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Antimony and arsenic partitioning during Fe^{2+}-induced transformation of jarosite under acidic conditions

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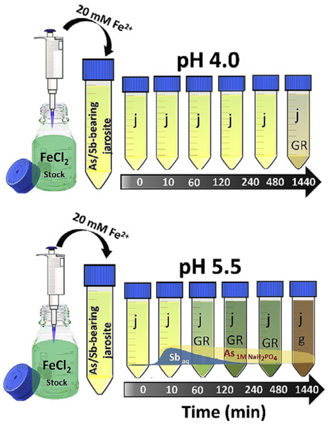
HIGHLIGHTS

- At pH 4.0, the addition of $Fe^{2+}_{(aq)}$ resulted in no significant transformation in jarosite.
- At pH 5.5, 60 min was sufficient for partial transformation of jarosite to green rust.
- Formation of green rust and goethite under pH 5.5, sequestered dissolved antimony.
- Arsenic was mostly repartitioned to the surface of green rust and goethite.

GRAPHICAL ABSTRACT



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ABSTRACT

Jarosite $[KFe_3(SO_4)_2(OH)_6]$ is considered a potent scavenger for arsenic (As) and antimony (Sb) under oxidizing conditions. Fluctuations in water levels in re-flooded acid sulfate soils (ASS) can lead to high $Fe^{2+}_{(aq)}$ concentrations (~10–20 mM) in the soil solution under acidic to circumneutral pH conditions. This may create favorable conditions for the Fe^{2+}-induced transformation of jarosite. In this study, synthetic arsenate [As(V)]/antimonate [Sb(V)]-bearing jarosite was subjected to $Fe^{2+}_{(aq)}$ (20 mM) at pH 4.0 and 5.5 for 24 h to simulate the pH and $Fe^{2+}_{(aq)}$ conditions of re-flooded freshwater ASS/acid mine drainage (AMD)-affected environments at early and mid-stages of remediation, respectively. The addition of Fe^{2+} at pH 5.5 resulted in the formation of a metastable green rust sulfate (GR- SO_4) phase within ~60 min, which was replaced by goethite within 24 h. In contrast, at pH 4.0, jarosite underwent no significant mineralogical transformation. Although the addition of $Fe^{2+}_{(aq)}$ induced the dissolution/transformation of jarosite at pH 5.5 and increased the mobility of Sb during the initial stages of the experiment ($Sb_{(aq)}$ = ~0.05 µmol L^{-1}), formation of metastable green rust (GR-SO_4) and subsequent transformation to goethite effectively sequestered dissolved Sb. Aqueous concentrations of As remained negligible in both pH treatments, with As being mostly repartitioned to the labile (~10%) and poorly crystalline Fe(III)-associated phases (~10–30%). The results imply that, under moderately acidic conditions (i.e. pH 5.5), reaction of $Fe^{2+}_{(aq)}$ with jarosite can drive the dissolution of jarosite and increase Sb mobility prior to the formation of GR-SO_4 and goethite. In addition, repartitioning of As to the labile

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fractions at pH 5.5 may enhance the risk of its mobilisation during future mineral transformation processes in Fe^{2+}-rich systems.

1. Introduction

Jarosite [$KFe_3(OH)_6(SO_4)_2$] is an Fe(III)-oxyhydoxysulfate mineral common in the sulfuric horizons of acid sulfate soil (ASS) and acid mine drainage (AMD) constructed wetlands (Bigham and Nordstrom, 2000; Burton et al., 2006; Lin et al., 2001). Various cations and anions can be incorporated into the structure of jarosite. The ability of jarosite to incorporate a variety of ions and its relative stability under oxidizing acidic conditions, makes jarosite group minerals potential scavengers for a wide range of toxic trace metal/metalloids in ASS/AMD sites. For example, jarosite can be an important host phase for both arsenic (As) and antimony (Sb) in oxidised ASS wetland sediments (Asta et al., 2010; Courtin-Nomade et al., 2012; Johnston et al., 2010; Tighe et al., 2013). Changes in environmental conditions that alter jarosite stability may enhance the environmental mobility and bioavailability of incorporated metal(loid)s (Gasharova et al., 2005: Kerr et al., 2015: Welch et al., 2008).

Iron oxides are considered important scavengers for many trace metals and metalloids (Pedersen, 2006). Various Fe(III) minerals can regulate the concentrations of dissolved trace metal(loid) species and thereby, influence surface/sub-surface water chemistry (Schwertmann and Cornell, 2000). However, Fe(III) minerals, including jarosite, can also be dissolved via either reductive or non-reductive pathways (Pedersen, 2006). The reductive dissolution of Fe(III) minerals in natural sediments can either be microbially mediated or accomplished with various organic (e.g. ascorbic acid) and inorganic reductants (e.g. HS^- and Fe^{2+}) (Pedersen, 2006).

