A

sites are partially vacant. Substitution of K in the plumbojarosite structure causes a slight increase in bond lengths of the A site, where K is located, due to the increased ionic size of K. There is also an increase in A2 bond lengths due to the partial vacancy.

Introduction

Plumbojarosite, Pb[Fe₃(SO₄)₂(OH)₆]₂, is primarily found in gossans, which overly massive sulfide deposits. Gossans are the residues of an intense acidic leaching, and are commonly enriched in some trace elements with respect to the original sulfide, such as Au, Ag, As and Pb. Gossan deposits are important because of their ability to fix potentially toxic elements such as Pb and As (Nieto et al. 2003). Plumbojarosite is often found closely associated with jarosite, KFe₃(SO₄)₂(OH)₆, in gossan deposits and in acid mine waste where lead is available for uptake (De Oliveira et al. 1996).

Plumbojarosite and jarosite are part of the jarosite group, which is part of the alunite supergroup. The alunite supergroup consists of over 40 different mineral species with the general formula of AB₃(TO₄)₂(OH)₆. There is extensive solid-solution in the A, B and T sites within the alunite supergroup, where A is H₃O⁺, Na⁺, K⁺, Rb⁺, Ag⁺, Tl⁺, NH⁴⁺, $\frac{1}{2}$ Ca²⁺ or $\frac{1}{2}$ Pb²⁺, B is Fe³⁺ or Al³⁺ and TO₄ is SO₄²⁻, PO₄³⁻ or AsO₄³⁻ (Scott 1987; Stoffregen and Alpers 1987). The jarosite group is characterized by B = Fe³⁺ and T = S. Jarosite (A = potassium) and natrojarosite (A = sodium) are the most prevalent naturally occurring jarosite group minerals. There is commonly substitution of hydronium in the A site of naturally occurring and synthetic jarosite group minerals, though end-member hydronium jarosite is quite rare.

Plumbojarosite was first described in 1902 as a species related to jarosite with a lead-rich composition (Hilebranad and Wright 1910). Plumbojarosite has been recognized as an economically important mineral as Ag commonly substitutes in the structure during oxidation of the original sulfide ore. The Pb and Ag content of

plumbojarosite have been large enough to be processed for Pb and Ag (Szymański 1985). The plumbojarosite structure was solved by Szymański (1985) using a natural sample from the Tintic Standard mine, Dividend, USA. The unit cell is doubled along the *c* axis of plumbojarosite as a result of divalent Pb^{2+} replacing univalent K⁺ in the jarosite structure. The doubling results in two crystallographically different cation positions and coordination polyhedra, which are half filled with Pb cations. The crystal structure of plumbojarosite showing the crystallographically distinct A sites is shown in Figure 5.1.

Three natural samples were analyzed along with the synthetic samples. Samples were supplied by CANMET, Natural Resources Canada, Ottawa, Canada. The first sample is from Apex Mine in Washington County, Utah. The second sample is from Chihuahua, Mexico and the third is from Rube Mine, Gold Hill, Utah.

The jarosite – plumbojarosite solid-solution series has been investigated in this study using synthetic samples of various compositions. The purpose of the study was to determine at what point in the solid-solution series the unit cell doubles to accommodate Pb²⁺ into the structure. A complete solid-solution series was not found as expected but a wide solvus between end-members was observed. Samples were characterized with powder X-ray diffraction, Rietveld refinement and chemical analysis.

Sample synthesis

Samples were synthesized in a chloride-rich medium, similar to Frost et al. (2005). The high chloride concentration eliminates PbSO₄ from precipitating with endmember plumbojarosite. Five ml of 1.23 M FeCl₃ solution and a 0.5g mixture of KCl and PbCl₂ were dissolved in 12 ml of concentrated LiCl solution. Six g of Fe(SO₄)₃• 5H₂O was dissolved in 25 ml deionized water and added to the chloride solution. Two sets of each starting solution were mixed and each was heated for 48 hours in a stainless steel pressure bomb at 140°C or 110°C. Samples were synthesized at two different temperatures to determine if there was a temperature dependence on the degree of substitution. The resulting powders are yellow and fine-grained and are either jarosite, plumbojarosite or a mixture of jarosite and plumbojarosite. A number of the samples also contained PbCl₂ or PbSO₄. The starting solutions, synthesis conditions and resulting solid phases are shown in Table 5.1. All of the samples were rinsed thoroughly before chemical analysis and data collection for Rietveld refinement to remove PbCl₂. The PbSO₄ has much lower solubility than PbCl and remained in the samples. The samples were filtered and then dried at 110°C.

In two previous studies of jarosite group minerals (Basciano and Peterson 2007; Basciano and Peterson, in press) it was found that there was peak broadening due to nonhomogeneity of the synthesized samples. The broadening was most evident in peaks where there is a large difference in peak position between end-member phases in the mixture (e.g. peak 006). When these samples were ground and re-heated in the reactant solution the samples became homogeneous. It was initially thought that the same behaviour would occur in the current study for samples that contained both jarosite and plumbojarosite. No peak broadening was noted in the samples; instead distinct peaks relating to either jarosite or plumbojarosite were seen. To ensure that the solid was in equilibrium with the solution, one sample was reheated in the original solution for 12 days at 140°C and analyzed with X-ray diffraction every 3 days to determine if any peak

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shifts occurred. The sample did not become homogeneous and remained the same after 12 days of annealing. From this it was determined that under these conditions jarosite and plumbojarosite are probably stable.

