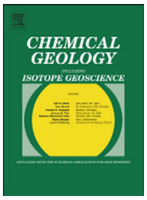
Chemical Geology 334 (2012) 9–24

Contents lists available at SciVerse ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo



Arsenic mobilization and iron transformations during sulfidization of As(V)-bearing jarosite

Scott G. Johnston [a,*], Edward D. Burton [a], Annabelle F. Keene [a], Britta Planer-Friedrich [b], Andreas Voegelin [c], Mark G. Blackford [d], Greg R. Lumpkin [d]

[a] Southern Cross GeoScience, Southern Cross University, Lismore, NSW 2480, Australia
[b] Environmental Geochemistry, Bayreuth University, Universitatsstrasse 30, Bayreuth 95440, Germany
[c] Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, CH-8600, Dübendorf, Switzerland
[d] Institute of Materials Engineering, Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia

ARTICLE INFO

Article history:
Received 14 August 2012
Received in revised form 24 September 2012
Accepted 26 September 2012
Available online 5 October 2012

Editor: J. Fein

Keywords:
Arsenic
Jarosite
Mackinawite
Sulfide
EXAFS
Orpiment

ABSTRACT

Jarosite ($KFe_3(SO_4)_2(OH)_6$) is an important host-phase for As in acid mine drainage (AMD) environments and coastal acid sulfate soils (CASS). In AMD and CASS wetlands, jarosite may encounter S(−II) produced by sulfate reducing bacteria. Here, we examine abiotic sulfidization of As(V)-bearing K-jarosite at pH 4.0, 5.0, 6.5 and 8.0. We quantify the mobilization and speciation of As and identify corresponding Fe mineral transformations. Sulfide-promoted dissolution of jarosite caused release of co-precipitated As and the majority of mobilized As was re-partitioned to a readily exchangeable surface complex (As_{Ex}). In general, maximum As mobilization occurred in the highly sulfidized end-members of all treatments and was greatest at low pH, following the order pH $5.0 \approx 4.0 > 8.5 > 6.5$. X-ray absorption spectroscopy revealed that most solid-phase As remained as oxygen-coordinated As(V) when pH values were >5.0 – even during latter stages of sulfidization and the presence of ≥ 100 μM dissolved S(−II). In contrast at pH 4.0, As transitioned from oxygen-coordinated As(V) to a sulfur-coordinated orpiment-like phase. This transition coincided with a marked decrease in As_{Ex}, attenuation of $As_{(aq)}$ and TEM-EDX spectra indicate concurrent formation of nano-scale zones variably enriched in As (~1–15%). Although discordant with geochemical modeling, the formation of an orpiment-like precipitate appears to be a primary control on As mobility during the late stages of complete jarosite sulfidization under acidic conditions (pH 4.0).

Mackinawite was the main Fe-mineral end product in all pH treatments. However, at pH 8.0, jarosite rapidly (<1 h) transformed to a lepidocrocite intermediary. Although lepidocrocite efficiently adsorbed $As_{(aq)}$, the transformation process itself was incongruent with electron transfer to Fe(III). Further investigation is required to determine whether the electron donor triggering this transformation was direct via S(−II), or indirect via surface complexed Fe(II) and hence akin to the widely-known Fe(II)-catalyzed transformation of Fe(III) minerals. The results demonstrate that abiotic sulfidization of As(V)-co-precipitated jarosite can mobilize substantial As and that pH exerts a major control on the subsequent As solid-phase speciation, electron transfer kinetics and Fe mineralization pathways and products. The findings are particularly relevant to heterogeneous sediments in which As-bearing jarosite encounters dissolved sulfide under a range of pH conditions.

1. Introduction

Jarosite is a common Fe(III)-mineral in coastal acid sulfate soils (CASS) and acid mine drainage (AMD) settings (Acero et al., 2006; Asta et al., 2009; Johnston et al., 2011a). Jarosite can effectively remove As from solution by sorption or co-precipitation mechanisms (e.g. Savage et al., 2005; Egal et al., 2009; Asta et al., 2010; Johnston et al., 2011b), and is therefore an important mineralogical control on aqueous concentrations of As in both AMD and CASS environments.

