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Reduction of antimony by nano-particulate magnetite and mackinawite

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ABSTRACT

The speciation of antimony is strongly influenced by its oxidation state (V, III, 0, –III). Redox processes under anaerobic groundwater conditions may therefore greatly alter the environmental behaviour of Sb. Employing X-ray absorption and photoelectron spectroscopy, we show here that Sb(V) is reduced to Sb(III) by magnetite and mackinawite, two ubiquitous Fe(II)-containing minerals, while Sb(III) is not reduced further. At the surface of magnetite, Sb(III) forms a highly symmetrical sorption complex at the position otherwise occupied by tetrahedral Fe(III). The Sb(V) reduction increases with pH, and at pH values >6.5 Sb(V) is completely reduced to Sb(III) within 30 days. In contrast, at the mackinawite surface, Sb(V) is completely reduced across a wide pH range and within 1 h. The Sb(V) reduction proceeds solely by oxidation of surface Fe(II), while the oxidation state of sulphide is conserved. Independent of whether Sb(V) or Sb(III) was added, an amorphous or nano-particulate SbS_3-like solid formed.

Keywords: antimony, reduction, mackinawite, magnetite, EXAFS.

Introduction

Antimony finds a wide range of industrial applications (e.g. in flame retardants, brake pads and as a lead-alloy in storage batteries and ammunition) and is consequently widely distributed in the environment (Watanabe *et al.*, 1999; Horrocks *et al.*, 2005; Scheinost *et al.*, 2006). Antimony may occur in different oxidation states (–III, 0, III, V) and each of these is capable of different environmental-behaviour characteristics (Raouf *et al.*, 1997; Leuz *et al.*, 2006; Li *et al.*, 2006); e.g. the anionic species $Sb^{V}(OH)_6^-$ is strongly sorbed by Fe(oxides), while the uncharged $Sb^{III}(OH)_3$(aq) is expected to be more mobile. At suboxic and anoxic conditions, Sb(V) and Sb(III) may be reduced by Fe(II) bearing minerals, further modifying their chemical behaviour. We therefore investigated the reaction of Sb(V) and Sb(III) with magnetite ($Fe^{II}Fe_2^{III}O_4$) and mackinawite ($Fe^{II}S$), minerals known to reduce e.g. Se (Scheinost and Charlet, 2008), Cr (Mullet *et al.*, 2004), As (Gallegos *et al.*, 2007), Tc and Re (Livens *et al.*, 2004) (mackinawite) and Se (Scheinost and Charlet, 2008), Pu (Powell *et al.*, 2004) and Np (Nakata *et al.*, 2004) (magnetite). Oxidation state and local structure of the reaction products were monitored by Sb-K-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine-structure (EXAFS) spectroscopy, respectively, and further supported by cryogenic X-ray photoelectron spectroscopy (XPS).

Experimental

Magnetite (Fe_3O_4) and mackinawite (FeS) were synthesized in a Jacomex glove box under anoxic conditions. After washing, they were reacted in 25 mm $CaCl_2$ with Sb(III) (Sb_2O_3 in 2 m HCl) or Sb(V) ($KSbOH_6$ in 2 M HCl or in H_2O) ([Sb] = 0.1 mm; 40 and 3 g/l Fe_3O_4; 25 and 1.9 g/l FeS) at several pH values and for different time periods

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TABLE 1. Reaction conditions of Sb(III) with magnetite.

Time	pH
1 h	7.1
15 d	4.7; 5.6
30 d	4.8
67 d	5.1; 6.1; 7.6
All at 40 g/l Fe_3O_4	

h = hours; d = days

TABLE 2. Reaction conditions of Sb(III) and Sb(V) with mackinawite.

Time	Sb(V)** pH	Sb(III)* pH
1 h	4.5; 6.3; 8.1	
22 h	5.4; 7.3; 8.3 // 25 h pH 5.4[a]	
15 d	5.6; 6.7; 8,3 // 7 d pH 5.2[b]	4.1; 4.2; 4.6
30 d	4.3; 5,3; 8,4	3.9; 4.1; 4.2

* All at 25 g/l FeS
** All at 25 g/l FeS, apart from a and b for which: 1.9 g/l FeS

