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Synthesis and properties of ternary (K, NH_4, H_3O)-jarosites precipitated from *Acidithiobacillus ferrooxidans* cultures in simulated bioleaching solutions

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ABSTRACT

The purpose of this study was to synthesize a series of solid solution jarosites by biological oxidation of ferrous iron at pH 2.2–4.4 and ambient temperature in media containing mixtures of K^+ (0, 1, 4, 6, 12, 31 mM) and NH_4^+ (6.1, 80, 160, 320 mM). The starting material was a liquid medium for *Acidithiobacillus ferrooxidans* comprised of 120 mM $FeSO_4$ solution and mineral salts at pH 2.2. Following inoculation with *A. ferrooxidans*, the cultures were incubated in shake flasks at 22 °C. As bacteria oxidized ferrous iron, ferric iron hydrolyzed and precipitated as jarosite-group minerals ($AFe_3(SO_4)_2(OH)_6$) and/or schwertmannite (idealized formula $Fe_8O_8(OH)_6(SO_4)\cdot nH_2O$). The precipitates were characterized by X-ray diffraction (XRD), elemental analysis, and Munsell color. Schwertmannite was the dominant mineral product at low combinations of K^+ ($\leq$4 mM) and NH_4^+ ($\leq$80 mM) in the media. At higher single or combined concentrations, yellowish jarosite phases were produced, and Munsell hue provided a sensitive means of detecting minor schwertmannite in the oxidation products. Although the hydrated ionic radii of K^+ and NH_4^+ are similar, K^+ greatly facilitated the formation of a jarosite phase compared to NH_4^+. Unit cell and cell volume calculations from refinements of the powder XRD patterns indicated that the jarosite phases produced were mostly ternary (K, NH_4, H_3O)-solid solutions that were also deficient in structural Fe, especially at low NH_4 contents. Thus, ferric iron precipitation from the simulated bioleaching systems yielded solid solutions of jarosite with chemical compositions that were dependent on the relative concentrations of K^+ and NH_4^+ in the synthesis media. No phase separations involving discrete, end-member K-jarosite or NH_4-jarosite were detected in the un-aged precipitates.

1. Introduction

Fe(III)-hydroxysulfate minerals are formed in biological leaching systems where acidophilic acidithiobacilli oxidize Fe^{2+} and Fe-sulfides as their energy sources. These microorganisms help maintain high Fe^{3+}/Fe^{2+} ratios in bioleaching solutions and thus produce conditions favorable for ferric iron-mediated oxidation of sulfide minerals [1,2]. Under appropriate environmental conditions, Fe(III)-hydroxysulfates, such as schwertmannite (idealized formula $Fe_8O_8(OH)_6(SO_4)\cdot nH_2O$) and the jarosite-group minerals ($AFe_3(SO_4)_2(OH)_6$), are common solid phase products of ferrous iron oxidation [3,4]. The specific phases produced and their properties depend on the concentrations of ferric iron, sulfate, and alkali cations as well as temperature, contact time, and pH [3–6]. Jarosite-group minerals are commonly precipitated from sulfate-rich waters in the pH range of 1–3 [7], whereas schwertmannite is more prevalent at somewhat higher pH values of 3–4 [8–10]. Schwertmannite synthesis at lower pH has previously been demonstrated in situations where alkali cation concentrations were inadequate for the formation of more ordered phases [11].

The direct formation of schwertmannite (log K_{sp} −18.0) by precipitation from ambient iron- and sulfate-rich systems is an acid-producing reaction described by:

$$8Fe^{3+} + SO_4^{2-} + 14H_2O \rightarrow Fe_8O_8(OH)_6SO_4 + 22H^+. \quad (1)$$

Schwertmannite may also be a precursor to jarosite mineral formation in acidic, sulfate-rich environments provided a suitable cation is available to occupy the “A” site in the jarosite structure. The transformation has been reported in laboratory systems as well as sediments impacted by acidic mine water discharge [12,13]. In bioleach solutions and liquid media for iron-oxidizing microorganisms, the dominant monovalent cations are usually K^+, NH_4^+, and Na^+, in addition to universally present H_3O^+, but some other monovalent as well as divalent cations (e.g., Ag^+, Pb^{2+}, Cu^{2+}, Ni^{2+} and Hg^{2+}) may also be present and can incorporate into the jarosite matrix [14–16].