The formula of jarosite can be represented as $MFe_3(SO_4)_2(OH)_6$, where M is usually K^+, Na^+, NH_4^+, or H_3O^+. Jarosite typically forms during oxic conditions at low pH (~1–3) and can transform to schwertmannite and goethite as pH increases (Bigham et al., 1996). Within the sediments of constructed AMD wetlands or re-flooded CASS wetlands, jarosite may be subjected to reducing and pH circum-neutral conditions that are well outside its stability field (Jones et al., 2006; Zhu et al., 2008; Johnston et al., 2011a). In such wetland environments there is potential for jarosite to encounter sulfide [S(−II)] produced by the metabolic activity of sulfate reducing bacteria (SRB) (Burton et al., 2011a).

Localization of organic matter and physical heterogeneity within wetland sediments can lead to extreme spatial variability in pH, redox

---

* Corresponding author.
E-mail address: scott.johnston@scu.edu.au (S.G. Johnston).

0009-2541/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemgeo.2012.09.045

potential and the development of distinct micro-niches (Zhu et al., 2006; Robertson et al., 2009). In AMD wetlands and re-flooded CASS wetlands there is potential for organic-rich zones with active SRB to overlap and occur in close proximity to jarosite (Johnston et al., 2009; Burton et al., 2011a). Hence, in such heterogeneous field environments, As-bearing jarosite may encounter dissolved sulfide under a range of pH conditions.

Sulfide is a powerful reductant. A variety of investigations have explored abiotic reduction of structural Fe(III) in iron oxides via electron transfer from dissolved S(−II) (e.g. Dos Santos Afonso and Stumm, 1992; Yao and Millero, 1996; Poulton et al., 2004; Hellige et al., 2012). This surface-controlled reaction is rapid and highly pH dependent and can be represented by Eq. (1) (Poulton et al., 2004):

$$2Fe(OH)_3 + H_2S + 4\,H^+ \leftrightarrow 2Fe^{2+} + S(0) + 6H_2O. \quad (1)$$

Electron transfer from surface complexed S(−II) leads initially to the generation of S(0) and Fe(II), driving the reductive dissolution of the iron oxide and eventual precipitation of Fe(II) species. Potential Fe(II) precipitates can include mackinawite (FeS_m), if there is sufficient HS^- to react with Fe(II) (Dos Santos Afonso and Stumm, 1992; Peiffer et al., 1992; Peiffer and Gade, 2007), or other intermediate Fe(II)/Fe(III) minerals such as magnetite (Hellige et al., 2012). The subsequent formation of FeS_m can be represented by Eq. (2) (Poulton et al., 2004):

$$Fe^{2+} + HS^- \leftrightarrow FeS_{(s)} + H^+. \quad (2)$$

Most previous work has focused on interactions between dissolved S(−II) and various iron oxides (i.e. Dos Santos Afonso and Stumm, 1992; Peiffer et al., 1992; Yao and Millero, 1996; Poulton et al., 2004; Peiffer and Gade, 2007; Hellige et al., 2012). In contrast, the reaction between dissolved S(−II) and jarosite has received relatively little research attention. Likewise, the consequences of this specific reaction for the subsequent mobilization or attenuation of any As associated with jarosite has not been investigated. Reaction between jarosite and dissolved sulfide should cause reduction of structural Fe(III) to Fe(II) and drive jarosite dissolution. As a result, sulfidization of jarosite has the potential to cause considerable mobilization of jarosite-associated As. Sulfidization may also change the proportional abundance of co-precipitated versus surface-complexed As during the subsequent precipitation of new Fe(II) mineral phases (Lee et al., 2005).

If there is sufficient sulfide to react with jarosite, Fe-sulfide minerals such as FeS_m are likely to form (Ivarson and Hallberg, 1976) and this newly-formed mackinawite may sequester dissolved As via pH-dependent sorption processes (Farquhar et al., 2002; Wolthers et al., 2005). Although mackinawite has a considerably lower sorption affinity for As when compared to Fe(III)-mineral phases such as ferrihydrite (Charlet et al., 2011), there are also widely contrasting sorption affinities for As between different iron-sulfide mineral phases (i.e. pyrite, mackinawite) (Wolthers et al., 2005; Kirk et al., 2010).