X-ray powder diffraction and Rietveld refinement

Powder-diffraction data were collected from 5°-100° 2 θ (Fe filtered CoKa radiation) from a back-packed sample using a PANalytical X'Pert theta-theta diffractometer and an X'celerator position-sensitive detector equipped with incident- and diffracted-beam soller slits, and $1/2^{\circ}$ divergence and 1° anti-scatter slits. The normalfocus Co X-ray tube was operated at 40 kV and 45 mA. Profiles were taken with a step interval of 0.008° 2 θ , and an effective counting time per step of 40 seconds. Data were refined with the Rietveld refinement program Topas Academic (Coelho 2004). Starting atomic parameters for jarosite and plumbojarosite were taken from Basciano and Peterson (2007) and Szymański (1985), respectively. The instrument parameters were modeled using a full axial divergence model defined by Cheary and Coelho (1998). CoK α source emission profiles were taken from Hölzer et al. (1997). Hydrogen positions (OH group) in jarosite samples were taken from the single crystal study of hydronium jarosite by Majzlan et al. (2004). Only unit cell parameters were refined for all samples except for Sample G. PbSO₄ was included in the model if needed to account for any PbSO₄ that precipitated from solution during synthesis.

Unit cell parameters were refined for all of the synthetic samples and natural samples. In addition, atomic positions and site occupancies and temperature factors were

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refined for Sample G (plumbojarosite with 32% potassium occupancy in the A site). Sample G was studied as there is no hydronium substitution in the A site. Hydrogen bond lengths were restrained to be 0.8 Å during the refinement. Displacement parameters of the oxygen atoms were set to equal each other and the displacement parameters of H were set to 2 and not refined. Final refinement gave the following agreement factors: $R_p = 4.975$, $R_{wp} = 6.759$, $R_{exp} = 4.080$ and Goodness of fit (Young 1993) = 1.656.

The X-ray diffraction patterns for jarosite and plumbojarosite are very similar and can be difficult to distinguish without high-quality data. Plumbojarosite does have an additional peak at d-spacing 11.25 Å due to the doubled unit cell dimension along c. When the sample consists of jarosite and plumbojarosite, subtle peak doubling due to the differences in unit cell dimensions can be noted.

Chemical Analysis

The iron, lead, potassium and sulfur content of the solid samples containing either jarosite or plumbojarosite were determined using a Varian Vista CCD Simultaneous ICP-OES at the Analytical Services Unit, Queen's University. The samples were digested in aqua regia and diluted for analysis. The average analytical accuracy and precision for each element is: Fe $\pm 2\%$, 4.1%; Pb $\pm 3\%$, 4.9%; K $\pm 5\%$, 4.7% and S $\pm 2\%$, 5.3%. From these data the stoichiometry of the alkali and iron sites were determined in the solid samples based on the ratio of alkali and iron to sulfur. The atomic % potassium, lead and iron in these sites were normalized to 2 sulfur atoms per chemical formula based on the

ideal chemical formula. The chemical compositions of synthetic samples are given in Table 5.2. Samples containing detectable jarosite and plumbojarosite or those with PbSO₄ were not chemically analyzed as potassium and lead content could not be accurately attributed to jarosite or plumbojarosite.

Results

Synthesis

At the synthesis temperatures (110 °C and 140°C) there is a solvus between jarosite and plumbojarosite. Jarosite and/or plumbojarosite precipitated in the synthesis experiments with no complete solid-solution between end-members. Synthesis conditions and the resulting solids are shown in Table 5.1. The mol% Pb in the starting solution vs the percent jarosite, plumbojarosite or PbSO₄ (as determined with Rietveld refinement) is show in Figure 5.2.

The starting solution must contain large amounts of PbSO₄ and very little K₂SO₄ for plumbojarosite to form with no jarosite. At 140°C and 110°C jarosite forms from a solution with up to79 mol% Pb. At 85 mol% Pb, jarosite and plumbojarosite both precipitated. The plumbojarosite structure crystallized in the solution containing 99 mol% Pb but not in the solution containing 95 mol% Pb, which contained a mixture of jarosite and plumbojarosite. At 79 mol% Pb, PbCl₂ crystallized out of solution as large white crystals with jarosite. At 85 mol% Pb, plumbojarosite formed with jarosite with no evidence of PbCl₂. Even though the mol% Pb is higher in the starting solution, PbCl did not form as the Pb is taken out of the solution with plumbojarosite. As the mol% Pb increased, PbSO₄ precipitated with the jarosite/plumbojarosite mixture. In samples containing both jarosite and plumbojarosite, only a finite amount of lead can be taken from solution by the plumbojarosite as there is limited substitution of Pb in the jarosite structure. The remaining lead must precipitate as PbSO₄ or PbCl₂. At 99 mol% Pb, plumbojarosite precipitated with no jarosite or PbSO₄. It is evident that at this concentration a sufficient amount of Pb is removed from solution by plumbojarosite. At 100 mol% Pb, plumbojarosite and minor PbCl₂ precipitated, due to excess Pb in solution.