(see Tables 1, 2 and Fig. 1). Samples were harvested either by centrifugation or filtration. The obtained solids were immediately placed into XAS sample holders and stored in liquid nitrogen until measurement in a closed-cycle helium cryostat at 15 K. The XANES and EXAFS spectra at the Sb-K-edge (30.491 keV) were collected at the Rossendorf Beamline at ESRF (Grenoble, France) using a high-purity 13 element Ge detector for fluorescence measurements. A Sb foil was used for energy calibration. Data treatment was carried out using the program packages *ITFA* (Rossberg *et al*., 2003), *SixPack* and *WinXAS*. The EXAFS data-fitting was carried out using theoretical backscattering amplitudes and phase-shifts calculated with *FEFF 7* from crystallographic data of tripuhyite ($FeSbO_4$), schafarzikite ($FeSb_2O_4$) and stibnite (Sb_2S_3). The oxidation states were quantified by monitoring the inflexion energy of XANES spectra, taking the edge positions of Sb(V) adsorbed on maghemite (γ-Fe_2O_3) and Sb(III) on magnetite as reference values for pentavalent and trivalent Sb on magnetite, respectively.

Results and discussion

Sb(V) and Sb(III) reacted with magnetite

The XAS spectra of this series (Fig. 1) were analysed using factor analysis. The $\chi(k)$-spectra contain only two eigenvectors, suggesting a continuous reaction from an initial state to one final reacted state. Two factors were extracted from the spectra ('Varimax-rotation' in the *ITFA* program). The first factor is expressed most strongly in the first sample, short-term reaction of Sb(V) (ads. SbV 1.25 h, pH 7.1), while the second factor is expressed most strongly in samples 8 and 9, short and long-term reaction of Sb(III) with magnetite (SbIII 67 d, pH 6.1, ads. SbIII 1.5 h, pH 7.1).

When Sb(III) was reacted with magnetite at pH 4.7–7.6 and reaction time 1 h–67 d (Table 1),

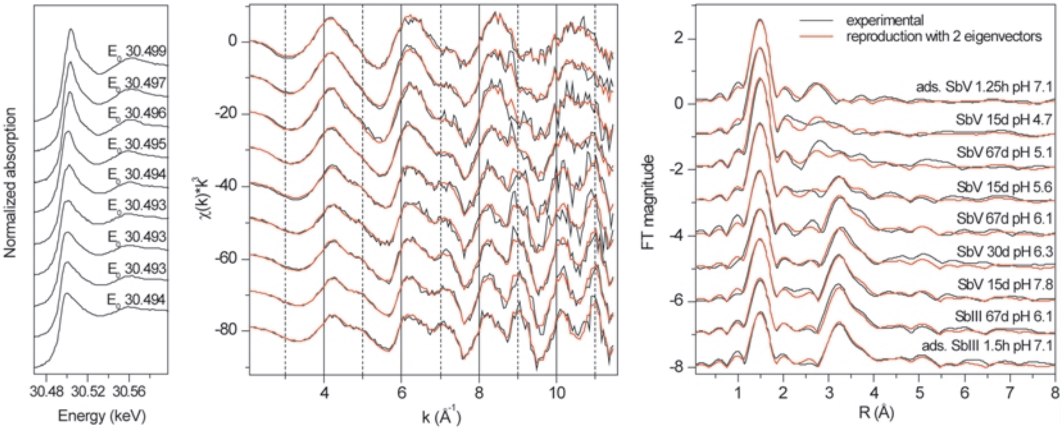

FIG. 1. Sb-XANES and EXAFS spectra of Sb(V) and Sb(III) reacted with magnetite. FT: Fourier transform.

