



## Scorodite precipitation in the presence of antimony



David Kossoff<sup>a</sup>, Mark D. Welch<sup>b</sup>, Karen A. Hudson-Edwards<sup>a,\*</sup>

<sup>a</sup> Department of Earth and Planetary Sciences, Birkbeck, University of London, Malet St., London WC1E 7HX, UK

<sup>b</sup> Department of Earth Science, The Natural History Museum, Cromwell Road, London SW7 5BD, UK

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### ABSTRACT

The effects of Sb on the precipitation of synthetic scorodite, and the resultant phases formed, were investigated. Nine synthetic precipitates with varying concentrations of Sb, together with As-only and Sb-only end members, were prepared using a scorodite synthesis method, and these were characterised using XRD, SEM, chemical digestion and  $\mu$ XRF mapping. XRD analysis shows that the end members are scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ) and tripuyhyite ( $\text{FeSbO}_4$ ), and that the intermediate members are not Sb-substituted scorodite, but instead are physical mixtures of scorodite and tripuyhyite, with tripuyhyite becoming more prominent with increasing amounts of Sb in the synthesis. Electron microprobe analysis on natural scorodites confirms that they contain negligible concentrations of Sb. With increasing Sb in the synthesis, the morphology of the scorodite changes from rosettes of intergrown crystals to anhedral masses of smaller crystallites. Chemical digestion of the series also became increasingly difficult with increasing Sb content. We conclude that Sb is not taken up in scorodite (perhaps due to its larger ionic radius and different co-ordination with O compared to As), that increasing amounts of Sb in the system affect scorodite morphology, and that tripuyhyite is a highly stable and perhaps underestimated Sb-sink.

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### 1. Introduction

Arsenic (As) and antimony (Sb) are classified as priority pollutants in the United States and European Union (Filella et al., 2002) because ingestion of As- and Sb-bearing fluids or inhalation of As- and Sb-bearing particles can lead to pathologies such as cardiovascular disease and lung cancer (Pershagen et al., 1987; Centeno et al., 2002; Yáñez et al., 2003; States et al., 2011; Maiti et al., 2012). One of the major sources of As and Sb in the environment is mine wastes, which contain 10s to 10,000s of ppm of As and 10s to 1000s of ppm of Sb (Smedley and Kinniburgh, 2002; Wu et al., 2011; Cidu et al., 2014). There has been a near exponential increase in the physical amount of waste rock extracted by modern mining principally as a function of the increasing use of open-cast methods (Mudd, 2010). This volume of waste is predicted to grow over the next 100 years due to increasing demand for mineral resources, and with the consequent exploitation of ever-lower ore grades (Gordon et al., 2006). Therefore, the amount of mine waste-derived As and Sb will correspondingly increase. Though precise numbers of people directly affected by mine waste-derived Sb are not available, they are likely to be in the range of 10s to 100s of thousands, given that 10,000 inhabitants are impacted in the Sb mining area of Xikuangshan, China alone (Fu et al., 2010). Large numbers of people are also affected by mining-related As contamination throughout the world. For example, in the former tin

mining area of Ron Phibun (Thailand) 1000 people were found to be directly affected by arsenicosis, with 30,000 more at risk.

One of the ways that the risks posed by exposure to As and Sb can be mitigated is by the precipitation of minerals and especially, those that are relatively insoluble and have resultingly low bioaccessibility. The two principal primary sources of As in mine tailings are arsenopyrite, with 46 wt.% As, and (arsenical) pyrite, with up to ~3 wt.% As (e.g., Savage et al., 2000; Kossoff et al., 2012). These minerals are hosts for Sb (Friedl et al., 1992) with, for example, <0.001–0.143 wt.% Sb (mean 0.34 wt.%) in arsenopyrite and <0.0002–0.039 wt.% Sb (mean 0.012 wt.%) in pyrite (Kossoff et al., 2012). The major primary host of Sb in mine wastes is stibnite ( $\text{Sb}_2\text{S}_3$ ) (e.g., Kossoff et al., 2012; Roper et al., 2012). These primary As and Sb minerals frequently occur together (e.g., Wilson et al., 2004; Anawar et al., 2011), and it is therefore likely that their secondary (alteration) phases will also be associated.

One of the major secondary As-bearing phases in mine wastes is scorodite, which has been shown to have the lowest bioaccessibility of common As-bearing mine waste minerals at pH values > 4 (Salzsauler et al., 2005; Meunier et al., 2010; Nordstrom et al., 2014). Scorodite is considered to be a stable phase, particularly under oxic conditions (Drahota and Filippi, 2009), but under reducing conditions ( $E_h < 100$  mV) it is destabilized, often as a result of the activity of organisms such as Fe(III)-reducing bacteria (Cummings et al., 1999). Although Sb is known to be present in mining-affected environments where scorodite occurs (e.g., Haffert and Craw, 2008), its potential effects on scorodite precipitation and character, and the resultant Sb phases formed, are

\* Corresponding author. Tel.: +44 203 073 8030.