Limited substitution in end-members jarosite and plumbojarosite

Unit cell parameters for jarosite and plumbojarosite are given in Table 5.3. Unit cell parameters a vs c are shown in Figure 5.3 showing the change in parameters with substitution. Samples have been categorized by synthesis temperature and whether jarosite and plumbojarosite precipitated independently or as a mixture. Unit cell parameter a shows very little change with K, Pb or H₃O substitution in the A site of jarosite and plumbojarosite. The total change in c in jarosite is 0.07 Å and in plumbojarosite it is 0.05 Å.

At the synthesis temperatures and conditions there is limited lead substitution in end-member jarosite. Chemical analysis and A site refinement of jarosite reveal that there is no Pb or H₃O substitution in Samples B or I and these samples are close to stoichiometric jarosite. A site occupancy of sample C is 91% K, 2% Pb, based on chemical analysis, and the remainder is assumed to be H₃O. A site occupancy of sample J is similar to sample C. Chemical analysis of samples that contain both jarosite and plumbojarosite was not done because substitution of K or Pb could not be attributed to the jarosite or plumbojarosite in the sample. Unit cell and A site occupancy refinement of samples D, E and F show that there is no substitution of Pb in the A site of jarosite. The increase in unit cell parameters seen is caused by substitution of H₃O. Details of the jarosite – hydronium jarosite solid-solution series can be found in Basciano and Peterson (2007).

Potassium substitution in plumbojarosite is more extensive than lead substitution in jarosite. Occupancy of the A site in end-member plumbojarosite (sample H) is 66% Pb by ICP-OES and the remainder is assumed to be 34% H₃O. A site occupancy of samples G and M are similar with G: 68% Pb and 32% K and M: 64% Pb, 26% K, 10% H₃O. As chemical analysis cannot be done on the remainder of the samples that contain both jarosite and plumbojarosite, it is assumed that the plumbojarosite in these samples contains K in the A site as opposed to H₃O. This is based on samples G and M, which were also synthesized with K available for uptake.

At synthesis temperature 140°C there is a progressive change in unit cell parameters of jarosite and plumbojarosite with increasing Pb content and decreasing K in the starting solution. As the Pb content of the starting solution increases unit cell parameter c of jarosite decreases due to increasing H₃O in the A site. This decrease also occurs in the samples where plumbojarosite precipitated as well. Unit cell parameter c of plumbojarosite increases with decreasing Pb and increasing K in the starting solution. This increase is caused by K substitution for Pb in the A site.

At synthesis temperature 110°C there is a similar trend in the jarosite series as that seen at 140°C. With increasing hydronium substitution in jarosite, unit cell

parameter c decreases. At 110°C there is little change in unit cell parameters in plumbojarosite with increased K in the starting solution. From this, it can be concluded that at 110°C less substitution of K occurs in plumbojarosite.

Unit cell parameters of three natural plumbojarosite samples were determined to compare with the synthetic samples. The unit cell parameters of the natural samples are included in Figure 5.3. Unit cell parameters were determined on the fine yellow powders using Rietveld refinement and the chemical analysis were done by CANMET, Natural Resources Canada, Ottawa, Canada. The natural samples from Apex Mine, Washington County, Utah and Rube Mine, Gold Hill, Utah have minor substitution and have unit cell parameters close to Sample G, grown in this study. Bulk composition of the Apex Mine sample is 14.0% Pb, 0.46% K, 0.16% Na, 26.23% Fe and 25.5% SO₄. Bulk composition of the Rube Mine sample is 17.48% Pb, 0.21% K, 0.30% Na, 0.29% Ag, 27.34% Fe, 0.10% Al and 26.17% SO₄. The sample from Chihuahua, Mexico has a bulk composition of 13.7% Pb, 2.00% K, 0.08% Na, 22.63% Fe and 22.32% SO₄. The sample from Chihuahua had minor gypsum and quartz mixed with the plumbojarosite sample, which were included in the refinement model. Due to the high acid insoluble content, the results are low for Fe and SO₄. The higher K content of this sample is reflected in the unit cell parameters. Unit cell c is larger than the samples synthesized in this study. There may be a small component of jarosite admixed in the sample based on the excess potassium measured during chemical analysis, though there are no obvious peaks that can be unquestionably attributed to jarosite. Due to the shift in cell parameters of the plumbojarosite and similarity of the plumbojarosite pattern to the jarosite pattern, jarosite could not be reliably added to the refinement. The increased amount of K substitution in

this natural sample than that achieved in the synthetic study is probably due to the slower growth conditions of the natural sample.

Crystal chemistry of K and H₃O substitution in plumbojarosite

The crystal structure of Sample G (plumbojarosite with 32% potassium A site occupancy) was determined using X-ray powder diffraction and Rietveld refinement. Sample G was chosen because it is a single phase, chemical analysis was done on the sample, and there is potassium substitution and no hydronium.