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In bioleaching systems, one important role for bacteria is the oxidation of Fe^{2+} to Fe^{3+} because ferric iron is a chemical oxidant of sulfide minerals.

$$4Fe^{2+} + 4H^{+} + O_2 \rightarrow 4Fe^{3+} + 2H_2O. \tag{2}$$

Bacterial oxidation of Fe^{2+} also precedes the precipitation of Fe(III) as hydroxysulfate minerals in sulfate-rich solutions. Iron-oxidizing bacteria in bioleaching systems and acid mine drainage include *Acidithiobacillus ferrooxidans* and *Leptospirillum* spp. [1,2]. In general, iron biomineralization is believed to involve bacterial cell surfaces serving as nuclei for initial crystal growth [17], with exopolysacccharides promoting Fe(III) deposition on cell surfaces. Although cell surface-facilitated nucleation and crystal growth has been demonstrated with poorly crystalline phases, such as schwertmannite, it has yet to be documented specifically for biogenic jarosites.

The solubilities of jarosites are limited in iron- and sulfate-rich solutions [18], and precipitation can occur at saturation with a variety of monovalent cations:

$$\text{K-jarosite } (\log K_{sp}\ -12.5) \quad 3Fe^{3+} + K^{+} + 2SO_4^{2-} + 6H_2O \rightarrow KFe_3(SO_4)_2(OH)_6 + 6H^{+} \tag{3}$$

$$NH_4\text{-jarosite } (\log K_{sp}\ -12.5) \quad 3Fe^{3+} + NH_4^{+} + 2SO_4^{2-} + 6H_2O \rightarrow NH_4Fe_3(SO_4)_2(OH)_6 + 6H^{+} \tag{4}$$

$$\text{Na-jarosite } (\log K_{sp}\ -8.56) \quad 3Fe^{3+} + Na^{+} + 2SO_4^{2-} + 6H_2O \rightarrow NaFe_3(SO_4)_2(OH)_6 + 6H^{+} \tag{5}$$

$$H_3O\text{-jarosite } (\log K_{sp}\ -8.67) \quad 3Fe^{3+} + 2SO_4^{2-} + 7H_2O \rightarrow H_3OFe_3(SO_4)_2(OH)_6 + 5H^{+}. \tag{6}$$

K-, NH_4-, and Na-jarosites can be synthesized at ambient temperatures, whereas synthesis of the hydronium end-member usually requires elevated temperatures in excess of 95 °C [19,20]. Nevertheless, the hydronium ion often partially substitutes for other monovalent cations in the “A” position of biogenic jarosite precipitates formed under ambient conditions.

Jarosite mineral precipitation can be employed as a means of controlling ferric iron and sulfate concentrations in recirculating acid leach solutions [21,22]. Jarosite type minerals can be problematic in the bioleaching of chalcopyrite ($CuFeS_2$), contributing to passivation of the leaching as they precipitate on chalcopyrite surfaces as secondary solid phase oxidation products [23,24]. Jarosite precipitation is also extensively used in the zinc industry to remove Fe and other impurities from metallurgical circuits [14,15,25]. As opposed to removing iron as hematite (α-Fe_2O_3) or goethite (α-FeOOH), the advantage of jarosite precipitation in the zinc industry is that there is less need for neutralization, and the precipitates settle and filter well with little loss of divalent metal ions (e.g., Ni, Cu, and Zn) in the washed residues [15]. Jarosite seed recirculation and the utilization of hot solutions (98 °C) usually ensure fast and efficient jarosite precipitation [26].

