

Experiment Report Form



	Experiment title: Ferrous iron oxidation in the presence of antimony: An XAS investigation into the speciation of antimony and iron oxide products	Experiment number: EV-494
Beamline: BM 20	Date of experiment: from: 2 November 2022 to: 7 November 2023	Date of report: 6 September 2023
Shifts: 15	Local contact(s): Dr. Andreas C. Scheinost, Dr. Damien Prieur	<i>Received at ESRF:</i>
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Report:

Motivation: The geochemical behavior of antimony (Sb), a priority pollutant of increasing concern, is closely linked to the redox cycling of iron (Fe). Microbial reduction of Fe(III) oxides and production of soluble Fe(II) under anoxic conditions has been shown to release co-associated Sb (occurring as Sb(V) and/or Sb(III)). In redox-dynamic environments, Fe(II) can be re-oxidized and precipitate as Fe(III) oxides. The extent to which these processes affect Sb mobility, however, is still poorly understood and likely depends on an array of factors such as pH, Sb species and the nature of the newly formed Fe(III) oxides.

Here, we investigated the effect of Fe(II) oxidation on Sb sequestration and on the mineralogy of the resulting Fe(III) precipitates in a pH range typical of Sb-contaminated systems (i.e. pH 6 and 7). To initiate the oxidation reaction, 0.5 mmol L⁻¹ Fe(II) was added to an oxygen-saturated electrolyte solution containing 0 or 50 μmol L⁻¹ Sb(V) or Sb(III). Changes in aqueous Sb, Sb speciation, and Fe(II) were tracked during the experiments, and solid phase samples were collected at the end of the oxidation reaction.

XAS experiments: The purpose of the beamtime was to collect Sb and Fe K-edge XAS data to identify oxidation states and local coordination environments of Sb during Fe(II) oxidation and to determine Fe speciation in the oxidation products. Sb K-edge (30,491 eV, $k_{\max} = 16 \text{ \AA}^{-1}$) and Fe K-edge EXAFS (7,112 eV, $k_{\max} = 14 \text{ \AA}^{-1}$) were recorded on pressed pellets at cryogenic temperatures (primarily) in fluorescence mode at BM20 (Rossendorf beamline) at ESRF using either a Si(111) or Si(311) monochromator. Sb K-edge X-ray

absorption near edge spectroscopy (XANES) spectra were analysed by LCF in Athena⁹ using Sb(III)-goethite, Sb(V)- goethite, and tripuhyte as reference specimen. Fe speciation was quantified by linear combination fittings (LCF) of the k^3 -weighted EXAFS oscillations, using ferrihydrite, goethite, feroxyhyte, and lepidocrocite as possible components. Sb K-edge EXAFS shell-by-shell fitting was performed using Artemis, as described in our papers from previous beamtimes at the Sb K-edge,¹⁰ and complemented by wavelet-transform analyses.¹¹

Results: In treatments with Sb(V) and in the absence of Sb, the Fe(II) concentration decreased immediately after its addition to the reactors and dropped below the detection limit within 60 hours at pH 6 and after 20 minutes at pH 7 (Fig. 1). In treatments with Sb(III), the oxidation of Fe(II) was significantly slower than in the Sb(V) or no-Sb experiments. Iron(II) oxidation also resulted in a decrease in aqueous Sb, with Sb(V) generally being faster removed from solution than Sb(III). The oxidation of Fe(II) caused the precipitation of orange to brown Fe(III) oxide particles. Using Fe EXAFS shell fitting, we were able to identify these Fe(II) oxidation products to be primarily lepidocrocite (γ -FeOOH) in no-Sb treatments. In contrast, the presence of Sb inhibited lepidocrocite formation, and instead resulted in the formation of short-range order Fe(III) oxides such as ferrihydrite ($\text{Fe}(\text{OH})_3$) and feroxyhyte (δ -FeOOH) (Fig. 2).

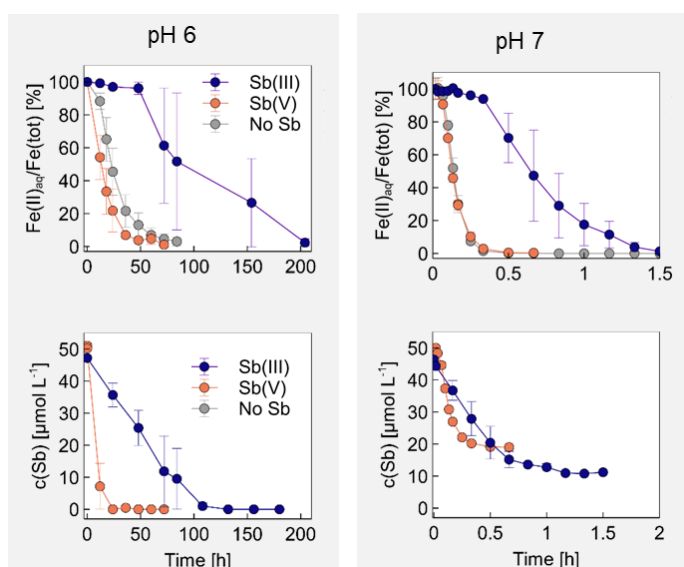


Fig. 1: Behaviour of aqueous Fe and Sb during Fe(II) oxidation at pH 6 and 7.