To determine if there is any ordering in sites A1 and A2, potassium occupancy was included in the refinement at (0, 0, 0) and (0, 0, 0.5), where lead is located. Pb1, Pb2, K1 and K2 were refined independently with no restrictions. It was found that no potassium is located at site (0, 0, 0.5) so this was removed from the refinement. Site occupancies of Pb1, Pb2 and K1 refined to 0.130(4), 0.547(4) and 0.371(4), respectively. Site occupancies of Pb1 and Pb2 add to 0.677. These values are very close to A site occupancies measured with ICP-OES, which are 68% Pb and 32% K. From these results it was concluded that there is ordering between A sites. The majority of lead is located in A2, with much less in A1, and all of the potassium is located in A1.

The refined structure of sample G is very similar to that of plumbojarosite, determined by Szymański (1985). The A1 polyhedra, which consist of Pb and K with the remainder vacant, have bond lengths of 2.896(8) and 2.913(8) Å. The Pb2 polyhedra, which are partially occupied by Pb and partially vacant, have bond lengths of 2.738(9) and 2.936(5) Å. It is expected that the site that contains potassium has longer bond

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lengths as K⁺ has a larger ionic radius than Pb²⁺. Both sites have some level of vacancy, which leads to longer bond lengths overall (Shannon 1976). The A1 polyhedra have marginally smaller bond lengths than those found by Szymański (1985) due to the higher occupancy. In the plumbojarosite structure solved by Szymański (1985), the Pb1 site is close to vacant, while Pb2 has close to fully occupancy by Pb. The Pb2 site in this study has slightly longer bond lengths than that of plumbojarosite due to partial occupancy.

The Fe atom is coordinated by four hydroxyl groups around the equatorial plane and two oxygen atoms in the axial positions. The Fe – O bond lengths are slightly shorter than those found by Szymański (1985) as there is partial occupancy in both A1 and A2 sites and K⁺ substitution in the A1 site. The lengthening in the A1 and A2 – O bond lengths causes a shortening in the Fe – O bond lengths.

Substitution of H_3O and K in plumbojarosite causes an increase in unit cell parameter *a* and *c*. The difference is more pronounced in the *c* direction, as is the case with substitution in the A site of other jarosite group members (Basciano and Peterson 2007).

Discussion

From chemical analysis and Rietveld refinement it was found under the synthesis conditions that there was essentially no substitution of Pb in the jarosite structure, but a substitution of H_3O instead. From this it can be concluded that for these synthesis conditions there is little substitution of Pb in the jarosite structure. From previous studies (Basciano and Peterson 2007, Nielson et al. 2007, Ripmeester et al. 1986; Drouet and Natrotsky 2003; Majzlan et al. 2004) it is known that there is extensive substitution of H_3O for K in jarosite. As K decreased in the starting solution there was less K available for substitution and H_3O substitution occurred, similar to results found by Basciano and Peterson (2007). Potassium is preferentially taken into the jarosite structure due to the marked difference in solubilities of jarosite over hydronium jarosite. Substitution of Pb²⁺ is extremely limited in jarosite due the difference in charge and size. An increase in charge in the A site causes a charge imbalance in the structure, resulting in a doubling of unit cell parameter *c*.

There is extensive substitution of K and H_3O in the plumbojarosite structure. The plumbojarosite synthesized in this study has 34% H_3O occupancy in the A site. In samples G and M where there was very little potassium added to the starting solution, samples have substantial K substitution in the A site. As is the case in jarosite, potassium is preferentially taken into the structure over hydronium (Basciano and Peterson 2007). As K^+ and H_3O^+ are univalent, substitution into the plumbojarosite structure is probably charge balanced in a similar fashion to that of hydronium jarosite that has vacancies in the A site. Charge neutrality is probably maintained by protonation of OH⁻ to form H_2O , which was proposed by Kubisz (1970) and Wills and Harrison (1996) for deficiencies in the B site in jarosite and alunite group structures.

Other structures in the alunite supergroup that have substitution of Pb^{2+} in the A site and no doubling of the unit cell must compensate for the charge discrepancy with different methods. In beudantite, $PbFe_3(SO_4)(AsO_4)(OH)_6$, which is part of the crandallite group (Jambor 1999), the Pb^{2+} is compensated by partial occupancy of As^{5+} in the T site. There is limited substitution of As in jarosite (Savage et al. 2005), but there is

a complete solid-solution between jarosite and beudantite (Scott 1987). There is a progressive substitution of trivalent for divalent anions in TO₄, which is accompanied with a concurrent change from monvalent to divalent cations in A sites. This progression most likely continues to form segnitite, $PbFe_3(AsO_4)_2(OH_6)$.

Evidence of an incomplete solid-solution between jarosite and plumbojarosite is noted in previous studies done on natural samples. Szymański (1985), who solved the crystal structure of plumbojarosite using a natural sample, noted that the single crystal used for the study had a rim of plumbojarosite and a small core of jarosite. The jarosite core has minor Pb substitution (wt%: 7.0 K, 1.2 Pb, 32.7 Fe and 12.9 S) and the rim of plumbojarosite shows no K substitution (wt%: 0.0 K, 18.4 Pb, 29.5 Fe and 11.7 S). They note in that study that Jambor and Dutrizac (1983) examined many samples from that locality (Tintic Standard mine, Dividend, USA) and found that the majority showed compositional zoning (jarosite core with a plumbojarosite rim).