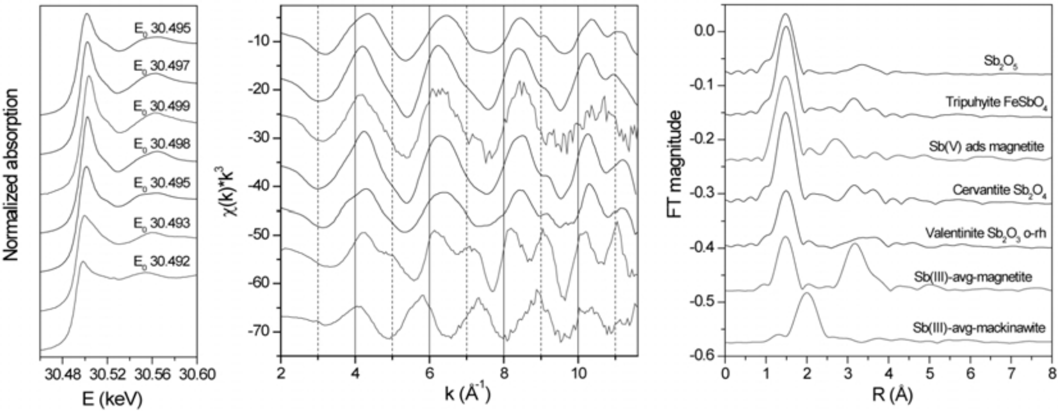

FIG. 2. Sb-K XANES and EXAFS spectra of Sb(III) reacted with magnetite and mackinawite in comparison to reference phases.

the trivalent oxidation state was conserved. Only one type of inner-sphere surface complex was identified wherein Sb^{III} is coordinated to 4–5 Fe atoms at a distance of 3.6 Å. The average spectrum of the Sb(III) spectra obtained under the conditions listed in Table 1 is displayed in Fig. 2 (SbIII-avg-magnetite).

Using FEFF Monte Carlo simulations, the structure of this sorption complex was further refined, revealing a highly ordered surface complex on the {111} faces of magnetite (Fig. 3). The trigonal pyramidal SbO_3 units occupy positions of Fe^{III} tetrahedra, which would ideally be coordinated to six FeO_6 octahedra via corner-sharing. The experimental Sb-Fe coordination numbers <6 suggest that Sb^{III} also occupies positions over incomplete FeO_6-octahedra-six-rings along surface edges.

The surface complex of Sb(V) on magnetite is characterized by the coordination of Sb to six oxygen atoms and the presence of three Fe atoms at a distance of 3.1 Å, characteristic of edge-sharing $Sb(O,OH)_6$ and $Fe(O,OH)_6$-octahedra.

In contrast to the invariant oxidation state of Sb(III) sorbed to magnetite, Sb(V) was progressively reduced to Sb(III) with increasing pH (Fig. 4). Reaction time had only a minor or no influence on Sb(V) reduction above 15 d. However, at reaction times of 1 h and 22 h, the observed degree of reduction was significantly smaller. The final surface complex is identical to the one formed after direct addition of Sb(III) (Fig. 3). At a solid/liquid ratio of 3 g/l, the reaction rate is initially slower compared to 40 g/l, but also achieves complete reduction of Sb(V) to Sb(III) within 7 d at pH 8 (Fig. 4).

Sb(V) and Sb(III) reacted with mackinawite

Independent of the initial oxidation state, pH and reaction time, only one type of spectra was observed with both XANES and EXAFS (Fig. 3). The XANES spectrum is indicative of trivalent Sb, hence Sb(V) is completely reduced to Sb(III) under all the experimental conditions

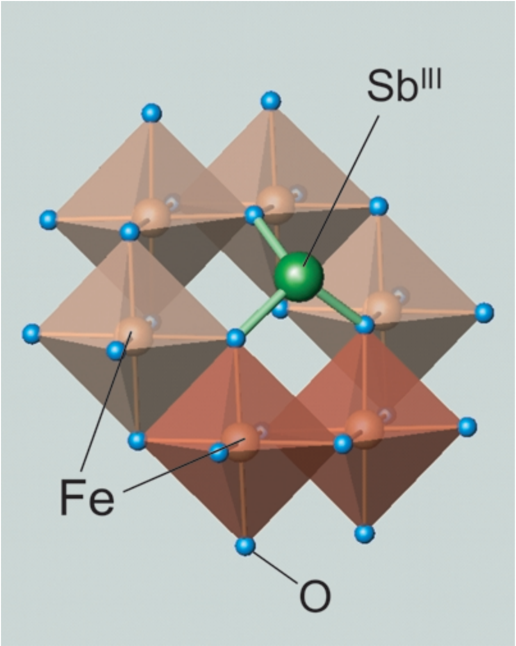

FIG. 3. Model of the Sb(III) complex at the {111} faces of magnetite as determined by FEFF Monte Carlo simulations of the EXAFS spectra.