The crystal chemistry of jarosite-group minerals is currently a topic of widespread interest because of their purported role as acid generators in mine wastes [27] and acid sulfate soils [28]; as sinks for iron and sulfate in metal processing circuits [15]; as proxies in remote-sensing studies [29]; and as solid-phase controls on contaminants (e.g., Pb, Ag, UO_2^{2+}, AsO_4^{3-}, and CrO_4^{2-}) associated with acid leach solutions from a variety of environmental sources (e.g., [30]). The sulfate entity in jarosite minerals is subject to partial substitution by other oxyanions such as selenate, chromate and arsenate [31–33]. With a few notable exceptions (e.g., [27]), most literature suggests that both natural and synthetic jarosite group minerals usually have significant substitution of hydronium in the alkali (A) site and also exhibit minor to major deficiencies in Fe with octahedral “B”-site occupancies as low as 86% [34,35]. Charge neutrality in iron deficient samples is apparently maintained by protonation of hydroxyl groups within the structure [36,37].

We have previously synthesized K-, NH_4-, and Na-jarosites under biological iron oxidation conditions [3,4,13,38]. These and other studies [e.g., 5] have shown that the solubility and mineralogical characteristics of common jarosite group minerals vary with the specific cation and its concentration in solution. Studies of natural jarosites suggest that ternary (K, Na, H_3O)-solid solutions are also common [7], and similar compounds have been synthesized under high temperature (95–120 °C) conditions [39,40]. Given that the hydrated radius of NH_4^+ (1.44 Å) is even closer to that of K^+ (1.32 Å) than Na^+ (0.95 Å) [41], (K, NH_4, H_3O)-solid solutions should also be possible. Therefore, the purpose of this work was to synthesize and characterize ternary (K, NH_4, H_3O)-jarosites precipitated under ambient conditions from iron-oxidizing cultures of *A. ferrooxidans*.

2. Materials and methods

2.1. Bacterial cultures and media for jarosite experiments

A mesophilic mixed culture of *A. ferrooxidans* was used in this study as previously described [3]. The iron-oxidizing culture was originally enriched from constructed wetland sediments impacted by coal mine drainage [4,10,42]. Since the bacterial consortium was only used for ferrous iron oxidation, no effort was made to use a pure culture of *A. ferrooxidans* in this study. The mixed culture was maintained in a mineral salts solution (0.4 g $(NH_4)_2SO_4$, 0.4 g $MgSO_4 \cdot 7H_2O$, and 0.36 g H_3PO_4 per liter 10 mM H_2SO_4) at pH 2.2–2.4. The medium was supplemented with 120 mM $FeSO_4 \cdot 7H_2O$ as the source of energy for the bacteria.

The solutions for jarosite synthesis were prepared as reported previously [3] and included a range of K^+ concentrations combined with 6.1, 80, 160 or 320 mM NH_4^+ added as $(NH_4)_2SO_4$. The baseline mineral salt solution contained 6.1 mM NH_4^+ to provide a nitrogen source for bacterial growth, but this concentration was insufficient for the formation of ammoniojarosite. The concentration of K^+ was adjusted with KH_2PO_4 to 0, 1, 4, 6, 12, and 31 mM. All media used for jarosite synthesis contained 160 mM Fe^{2+} added as $FeSO_4$. The media were inoculated (3.3% v/v) with cultures that had been previously maintained in K-free media, and the inoculated samples were then incubated at 22 ± 2 °C in shake flasks at 120 rev/min. Precipitates were collected after 2 weeks of incubation, even though Fe^{2+} was completely oxidized within 3–4 days as determined by color change, Fe(III)-precipitation, and lack of residual ferrous iron. The extended time course of 2 weeks was adopted to improve the yield of the precipitates. The solids were concentrated by centrifugation at 15,300 × g for 10 min, followed by washing with 10 mM H_2SO_4 and double distilled H_2O. The samples were then air dried and stored in a desiccator at 22 °C until analyzed.

2.2. Analytical methods

Powder X-ray diffraction (XRD) was performed using a Philips PW 1316/90 diffractometer (Philips Electronics, New York, NY) with CuKα radiation in combination with a diffracted-beam monochromator. All samples were packed into a zero background quartz sample holder and step-scanned from 3 to 80 °2Θ using a step interval of 0.05 °2Θ and a counting time of 4 s. A quartz reference material served as a calibration standard. The DIFFRAC.EVA (Release 2009, Bruker AXS GmbH, Karlsruhe, Germany) evaluation software module, part of the DIFFRAC.SUITE software platform for phase identification and X-ray data analysis, was used in scan processing and for obtaining