De Oliveira et al. (1996) looked at natural samples from gossans related to the Pb-Zn mineralization in the Canoas district; they found many of the samples are distinctly zoned with close to end-member jarosite or plumbojarosite. A number of the samples have mid-point chemistry between jarosite and plumbojarosite, and probably have the plumbojarosite structure with potassium substitution in the A site. None of the samples were examined in detail with X-ray diffraction.

From this study and previous studies it can be concluded that there is limited Pb^{2+} substitution in the jarosite structure. There is extensive substitution of univalent cations in the plumbojarosite structure, which can maintain charge balance by converting OH⁻ groups to H₂O.

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Starting solution	K ₂ SO ₄	0.5	0.4	0.25	0.2	0.15	0.08	0.02	0.0
composition (g)	PbSO ₄	0.0	0.1	0.25	0.3	0.35	0.42	0.48	0.5
Mol% Pb		0	48	79	85	90	95	99	100
Sample name	140°C	Α	B	С	D	Ε	F	G	Н
		jar	jar	jar, PbCl ₂	jar, Pb jar	jar, Pb jar	jar, Pb jar,	Pb jar	Pb jar, PbCl ₂
							PbSO ₄		
Sample name	110°C	-	Ι	J	-	K	L	Μ	-
		-	jar	jar, PbCl ₂	-	jar, Pb jar	jar, Pb jar	Pb jar	-
						PbSO ₄	PbSO ₄		

Table 5.1. Chemical compositions of starting solutions and resulting solid

Note: jar = jarosite, Pb jar = plumbojarosite, synthesis conditions in text.

	Analytical results (ICP-OES)
Sample	Formula
A*	$(K_{0.95}H_3O_{0.05})Fe_{2.87}(SO_4)_2(OH)_6$
В	$(K_{0.99}H_3O_{0.01})Fe_{2.96}(SO_4)_2(OH)_6$
С	$(K_{0.91}Pb_{0.02}H_3O_{0.07})Fe_{2.95}(SO_4)_2(OH)_6$
G	$(Pb_{0.68}K_{0.32})[Fe_{2.95}(SO_4)_2(OH)_6]_2$
Н	$(Pb_{0.66}H_{3}O_{0.35})[Fe_{3.01}(SO_{4})_{2}(OH)_{6}]_{2}$
I	$(K_{0.99}H_3O_{0.01})Fe_{2.97}(SO_4)_2(OH)_6$
J	$(K_{0.92}Pb_{0.01}H_3O_{0.14})[Fe_{3.08}(SO_4)_2(OH)_6]_2$
Μ	$(Pb_{0.64}K_{0.26}H_3O_{0.10})[Fe_{3.00}(SO_4)_2(OH)_6]_2$
* Data ta	ken from Basciano and Peterson, 2007

Table 5.2: Chemical compositions of synthetic jarosite and plumbojarosite samples

Sample	a (Å)	c (Å)
Plumbojarosite -	7.3055(7)	33.675(2)
Szymański, 1985		
A* – jarosite	7.30293(8)	17.2043(2)
B – jarosite	7.3072(1)	17.2099(3)
C – jarosite	7.3089(1)	17.1930(3)
D – jarosite	7.3110(2)	17.1764(4)
D – plumbojarosite	7.3173(5)	33.770(2)
E – plumbojarosite	7.3151(2)	17.1504(6)
E – plumbojarosite	7.3160(2)	33.740(1)
F – jarosite	7.3156(3)	17.1439(8)
F – plumbojarosite	7.3168(2)	33.741(1)
G – plumbojarosite	7.3185(2)	33.7274(8)
H – plumbojarosite	7.3199(2)	33.7116(8)
I – jarosite	7.3046(1)	17.2120(3)
J – jarosite	7.3107(1)	17.1902(3)
K – jarosite	7.3142(2)	17.1605(5)
K – plumbojarosite	7.3166(2)	33.717(1)
L – jarosite	7.3174(2)	17.1333(7)
L – plumbojarosite	7.3190(2)	33.715(1)
M – plumbojarosite	7.3186(2)	33.706(1)

Table 5.3. Unit cell parameters of synthetic samples, determined by Rietveld refinement

* Data from Basciano and Peterson, 2007

Site	W	х	У	Z	В	Ν
Pb1	3b	0	0	0	0.8(5)	0.130(4
K1	3b	0	0	0	0.5(8)	0.371(4
S1	6c	0	0	0.1549(3)	1.3(3)	1
01	6c	0	0	0.1987(5)	2.2(1)	1
02	18h	0.2182(6)	2x	0.0270(3)	2.2(1)	1
O3	18h	0.1226(6)	2x	-0.0725(2)	2.2(1)	1
H1	18h	0.141(3)	2x	-0.051(1)	2	1
Pb2	3a	0	0	0.5	3.1(2)	0.547(4
S2	6c	0	0	0.6546(2)	3.2(4)	1
O4	6c	0	0	0.6981(3)	2.2(1)	1
05	18h	0.2212(6)	2x	0.5258(3)	2.2(1)	1
O6	18h	0.1312(6)	2x	0.4355(3)	2.2(1)	1
H2	18h	0.189(3)	2x	0.444(1)	2	1
Fo	18h	0 1677(4)	2x	0.0830(2)	1.7(1)	1