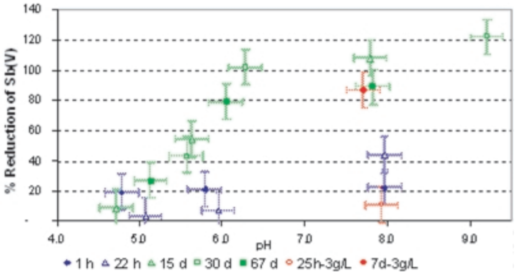

FIG. 4. Reduction of Sb(V) by magnetite as a function of pH and time at two solid/liquid ratios (40 g/l for 1 h to 67 d samples).

investigated (Table 2), while Sb(III) maintains its oxidation state. The Fourier transform shows only one strong backscattering peak, which was fitted with ~3 S atoms at a distance of 2.46 Å, suggesting formation of an highly-disordered or nano-particulate SbS_3 phase at the surface of mackinawite. No pH dependence of the reaction rate could be observed as soon as 1 h after Sb(V) was completely reduced to Sb(III) (Fig. 5).

Cryo-XPS measurements were carried out to observe changes in oxidation state of Fe, S and O at the surface of mackinawite during reaction with Sb. The Fe 2p spectrum of pure mackinawite exhibits a dominant peak at 707.2±0.1 eV, which is assigned to Fe^{II} bound to monosulphide species. Minor contributions from Fe^{III} bound to monosulphides are present as multiplet peaks starting from 708.4±0.1 eV. After reaction with Sb^{V}, the Fe 2p spectrum of mackinawite remained similar to the unreacted sample with two exceptions: an increased abundance of Fe^{III}-S species and the presence of Fe^{III}-O species on the surface at the expense of Fe^{II}-S species, suggesting Fe oxidation coupled to Sb reduction. According to the O 1s spectra, there is a small contribution of surface hydroxyl groups after the reaction, which is most likely due to the formation of Fe^{III} hydroxides. The fitted S 2p spectrum of pure mackinawite reveals three main doublets arising from the spin-orbit splitting of $2p_{3/2}$ and $2p_{1/2}$ peak (separated by 1.18 eV) of three different types of S species at the surface. The main contribution, at 162.3±0.1 eV is assigned to bulk monosulphide and the minor contribution at 161.5±0.1 eV is surface monosulphide. A minor contribution at higher energy, at ~163.5±0.1 eV, is attributed to surface polysulphide species. The presence of S^0 was observed on the surface after reaction with Sb^V. Therefore, Sb^V is reduced by electron transfer from both Fe(II) and S^{II-}.

Conclusion

Tri- and pentavalent antimony was reacted with the minerals magnetite and mackinawite under anoxic conditions. Time and pH dependence of the occurring reduction reactions as well as the nature of the resulting surface complexes was investigated using X-ray absorption spectroscopy.

Sb(V) is reduced to Sb(III) by both magnetite and mackinawite. On magnetite, the degree of reduction increased with pH and is complete at pH $\geqslant 6.5$. Two inner-sphere Sb surface complexes ($Sb^{V}O_6$-Fe_3 and $Sb^{III}O_3Fe_{4-5}$) could be identified. On mackinawite, a Sb^{III}-S_3 complex forms.

The same surface complex on Fe_3O_4 resulted when Sb(III) was added directly to magnetite or when Sb(V) was reduced at the surface. Irrespective of the experimental conditions, Sb(III) was never found to be further reduced.

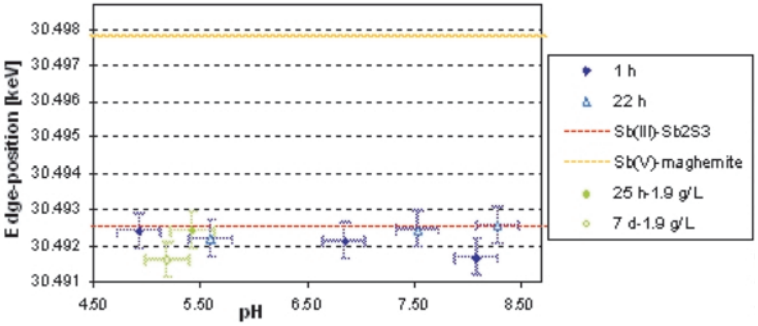

FIG. 5. Reduction of Sb(V) by mackinawite as a function of pH and time at two solid/liquid ratios (25 g/l for 1 h and 22 h samples).

For mackinawite, cryo-XPS measurements suggest that the reduction of Sb^{V} proceeds by coupled oxidation of Fe^{II} and Fe^{III} and S^{II-} to S^{0}.

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