Iron(III) reduction is an important terminal electron accepting process occurring following inundation of ASS/AMD-affected wetlands sediments. Some notable geochemical consequences of Fe(III) reduction include, increased pH, increased $Fe^{2+}_{(aq)}$ concentrations and formation of new mineral phases (Ponnamperuma, 1972). In particular, in environments with seasonal changes in water table levels and frequent changes in redox potential, pH can be highly dynamic. This can in turn influence the mineral stability as well as the mobility of the metals in these environments (Frohne et al., 2011; LeMonte et al., 2017).

Abundant $Fe^{2+}_{(aq)}$ itself may trigger Fe^{2+}-induced transformation of metastable Fe(III) minerals. This occurs via different reactions including isostructural substitution, surface sorption of Fe^{2+} to Fe(III) minerals and subsequent electron flow to Fe(III), which can lead to dissolution followed by re-precipitation of more thermodynamically stable phases (Burton et al., 2008; Pedersen et al., 2005; Schwertmann and Cornell, 2000). Given that the pH-dependent surface-charge characteristics of Fe(III) minerals influence the degree of $Fe^{2+}_{(aq)}$ and structural Fe(III) interaction (and thus the rate of mineral transformation), it is expected that both the rate of Fe^{2+}-induced transformation and the Fe(III) mineral end-products formed, will be influenced by variations in solution pH (Burton et al., 2008; Hansel et al., 2005; Jones et al., 2009).

Jarosite may undergo such Fe^{2+}-induced mineralogical transformations under Fe^{2+}-rich conditions found in inundated ASS/AMD-affected wetlands sediments, thereby influencing the mobility and bioavailability of any associated As and Sb (Johnston et al., 2010, 2012; Tighe et al., 2013). Because the Fe^{2+}-induced transformation involves a dissolution/re-precipitation reaction, incorporated metalloids such as As or Sb can repartition from co-precipitated to aqueous or surface-complexed species, or alter their oxidation states (Amstaetter et al., 2010; Mitsunobu et al., 2008), thereby increasing or attenuating their environmental bioavailability (Johnston et al., 2012; Tufano and Fendorf, 2008).

Both As and Sb possess several similar chemical and toxicological properties, for example, the trivalent species of both metalloids [As(III) and Sb(III)] are carcinogenic (Beyersmann and Hartwig, 2008; Casiot et al., 2007; Eiche et al., 2008; Wilson et al., 2010). Therefore, understanding the geochemical behavior of these two elements in conditions relevant to ASS and AMD environments, with seasonal oscillations in water level and fluctuations in pH, is worthy of consideration.

In the environment, the stability and reactivity of jarosite depends on a range of physiochemical factors including, the degree of isomorphous substitution and the nature and concentration of the ions substituted into the A and B sites of the mineral, pH, redox condition and the presence of organic agents (Welch et al., 2008; Gasharova et al., 2005; Knorr and Blodau, 2007; Smith et al., 2006). While the effect of pH on Fe^{2+}-induced transformation of various Fe(III)-minerals (e.g. schwertmannite, hematite and goethite) have been studied previously (Burton et al., 2008; Catalano et al., 2011; Handler et al., 2014), jarosite has received less attention. In a previous study by Johnston et al. (2012), pH played a significant role in regulating the behavior of As during abiotic sulfidisation of As-bearing jarosite, with greater mobility of As(V) observed under acidic pH (~4.0) conditions (Johnston et al., 2012). While the abiotic mineralogical transformation of As/Sb-bearing jarosite under Fe^{2+}-rich and pH circumneutral conditions has been examined (Karimian et al., 2017), the geochemical behavior of As and Sb in Fe^{2+}-and jarosite-rich systems under acidic pH conditions has not been directly addressed. Likewise, the consequences of this specific reaction for the mobilisation or sequestration of As(V)/Sb(V) associated with jarosite has not been investigated. Therefore, the resultant mineralogical products of jarosite transformation and the consequences for As and Sb bioavailability are poorly constrained.

The objective of this study is to systematically explore these interactions via investigation of solid and aqueous phase geochemistry during reaction of As and Sb-bearing jarosite with $Fe^{2+}_{(aq)}$ (20 mM) over 24 h under controlled pH 4.0 and 5.5 conditions. The results provide insight into a) mineralogical products of the Fe^{2+}-induced transformation of jarosite under acidic conditions, and b) As and Sb partitioning and mobility during such transformations. These insights have relevance for freshwater reflooded ASS- and AMD-affected environments and will assist in the development of appropriate risk assessment and management options at early and mid-stages following inundation of these systems.

2. Methods

2.1. As(V)/Sb(V)-bearing jarosite synthesis

K-jarosite was synthesised according to Baron and Palmer (1996). This involved dissolving 0.2 g of $Na_2HAsO_4 \cdot 7H_2O$ and 0.6 g of $KSb(OH)_6$ along with 112 g of KOH and 344.2 g of $Fe_2(SO_4)_3 \cdot 5H_2O$