Table 5.4. Refined atomic positions, displacement dimensions and occupancies of synthetic sample G – plumbojarosite with 16% K substitution in the A site
A1* - O3 x 6	2.896(8)	Pb2 - O6 x 6	2.738(9)
A1* - O2 x 6	2.913(8)	Pb2 - O5 x 6	2.936(5)
Average	2.904		2.837
04 04	4.47(0)	00.04	4 47(4)
51-01	1.47(2)	S2 - 04	1.47(1)
S1 - O5 x 3	1.498(9)	S2 - O2 x 3	1.543(9)
Average	1.491	Average	1.524
O1 - S1 - O5 x 3	108.4(3)	O4 - S2 - O2 x 3	109.1(5)
O5 - S1 - O5 x 3	110.5(5)	O2 - S2 - O2 x 3	109.9(5)
Average	109.4	Average	109.5
F- 000	4 000(5)	00.114	0.75(5)
Fe - 03 x 2	1.938(5)	O3 - H1	0.75(5)
Fe - O2	1.99(1)	O3 - H1 … O4	2.528(2)
Fe - O6 x 2	2.025(4)		
Fe - O5	2.07(1)	O6 - H2	0.79(4)
Average	2.00	O6 - H2 ··· O3	2.69(3)
* A1 = Pb and K			

Table 5.5. Selected interatomic distances (Å) and angles (°) of Sample G (plumbojarosite with 32% K occupancy in the A site) as determined by powder X-ray diffraction and Rietveld refinement.



Figure 5.1. Polyhedral representation of the plumbojarosite structure. Sulfate tetrahedra are dark grey, iron octahedra are light grey, lead atoms are grey and white spheres and hydrogen atoms are white spheres. The lead occupies two crystallographically distinct cation positions, resulting in a doubling of the unit cell along c compared to other jarosite group minerals.



Figure 5.2 Mol% Pb in starting solution vs % jarosite, plumbojarosite and $PbSO_4$ in the final washed synthesized product.



Figure 5.3. Unit cell parameters a vs c of synthetic jarosite and plumbojarosite samples from the current study and three natural plumbojarosite samples. The change in unit cell parameters as a result of K or Pb substitution can be seen across the series.

Chapter 6: Preliminary investigation of hydronium jarosite – water hydrogen isotope fractionation

Abstract

The stable isotope (H and O) geochemistry of hydronium jarosite, (H₃O,K)Fe₃(SO₄)₂(O,OH)6, and the effect that the presence of hydronium in the crystal structure has on exchange rates of stable isotope values of jarosite with hydronium substitution has been investigated in this study. Hydronium (H₃O⁺) commonly substitutes into the A site of jarosite, (K,H₃O)Fe₃(SO₄)₂(O,OH)₆, increasing the number of oxygen and hydrogen atoms in the structure. Preliminary δ D values have been measured from samples of synthetic hydronium jarosite and potassium jarosite with hydronium substitution. Additionally, controlled isotopic exchange experiments were done using hydronium jarosite. It was found that hydronium substitution does influence δ D values significantly. Additionally, it was found that H exchanges readily in air and water at room temperature.

Introduction

Jarosite, $KFe_3(SO_4)_2(OH)_6$ is common in high-sulfate acid environments generated through the oxidation of sulfides in the supergene environment. End-member hydronium jarosite, $(H_3O)Fe_3(SO_4)_2(OH)_6$, is rare, but partial H_3O substitution of K in jarosite is relatively common (Ripmeester et al. 1986; Drouet and Natrotsky 2003; Majzlan et al. 2004). A number of previous studies have investigated the stable isotope geochemistry of jarosite and alunite (Rye and Stoffregen, 1995; Rye and Alpers, 1997; Stoffregen et al. 1994; Wasserman et al. 1992).

The stable isotope semantics of alunite and jarosite are informative as there are four stable isotope sites that can be analyzed, δ^{34} S from the SO₄ site, δ^{18} O from the SO₄ and OH sites, and δ D from the OH site (Rye et al. 1992; Rye and Alpers 1997). In hydronium jarosite δ^{18} O and δ D can be analyzed from the H₃O group. The jarosite and alunite have unique stable isotope characteristics based on the environment of formation (Seal et al. 2000). In supergene alunite and jarosite, the sulfur and oxygen in the sulfate group are indicative of the oxidation of the original sulfide mineral (such as pyrite) and reflect disequilibrium reactions (Seal et al. 2000). The stable isotope values of the oxygen and hydrogen of the OH group result from the waters associated with oxidation. Expected isotopic values for jarosite and alunite compositions were defined by Rye et al. (1992) and Rye and Alpers (1997) as the supergene alunite SO₄ field (SASF), a supergene SO₄ field (SJSF), a supergene alunite OH zone (SAOZ) and a supergene jarosite OH field (SJOZ).

Stoffregen et al. (1994) found that oxygen isotope exchange between alunite and water occurs by dissolution-reprecipitation at rates one to three orders of magnitude faster with alkali exchange than without. They also noted that K/Na substitutions in alunite have negligible effect on oxygen isotope fractionation in the SO₄ group at 350 to 450°C. As sulfate-water oxygen isotope exchange is very slow, aqueous sulfate should preserve a record of the sources of oxygen from which the oxygen originated in the precipitated alunite or jarosite.