E-mail address: [k.hudson-edwards@bbk.ac.uk](mailto:k.hudson-edwards@bbk.ac.uk) (K.A. Hudson-Edwards).

not well-known. To fill this knowledge gap, we conducted co-precipitation experiments with Sb and scorodite, and we examined natural scorodite samples for the presence of Sb. This study therefore aimed to determine how the presence of Sb affects scorodite precipitation, and to characterise the solid phases produced.

## 2. Methods and materials

### 2.1. Synthetic Fe–As–Sb–O compounds

#### 2.1.1. Synthesis methods

The method of Paktunc et al. (2008) was used to synthesise scorodite-type compounds with zero to 100 M Sb/(As + Sb). The method was modified by carrying out the synthesis in sealed reaction bombs with PTFE liners, rather than on a hotplate. The bombs were set in a  $140 \pm 3$  °C oven for three days (72 h). Eleven precipitates containing various proportions of As and Sb were synthesised (Table 1). The syntheses were carried out using 0.1 M HCl solution (pH 1) and 0.2 M sodium arsenate heptahydrate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ) and sodium antimonate trihydrate ( $\text{Na}_3\text{SbO}_4 \cdot 3\text{H}_2\text{O}$ ), depending on the relative amounts of As and Sb desired in the precipitates (Table 1), and 0.1 M ferric sulphate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ) pentahydrate (equivalent to 0.2 M  $\text{Fe}(\text{SO}_4)_{1.5} \cdot 5\text{H}_2\text{O}$ ).

#### 2.1.2. Characterisation of synthetic precipitates

The precipitates were photographed using a Nikon D300S camera and their colours were recorded using a Munsell colour chart. The precipitates were then identified by X-ray powder diffraction using a PANalytical XPERT-PRO diffractometer (45 kV, 40 mA) with  $\text{CuK}\alpha$  radiation monochromated by a Ge(111) plate. Anti-scatter Soller slits were used and the precipitates were spun at  $0.5 \text{ rev s}^{-1}$ . A constant step-scan interval of  $0.0167^\circ$  was used from 10 to  $80^\circ 2\theta$  corresponding to 4189 data points. Total exposure times of 5 h were used to obtain patterns for Rietveld refinement of precipitates  $\text{As}_{100}\text{Sb}_0$ ,  $\text{As}_{98.75}\text{Sb}_{1.25}$ ,  $\text{As}_{95}\text{Sb}_5$ ,  $\text{As}_{90}\text{Sb}_{10}$ ,  $\text{As}_{60}\text{Sb}_{40}$  and  $\text{As}_{50}\text{Sb}_{50}$ , comprising mixtures of well-crystallised scorodite (with or without minor poorly crystallised tripuhyte). An exposure time of 3 h was used for those precipitates containing poorly crystallised tripuhyte that were unsuitable for Rietveld refinement, but allowed peaks to be identified and indexed. The detection limit of the diffractometer based upon scorodite: tripuhyte ratio (by mass) was estimated by preparing mixtures of precipitates  $\text{As}_{100}\text{Sb}_0$  (pure scorodite) and  $\text{As}_0\text{Sb}_{100}$  (pure tripuhyte). It was found that scorodite peaks could be detected and peak positions determined at the 2 wt.% level, which we take to be a good indication of the phase detection limit for our diffraction experiments.

The morphology and size of the precipitates were analysed using scanning electron microscopy (SEM, JEOL JSM-6480LV) following Au coating. For the imaging secondary electrons were collected using a 7 kV acceleration voltage. The relative proportions of As, Sb, Fe and O in the synthetic precipitates were determined by Wavelength-dispersive X-ray spectroscopic (WDS) analysis (EMPA; Jeol 8100

Superprobe) on polished resin blocks. Analyses were carried out using an accelerating voltage of 15 kV, a current of 2.5 nA and a beam diameter of 1  $\mu\text{m}$ . The counting times for all elements were 20 s on the peak, and 10 s each on the high and low backgrounds. The analyses were calibrated against standards of natural silicates, oxides and Specpure® metals, with the data corrected using a ZAF program (Gill, 1997).

