Chemical Geology 215 (2005) 473–498

CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

www.elsevier.com/locate/chemgeo

Arsenic speciation in synthetic jarosite

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Accepted 1 June 2004

Abstract

Iron sulfate minerals may incorporate arsenic released from oxidizing arsenian pyrite and other sulfide minerals. For example, in the southern Mother Lode gold district of California, As is concentrated in jarosite, ideally $KFe_3(SO_4)_2(OH)_6$, that formed by the oxidation of sulfides in mineralized outcrops and mine tailings containing ~100 to ~2000 ppm As. These weathering crusts, which are vulnerable to storm erosion, are of concern as a source for the transport of As into watersheds. Both arsenatian jarosite and scorodite [$FeAsO_4 \cdot 2H_2O$] provide only temporary storage mechanisms for As in the environment because of the limited pH and redox conditions over which they are stable. To evaluate the extent of incorporation of As into jarosite, a series of jarosites in the system K_2O–Fe_2O_3–As_2O_5–H_2SO_4–H_2O was synthesized at 95 °C and 1 bar. Potassium arsenate was included at relative molar proportions of 1–50% $As_{T,aq}$ (defined as 100*As/(As+S)) in the starting solutions. Arsenic was incorporated into all samples at higher proportions relative to S than in the starting solutions. Synchrotron X-ray diffraction results indicated that jarosite was formed from starting solutions that contained up to 20% $As_{T,aq}$. An X-ray amorphous phase also formed in samples containing As and, at 25% $As_{T,aq}$ in the starting fluid, only an amorphous phase was obtained. Starting fluids with 33% and 50% $As_{T,aq}$ produced poorly crystalline scorodite. Scanning electron microscope (SEM) images show textural differences among the jarosite samples, from relatively uniform anhedral to subhedral particles 0.5–1 μm across in low-As jarosite samples, to smaller grains (<0.2 μm) dispersed in a groundmass in the samples richer in As. Results from SEM, SXRD and Raman spectroscopy suggest that most As in the synthetic samples enters the amorphous phase, but quantitative analytical electron microprobe (AEM) analyses showed that the grains of jarosite contain up to ~30% $As_{T,s}$. Iron *K*-edge and As *K*-edge extended X-ray absorption fine-structure (EXAFS) spectra of the arsenatian jarosite showed As and Fe environments consistent with substitution of As for S. SXRD indicated unit-cell expansion with increased substitution of As in jarosite. The extent to which As is accommodated in the jarosite structure may be limited by the charge-balance mechanism and deficiency of Fe in octahedral sites. The X-ray amorphous material produced in the syntheses exhibits short-range order and is similar to scorodite over small domains, on the order of 10–14 Å. Raman spectroscopy showed several broad peaks in the 750–950-cm^{-1} Raman shift spectral region, associated with As–O vibrations. The relative intensities of bands related to As–OFe and As–O vibrations are also consistent with substitution of As for S in jarosite, and with small, scorodite-like domains in the amorphous material. Collectively, these data show that the strong association between Fe and arsenate during nucleation of the

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doi:10.1016/j.chemgeo.2004.06.046

solid materials leads to As retention in the oxidized Fe minerals produced during weathering of arsenian pyrite and other As-rich sulfide minerals.

Keywords: Jarosite; Arsenic; Spectroscopy; Crystallography; Synchrotron; Environmental geochemistry

1. Introduction

The fate of As during the weathering of As-rich sulfide minerals is ecologically significant for environments exposed to coal and metal-mining operations, especially those related to the production of gold. Recent contributions to the literature on environmental geochemistry have elucidated the influence of iron oxyhydroxides on the geochemical cycling of As in weathering environments, largely by adsorption (e.g., De Vitre et al., 1991; Azcue et al., 1994; Balistrieri et al., 1994; Bowell, 1994; Rodie et al., 1995; McGeehan et al., 1998). However, Fe-sulfate minerals also sequester As, thereby providing a mineralogical attenuation mechanism during weathering of As-rich pyrite (Huggins et al., 1997; Foster et al., 1998; Savage et al., 2000a). Jarosite [$KFe_3(SO_4)_2(OH)_6$] occurs commonly where pyrite is exposed to atmospheric weathering. Depending on aqueous activities of potassium, iron and sulfate, it is generally stable in the pH range of 1–3 (Alpers et al., 1989; Bigham et al., 1996). Uptake of As in jarosite derived from the weathering of arsenian pyrite is common in the southern Mother Lode gold district of California. Jarosite-rich samples from this area contain up to ~2000 ppm As in the fine (<63 μm) size fraction (Savage et al., 2000a). In this region, fine-grained friable weathering crusts incorporate the oxidation products of pyrite, including arsenatian jarosite, as well as detrital minerals. These materials may be transported from outcrops and mine tailings into surface waters during winter storms (Savage et al., 2000b).

Jarosite has three crystallographic structural cation sites with differing coordination environments in which various impurity elements may reside. Use of jarosite has therefore proved to be beneficial in waste-disposal settings, where it is employed to sequester Fe, S and Na in coal-cleaning process wastes (Norton et al., 1991), and is also employed in metallurgical processes to immobilize Fe and heavy metals, e.g., from Zn ores (Buckle et al., 1996; Garcia and Valdez, 1996; Dutrizac and Jambor, 2000 and references therein) and from Ni ores (Plasket and Dunn, 1986). Jarosite has also been suggested as a storage mineral for radioactive nuclides (DePutter et al., 2000; Kolitsch and Pring, 2001). Baron and Palmer (2002) and Drouet et al. (2003) demonstrated that jarosite forms a complete solid solution in which chromate substitutes for sulfate, making the mineral a good candidate for waste disposal from chrome-plating and leather-tanning operations.

The mode of incorporation of As in or on jarosite may influence the mobility and bioavailability of As in both natural and controlled environments. Arsenate (AsO_4^{3-}) sorbed onto the mineral surface may desorb under the near-neutral pH conditions associated with many natural waters. By contrast, As incorporated into the mineral structure could influence the solubility of jarosite, potentially stabilizing the structure over a wider range of conditions than is tolerated by pure jarosite. Baron and Palmer (2002) found decreased solubility for solid solution analogues to jarosite when chromate substitutes for sulfate. However, charge imbalance imposed by arsenate for sulfate substitution might also decrease arsenatian jarosite stability relative to end-member jarosite. To aid in predicting the stability of arsenatian jarosite, a series of As-bearing jarosite samples was synthesized to investigate the extent and mode of As substitution. Synthetic samples produced from starting solutions containing a range of As concentrations were characterized using synchrotron X-ray powder diffraction (SXRD), X-ray absorption spectroscopy (XAS), Raman spectroscopy, transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). This combination of bulk and spatially resolved techniques enabled physical and chemical characterizations of jarosite, scorodite and an amorphous phase that were produced during the experiments.