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None of the previous studies have addressed the effect of hydronium substitution on the stable isotope composition of natural jarosite samples. Rye and Alpers (1997) did note in their isotopic study that jarosite samples must be heated before analysis to outgas any possible hydronium that had substituted into the structure. The effect of hydronium substitution for potassium in jarosite increases the number of oxygen isotope sites from two (sulfate group and a hydroxyl group) to three, and the hydrogen sites from one to two. The isotopic composition of all can potentially be determined separately. Techniques for stable isotope analysis are presented in Wasserman et al. (1992).

As δD_{OH} and $\delta^{18}O_{OH}$ values can be used to investigate the isotopic composition of the fluid from which the jarosite precipitated (Rye and Stoffregan 1995; Rye et al. 1992), H₃O substitution in the jarosite structure significantly alters the predicted $\delta D_{jarosite}$ of potassium jarosite. Thus, isotopic fractionation of hydrogen and oxygen between water and the hydronium ion substituted into the K-site in jarosite needs to be modeled in order to interpret isotopic results of H₃O-bearing jarosite samples unless all of the H₃O is driven off by heating before analysis. As the H₃O group exchanges differently than the OH group isotopic fractionation of O and H of the H₃O group increases the information about the formation and equilibration of the jarosite.

In this study preliminary data were collected in the determination of δD for synthetic (H₃O)Fe₃(SO₄)₂(OH)₆, (H₃O)_{0.5}K_{0.5}Fe₃(SO₄)₂(OH)₆, and K_{0.85}(H₃O)_{0.15}Fe₃(SO₄)₂(OH)₆. These compositions are based on previous work done by Basciano and Peterson (2007). Additionally δD values were determined for several synthetic samples of hydronium jarosite after undergoing isotopic exchange.

Experimental Methods

The samples were synthesized using the method of Basciano and Peterson (2007). Forty grams of $Fe_2(SO_4)_3 \cdot xH_2O$ and varying amounts of K_2SO_4 were mixed with deionized water of varying hydrogen isotopic compositions (discussed below), to a volume of 100 ml. The samples were heated in polypropylene containers inside stainlesssteel bombs at 140°C for 48 hours. The bombs were quenched and the reaction fluid was decanted off and the resultant fine-grained amber powder was rinsed, filtered and airdried. The solid samples were analyzed for δD within hours of drying to ensure that no exchange occurred before analysis.

Two waters were used during synthesis. Water A is deionized water ($\delta D = -61\%$) and water B is deionized water spiked with D₂O ($\delta D = +92\%$). Water B was used to synthesize (H₃O)Fe₃(SO₄)₂(OH)₆, (H₃O)_{0.5}K_{0.5}Fe₃(SO₄)₂(OH)₆, and K_{0.85}(H₃O)_{0.15}Fe₃(SO₄)₂(OH)₆. End-member potassium jarosite was not synthesized because a two-step method must be used to create a sample with full potassium occupancy in the alkali site (Basciano and Peterson, 2007). Waters A and B were used to synthesize the hydronium jarosite used for exchange experiments. The preliminary results determined in this study will be extrapolated to end-member potassium jarosite. All samples in this study were analyzed with X-ray diffraction to confirm that a single phase of homogeneous composition was created for each jarosite composition.

The resulting decanted liquid from the synthesis of hydronium jarosite grown in water A and B were used for exchange experiments instead of water as jarosite is not stable at 140°C and will convert to hematite. Hydronium jarosite grown in water A was

exchanged with the synthesis liquid of jarosite B, and hydronium jarosite B was exchanged with the synthesis liquid of jarosite A. One gram sub-samples were exchanged at 140°C for 3 days in approximately 80 ml of fluid.

Samples of hydronium jarosite synthesized with water B were left to exchange in air and deionized water for 60 days at 20°C. All of the samples used for exchange experiments were finely ground by hand with a mortar and pestle before exchange.

Samples were analyzed for hydrogen at the Queen's University Facility for Isotope Research (QFIR) on a TCEA coupled to a Thermo Finnigan Delta Plus XP. Hydrogen isotopic compositions are reported in units of ‰ relative to standard mean ocean water (SMOW).

Preliminary Results

The preliminary results are shown in Table 6.1. The three samples from the hydronium jarosite – potassium jarosite solid-solution series grown in water B show a trend of increasing δD values with increasing potassium content. δD values for $(H_3O)Fe_3(SO_4)_2(OH)_6$, $(H_3O)_{0.5}K_{0.5}Fe_3(SO_4)_2(OH)_6$, and $K_{0.85}(H_3O)_{0.15}Fe_3(SO_4)_2(OH)_6$ are -59 ‰, +15 ‰ and +40 ‰ respectively. The trend can be extrapolated for end-member potassium jarosite. From these results it can be seen that substitution of hydronium in the A site of potassium jarosite does significantly effect the δD value.

Hydronium jarosite grown in waters A and B resulted in samples with δD of -133 ‰ and -56 ‰, respectively. Exchange occurred readily in the synthesis solution at 140°C. Hydronium jarosite grown in water B was left at room temperature in water A and in air for 60 days. Both showed exchange with the sample left in air with a δD of -103 ‰ and the sample in water A with a δD of -86 ‰.

