 ROBL-CRG	Experiment title: Abiotic antimony reduction by Fe(II) systems	Experiment number: 20-01-668
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Shifts: 29	Local contact(s): A.C. Scheinost, H. Funke	<i>Received at ROBL:</i>
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Report:

Iron(II)minerals occur naturally in anoxic soils or form as corrosion products of reactive barriers and waste containers. They may react with metal contaminants via sorption and electron-transfer reactions. Redox reactions with selenium, arsenic, chromium, plutonium or neptunium have been shown ^[1,2,3,4,5]. The mobility of these contaminants is either reduced (if the resulting species is less soluble than the original one), enhanced (if the resulting species is more mobile) or left unaffected. Furthermore, surface sorption/precipitation reactions play a considerable role in determining environmental contaminant mobility. Through the present experiments it could be shown that aqueous Sb^{III} and Sb^V species form inner-sphere sorption complexes on the surface of magnetite (Fe^{II}Fe^{III}₂O₄), mackinawite (Fe^{II}S) and siderite (Fe^{II}CO₃), and that Sb^V is reduced to Sb^{III} by magnetite and mackinawite, the former reaction taking place on a much longer timescale than the latter.

Experimental:

Magnetite^[6], mackinawite^[7] and siderite^[8] were synthesized in a glove box under anoxic conditions (< 2 ppmv O₂). They were reacted in 25 mM CaCl₂ with Sb(III) (Sb₂O₃ in 2M HCl) or Sb(V) (KSbOH₆ in 2M HCl or H₂O) ([Sb]=0.1mM; 40 or 3 g/L Fe₃O₄; 25 or 1.9 g/L FeS, 10g/L FeCO₃) in the pH range 4 to 9 and for time periods from 1h to 67d. The wet pastes resulting from centrifugation were put into XAS sample holders and stored in liquid nitrogen until measurement in a closed-cycle helium cryostat at 15K. XANES and EXAFS spectra at the Sb-K-edge 30.491 keV were collected in fluorescence mode using a 13-element Ge detector; an Sb foil was used for energy calibration.

Results:

Reaction of siderite with Sb(V) for up to 7 days at near-neutral pH resulted in no reduction of Sb(V) as observed by XANES (not shown). Sb(V) is adsorbed via inner-sphere surface complexation with Sb-Fe distances of 3.18 Å and 3.55 Å, characteristic of edge and corner-sharing arrangements between Sb(O,OH)₆ and Fe(O,OH)₆ octahedra (Fig. 1).

Reaction of mackinawite with Sb(V) caused a fast (~ 1 h) and complete reduction to Sb(III) and formation of a surface complex with a $\text{Sb}(\text{S})_3$ -structure, characterized by a (Sb-S) distance of 2.48 Å (Fig. 2).

Reaction of magnetite with Sb(V) also produced Sb(III), the extent of reduction being dependent on reaction pH and time. Under our experimental conditions antimony reduction was complete for $\text{pH} > 6.5$ and reaction times > 7 days (further depending on the solid/liquid ratio and loading with antimony). The reduction process is orders of magnitude slower than adsorption of Sb(V) to the surface, which is complete within 30 minutes. The resulting surface complex of Sb(III) is characterized by corner sharing of an $\text{Sb}(\text{III})\text{O}_3$ -pyramide with up to 6 $\text{Fe}(\text{O},\text{OH})_6$ -octahedra, a position else occupied by $\text{Fe}(\text{III})\text{O}_4$ tetrahedra in the magnetite-structure (Fig. 3). The identified structure of the Sb(III) surface complex is similar to the one found for As(III) on {111} faces of magnetite [9].

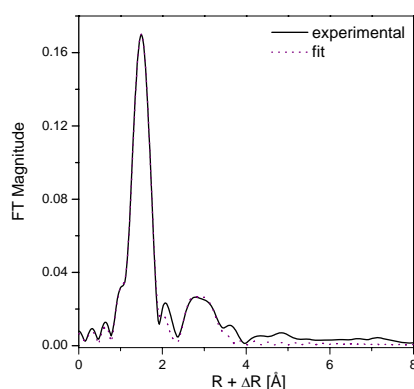


Fig. 1: Experimental FT and fit of Sb(V) sorbed on siderite

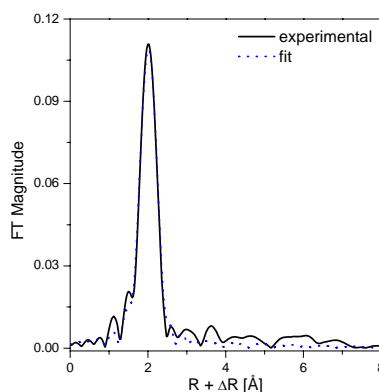


Fig. 2: Experimental FT and fit of Sb(III) on mackinawite

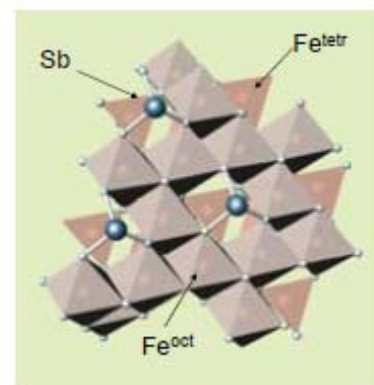


Fig. 3: Model of Sb(III)-complex on {111}-faces of magnetite

Conclusion:

The structure of the surface complexes of Sb(III) and Sb(V) on the surface of magnetite, mackinawite and siderite could be elucidated by shell fitting [10]. However, a number of questions remain open concerning the reduction mechanisms of Sb by magnetite and mackinawite. While Sb(V) is reduced by FeS over a wide pH range, it remains to be elucidated whether this reduction is due to oxidation of Fe^{II} or S^{2-} or a combination of both. It also remains open whether the lower reactivity of magnetite at low pH is solely due to (surface) oxidation of the mineral to maghemite or whether other mechanisms come into play.

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