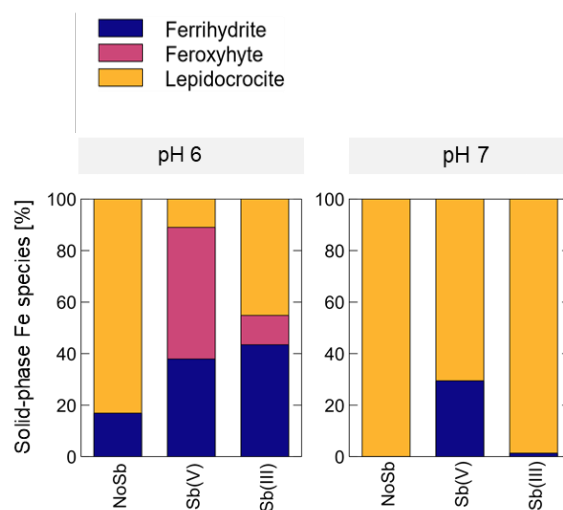
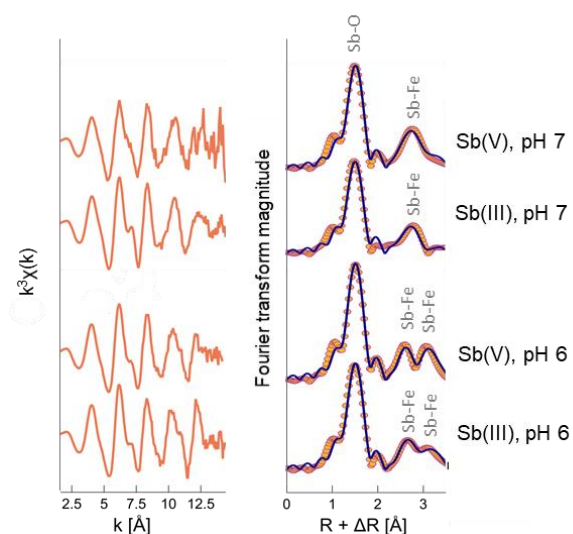


Fig. 2: Fe speciation of the precipitated Fe(III) oxide products at pH 6 and 7. Speciation data are expressed as a proportion of total and are calculated by LCF of Fe EXAFS spectra



Analysis of Sb K-edge XANES data showed that Sb was exclusively present in its pentavalent oxidation state (data not shown). This agrees with results from Sb K-edge EXAFS analysis (Fig. 3), where the first peak of the Fourier-transformed (FT) spectrum was fitted with an Sb-O shell of ~ 6 O atoms at a distance of 1.98 \AA in all samples, suggesting octahedral coordination of pentavalent Sb with oxygen. In samples containing predominantly lepidocrocite, EXAFS analysis revealed an Sb-Fe shell with 3-4 Fe atoms at approximately 3.1 \AA , which is indicative of Sb incorporation into the structure of lepidocrocite. Analogously, in samples containing also feroxyhyte (i.e. in pH 6 treatments) the FT spectra were best fitted with two Sb-Fe shells at distances of 3.1 \AA and 3.5 \AA , respectively.

Discussion and environmental significance: Our results show that that Sb(V) was incorporated into the structure of the newly formed Fe(III) precipitates via heterovalent substitution for octahedral Fe(III)–O. In the case of Sb(III) addition as the initial Sb species, trivalent Sb was fully oxidized to Sb(V), which was similarly incorporated into the precipitating Fe(III) oxides. Our results also showed that Sb(V) incorporation inhibited precipitation of lepidocrocite and instead resulted in the formation of ferrihydrite.

Our findings are significant as they imply that Fe(III) oxide formation pathways in Sb-contaminated systems may strongly differ from the well-known pathways under Sb-free conditions. Also, the research outcomes from this beamtime provide important information for risk assessment of Sb-contaminated sites, because sorption of Sb via structural incorporation would greatly enhance the sink-type capability of the newly-formed Fe(III) oxides by retaining Sb within a mineral lattice and thereby limiting direct, short-term interactions with the aqueous phase.