These results strongly imply that hydronium in the A site of naturally occurring potassium jarosite could result in erroneous isotopic values, as isotopic exchange has been shown to occurs readily at low temperatures with both air and water.

Suggested Future Work

Future work could include measuring δ^{18} O values in all of the liquid and solid samples. The time used for the exchange experiments should be increased to allow the isotopic values to more closely approach equilibrium. The exchange between H₃O and OH at 140°C between the samples of hydronium jarosite grown in waters A and B should be extended to determine the hydrogen and oxygen – isotope fractionation factors. The isotopic value of hydrogen and oxygen of hydronium in hydronium jarosite will be determined by driving off the hydronium but not the hydroxyl group or sulfate group by heating the sample. The difference in the isotopic values determined for jarosite for which the hydronium has not been driven off and the samples that have been heated to remove the hydronium will determine the difference in fractionation. The fractionation factor of hydrogen and oxygen for hydronium jarosite will be determined from the experimental data after a complete data set is completed.

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Waters and synthesis products	Hydronium jarosite B after exchange		
Water A	-61	Water B (140°C)	-36
Water B	+92	Water A (140°C)	-121
Hydronium jarosite (A)	-133	Air	-103
Hydronium jarosite (B)	-56	Water A (20°C)	-86
$(H_3O)_{0.5}K_{0.5}Fe_3(SO_4)_2(OH)_6(B)$	15		
$K_{0.85}(H_3O)_{0.15}Fe_3(SO_4)_2(OH)_6$ (B)	40		

Table 6.1 δD values of jarosites and waters (in ‰)

Chapter 7: General Conclusion

Jarosite group minerals are common in many different geological environments and are thought to exist on the surface of Mars. The goal of this study was to look carefully at how synthetic minerals in this group adjust to changes in chemical composition for the commonly observed end-members. By studying carefully synthesized minerals in different solid solution series it allows us to recognize the properties of more complex natural samples and interpret natural assemblages and processes. The complete solid solution series between the most common jarosite group members, potassium jarosite, natrojarosite and hydronium jarosite are described in Chapters 2 and 3. The samples were synthesized and analyzed by X-ray diffraction, Rietveld analysis, chemical analysis, SWIR and MIR spectroscopy. The samples synthesized in this study have full iron occupancy and the samples in the Na - K jarosite series have no hydronium substitution, making the unit cell parameters significantly different than those reported in the majority of previous studies. The samples are very well characterized and as a result these data will be a useful guide in future studies to determine the composition of natural samples.

The crystal structure of ammoniojarosite has been solved and the solid solution between ammoniojarosite and hydronium jarosite is examined using X-ray diffraction, Rietveld analysis, chemical analysis, SWIR and MIR spectroscopy (Chapter 4). The unit cell dimensions of the synthetic ammoniojarosite are larger than those synthesized in previous studies as a result of full iron occupancy and no hydronium substitution in the A site. Hydrogen positions of the OH and NH₄ groups were determined. In Chapter 5, the incomplete solid solution between jarosite and plumbojarosite is discussed. At the studied synthesis conditions, lead substitution in jarosite is extremely limited while potassium substitution in plumbojarosite is more extensive. Jarosite and plumbojarosite are often found closely associated in nature and it was assumed that there was a complete solid solution series between end-members. It was found during the course of synthesizing the samples that plumbojarosite will only precipitate with large amounts of lead in the starting solution. The jarosite structure will preferentially form over plumbojarosite.

Preliminary isotopic data on hydronium jarosite was collected and is discussed in Chapter 6. Stable isotope data for hydronium jarosite has not been determined previously and as hydronium readily substitutes for potassium in the jarosite structure, hydronium greatly effects stable isotope values of jarosite with hydronium substitution.

As jarosite is an important mineral group in mineralogical and geological sciences the data presented in this thesis provides basic information that can be used to understand more complex natural processes. The characterization of the three most common minerals in the jarosite group, (potassium) jarosite, natrojarosite and hydronium jarosite, is vital for accurate characterization and further research in the jarosite group of minerals. The Mars Science Laboratory scheduled to launch in October of 2009 will have an X-ray diffractometer on board as a payload instrument. If jarosite is observed, as expected, in sediments on the Martian surface, the results of this thesis will be directly applicable to the interpretation of the diffraction data created by this NASA mission.

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Appendix A Analytical procedure – additional detail

Synthesis

Details of individual syntheses can be found within the text of the thesis. The temperature of 140°C was chosen for the majority of the syntheses as a higher temperature is optimal to achieve full iron occupancy in the A site. A higher temperature was not used due to physical and chemical limitations. The polypropylene containers slumped slightly at 140°C and failed beyond this temperature. Additionally, at higher temperatures iron oxide formed in addition to jarosite group minerals. After heating, the bombs were cooled over approximately 4 hours at room temperature.

Chemical Analysis

All of the samples were digested in *aqua regia*, which was a mixture of HCl and H_2SO_4 . As iron and A site occupancies of the jarosite samples can be less than ideal, chemical formulas were determined based on 2S per formula unit. In a number of the samples, iron occupancy is more than 3 per formula unit. This may be caused by the assumption that the occupancy of S is 2.