For quantitative total element analysis, approximately 200 mg of the synthetic precipitates were dissolved in a PTFE beaker by adding 10 mL of concentrated  $\text{HNO}_3$ . This digestion methodology proved difficult, however, for the more Sb-rich members of the series. The concentrated  $\text{HNO}_3$  digestion was successful only with precipitates  $\text{As}_{100}\text{Sb}_0$ ,  $\text{As}_{98.75}\text{Sb}_{1.25}$ ,  $\text{As}_{95}\text{Sb}_5$ ,  $\text{As}_{90}\text{Sb}_{10}$  and  $\text{As}_{60}\text{Sb}_{40}$ ; for the remaining precipitates the  $\text{HNO}_3$  was evaporated, 5 mL HF and a further 2 mL of concentrated  $\text{HNO}_3$  were added, and the mixture was then complexed with 1 mL perchloric acid ( $\text{HClO}_4$ ) and evaporated. Subsequently, 5 mL of concentrated  $\text{HNO}_3$  was added and the solution was made up to 100 mL with 18  $\text{M}\Omega \text{ cm}^{-1}$  deionised water to give a 5% (vol:vol)  $\text{HNO}_3$  matrix suitable for inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis. This additional procedure successfully digested precipitates  $\text{As}_{50}\text{Sb}_{50}$ ,  $\text{As}_{40}\text{Sb}_{60}$  and  $\text{As}_{10}\text{Sb}_{90}$ , but portions of precipitates  $\text{As}_5\text{Sb}_{95}$ ,  $\text{As}_{1.25}\text{Sb}_{98.75}$  and  $\text{As}_0\text{Sb}_{100}$  increasingly remained as milky-coloured precipitates. A heated ultrasonic bath was employed over a period of 6 h in a final attempt to dissolve these precipitates.

### 2.2. Collection and electron microprobe analysis of natural scorodite and tripuhyte samples

Natural samples of scorodite ( $n = 36$ ) were obtained from museum collections at Birkbeck College (London, UK), the Natural History Museum (London, UK), the Manchester Museum (Manchester, UK), the Smithsonian Institution (Washington DC, USA), the Victoria Museum (Melbourne, Australia), the American Museum of Natural History (New York, New York, USA) and the Natural History Museum (Salt Lake City, Utah, USA) and from mineral dealers. The samples were photographed using a Nikon D300S camera and their relative proportions of As, Sb, Fe and O were determined by electron microprobe analysis using the same instrument as described above.

### 2.3. $\mu\text{XRF}$ analysis of synthetic precipitates

To investigate the distribution and association of As and Sb in the synthetic precipitates, we carried out micro-X-ray fluorescence ( $\mu\text{XRF}$ ) mapping at the Sb  $L^{\text{III}}$  and As K edges at the Diamond Light Source on beamline I18 on polished blocks previously analysed by EPMA. Operating conditions for the storage ring were 3 GeV and 200 mA. On I18, which is an undulator beamline, the X-rays are focused by a pair of Kirkpatrick–Baez (KB) mirrors after being monochromated by a Si(111) double-crystal monochromator. Harmonic rejection for Sb was achieved by reflecting off the silicon substrate of the KB mirrors. The beam size for the  $\mu\text{XRF}$  was 5  $\mu\text{m}$ .

**Table 1**  
Details of synthesis of As–Sb–Fe–O compounds.

Precipitate	$\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ (mg)	$\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (mg)	$\text{Na}_3\text{SbO}_4 \cdot 3\text{H}_2\text{O}$ (mg)	As (mol/L)	Sb (mol/L)	As/(As + Sb) molar	Sb/(As + Sb) molar
$\text{As}_{100}\text{Sb}_0$	0.490	0.624	0.000	0.2000	0.0000	100	0
$\text{As}_{98.75}\text{Sb}_{1.25}$	0.490	0.609	0.012	0.1975	0.0025	98.75	1.25
$\text{As}_{95}\text{Sb}_5$	0.490	0.593	0.025	0.1950	0.0050	95	5
$\text{As}_{90}\text{Sb}_{10}$	0.490	0.562	0.049	0.1900	0.0100	90	10
$\text{As}_{60}\text{Sb}_{40}$	0.490	0.374	0.197	0.1200	0.0800	60	40
$\text{As}_{50}\text{Sb}_{50}$	0.490	0.312	0.247	0.1000	0.1000	50	50
$\text{As}_{40}\text{Sb}_{60}$	0.490	0.250	0.296	0.0800	0.1200	40	60
$\text{As}_{10}\text{Sb}_{90}$	0.490	0.063	0.444	0.0100	0.1900	10	90
$\text{As}_5\text{Sb}_{95}$	0.490	0.031	0.469	0.0050	0.1950	5	95
$\text{As}_{1.25}\text{Sb}_{98.75}$	0.490	0.016	0.487	0.0025	0.1975	1.25	98.75
$\text{As}_0\text{Sb}_{100}$	0.490	0.000	0.490	0.0000	0.2000	0	100

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