

 ROBL-CRG	Experiment title: Identification of thioantimonate and thioantimonite XAS spectra in liquid samples	Experiment number: 20-01-709
Beamline: BM 20	Date of experiment: from: 29/01/2011 at 08:00 to 01/02/2011 at 08:00	Date of report: 27.01.2012
Shifts: 9	Local contact(s): Dr. Andreas Scheinost	<i>Received at ROBL:</i>
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Report:

The study was initiated in analogy to studies we have previously conducted at ESRF on thioarsenic species which have recently received increasing attention in the scientific community. We have shown that thioarsenites and thioarsenates can co-exist in solution and that actually trithioarsenite forms upon acidic dissolution of tetrathioarsenate, thus finally settling a decade-long debate about the sole existence of either one OR the other homologue series (SUESS et al., 2009). In our latest paper we reconciled why when analysing the same arsenite-sulfide solutions, trithioarsenite predominance is determined by XAS and dithioarsenate by IC-ICP-MS (PLANER-FRIEDRICH et al., 2010).

In general, much less is known about antimony compared to its notorious group 15 cohort arsenic. Thioantimony species have been reported in some key papers: Solubility studies with theoretical species stability calculations (HELZ et al., 2002; SPYCHER and REED, 1989; TOSSELL, 1994), an early XAS study (MOSELMANS et al., 2000) on dissolution of stibnite yielding a tetrathioantimonate, a multimeric Sb(V)thioantimonide, and a $Sb_2S_2(SH)_2$ species and EXAFS evidence for tetrathioantimonate occurrence in hydrothermal solutions (SHERMAN et al., 2000). No clear evidence for thioantimonites was reported. We have been able to detect two thioantimonates as predominant antimony species in geothermal waters in Yellowstone Nationalpark (assigned Sb-S1 and Sb-S2). Their retention times are comparable to those of the respective thioarsenates, which was why we initially assigned them somewhat arbitrary as mono- and dithioantimonate. Calculating S/Sb ratios yielded average ratios of 2 and 3 for Sb-S1 and Sb-S2, respectively, seemingly

identifying them as di- and trithioantimonate, while preliminary evidence from electrospray-MS showed spectra of tri- and tetrathioantimonate.

The primary goal of our studies this time was to determine fundamental XAS spectra (XANES and EXAFS) for aqueous thio-antimonate and thio-antimonite complexes and relate their structure to thioarsenic species already determined in our group as well as to structural investigations of different antimony (-sulfur) species (e.g. (FAWCETT et al., 2009; WOOD, 1989)). Mixes exposed to different redox-conditions were used to evaluate the formation mechanisms of Sb(III)- and Sb(V)-species and their importance for natural sulfidic systems. Furthermore we intended to clearly identify the two Sb-S-species already observed by IC-ICP-MS under natural conditions. A major motivation was furthermore to clarify, like for the thioarsenic species, the controversy whether the species in geothermal systems are thioantimonates or thioantimonites.

In comparison between XAS and IC-ICP-MS studies we finally assigned the two thioantimony species detected by AEC-ICP-MS in oxic synthetic antimonite-sulfide solutions to tri- and tetrathioantimonate based on their S/Sb ratios and structural characterization by XAS. XAS confirmed that the initial species formed under anoxic conditions from antimonite at a 10-fold sulfide excess is trithioantimonite. Trithioantimonite rapidly transforms to tetrathioantimonate in the presence of oxygen or to antimonite at excess OH⁻ versus SH⁻ concentrations, and escapes chromatographic detection. In natural geothermal waters, up to 30% trithioantimonate and 9% tetrathioantimonate were detected. Their occurrence increased at increasingly alkaline pH and with increasing sulfide and decreasing oxygen concentrations. Considering the large sulfide excess (100 to 10,000-fold) the proportion of thioantimonates formed under natural conditions is lower than expected from synthetic solutions. Together with the observed high thioarsenate concentrations (>80% of total arsenic), this indicates that in direct competition with arsenic for a limited source of sulfide, thioantimonates form less spontaneously than thioarsenates. Interactions of arsenic and antimony with sulfur can therefore be decisive for similarities or differences in their environmental behavior.

The results of this study at ESRF have already been published (Planer-Friedrich and Scheinost, 2011).

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