In addition, free sulfide may facilitate the precipitation of discrete As-sulfide phases — a process which is strongly influenced by pH and reaction kinetics (e.g. Rochette et al., 2000; Gallegos et al., 2007; Renock et al., 2009). Indeed, sulfidogenesis can be an important mechanism for attenuating As in sulfur-rich sediments (e.g. Bostick et al., 2004; O'Day et al., 2004a; Root et al., 2009; Johnston et al., 2010). Nano-particulate FeS_m is typically one of the first iron-sulfides to form in natural sulfidogenic environments and is regarded as an important mineralogical control on As mobility (Wolthers et al., 2005; Gallegos et al., 2007).

However, it is overly simplistic to regard sulfidogenic environments as generally unfavorable for As mobility (Kirk et al., 2004). For example, several recent studies demonstrate that there is considerable potential for mobilization of As when sulfide produced by SRB reacts with As-bearing iron oxides (e.g. Kocar et al., 2010; Burton et al., 2011b). As mobilization and speciation in sulfidic systems is complex, with interactions between S(−II) and As leading to formation of a variety of thiolated As(III) and As(V) anion species (Planer-Friedrich et al., 2007; Wallschläger and Stadey, 2007; Helz and Tossell, 2008). Contemporary understanding of As–S systems has evolved substantially in the last decade and analytical differentiation between thiolated As(III) and As(V) species is a relatively recent development (Suess et al., 2009; Planer-Friedrich et al., 2010).

In this study, we subjected synthetic K-jarosite containing co-precipitated As(V) to abiotic reactions with dissolved S(−II) at pH 4.0, 5.0, 6.5 and 8.0. Our aim was to examine the effects of pH on the subsequent mobilization and aqueous/solid-phase partitioning and speciation of As. In addition, we investigated the composition and Fe mineralogy of the precipitates that formed under different pH regimes and explored how their formation influenced the observed aqueous behavior of As.

2. Methods

2.1. General methods

All laboratory glass-ware was soaked in 5% (v/v) HNO_3 for at least 24 h, followed by repeated rinsing with deionized water. All chemicals were analytical reagent grade. All reagent solutions were prepared with deionized water (MilliQ). Solid-phase samples were prepared and dried under oxygen-free conditions in an anaerobic chamber (1–5% H_2 in N_2), containing an O_2 consuming Pd catalyst.

2.2. Experimental design

Approximately 500 g of K-jarosite was synthesized according to Baron and Palmer (1996). Sufficient $Na_2HAsO_4.7H_2O$ was dissolved in the initial solution (prior to the addition of reagents) to generate a synthetic jarosite containing between 500 and 1000 ppm of co-precipitated As(V). Although this is well below the demonstrated capacity of jarosite to incorporate As(V) (Paktunc and Dutrizac, 2003), this concentration range was selected to be consistent with prior observations of As concentrations in naturally occurring jarosite (e.g. Dudas, 1984). The resulting suspension was allowed to settle, the supernatant decanted and replaced with deionised water and the suspension thoroughly mixed. This was repeated 4 times to remove soluble ions, prior to drying the final concentrated slurry at 40 °C. The resulting dry material was finely ground using a mortar and pestle.

An airtight 2 L glass reaction vessel (Asynt) with PTFE access ports and a PTFE paddle stirrer was used for all reaction series. A 2 L solution of 0.1 M NaCl, buffered using 0.025 M MES 2(N-morpholino) ethanesulfonic acid and 0.025 M DEPP (N,N′-diethylpiperazine), was placed in the reaction vessel and purged with high purity N_2 for 16 h. These buffers were chosen for their non-complexing properties and the wide pH range spanned by their respective pK_a values (Kandegedara and Rorabacher, 1999).

A Metrohm 836 Titrando pH stat was integrated with the reaction vessel enabling pH to be maintained (±0.05 pH units) via the addition of N_2 purged 0.5 M HCl or 0.5 M NaOH. The atmosphere equilibration ports on the Metrohm 836 Titrando pH stat were connected to a N_2 filled gas-bag during each experiment, thereby ensuring that the headspace of the HCl and NaOH supply vessels remained composed of N_2 throughout the experiments.

The desired experimental pH of the 2 L solution (4.0, 5.0, 6.5 or 8.0) was established using the pH stat, immediately prior to adding 10.0 g (~26.2 mM L^{-1} Fe equivalent) of synthetic As(V)-bearing jarosite to the reaction vessel while simultaneously purging the solution and headspace with high purity N_2. The suspension was stirred continuously at 300 rpm and purged with high purity N_2 for an additional 1 h. After 1 h, N_2 purging was ceased and the reaction vessel