| | | |
|---|---|---|
| ROBL-CRG | **Experiment title:**<br>Identification of thioarsenate XAS spectra in liquid and solid samples | **Experiment number**:<br>20-01-680 |
| **Beamline**:<br>BM 20 | **Date of experiment**:<br>From: 27/07/2008 to: 30/07/2008 | **Date of report**:<br>23/12/2008 |
| **Shifts:**<br>9 | **Local contact(s)**:<br>Dr. Andreas Scheinost | *Received at ROBL:* |

Names and affiliations of applicants (* indicates experimentalists):

**E. Suess[1], G. Bernhard[2], WA. Gezahegne[1], BJ. Merkel[1], B. Planer-Friedrich[3], AC. Scheinost*[2,4]**

[1]Institute for Geology, TU Bergakademie Freiberg, 09599 Freiberg, Germany

[2]Institute for Radiochemistry, Research Center Dresden, 01314 Dresden, Germany

[3]Environmental Geochemistry, University of Bayreuth, 95447 Bayreuth, Germany

[4]ESRF-ROBL/CRG, 38043 Grenoble Cedex, France

## Report:

*Background.* In natural systems As and S often occur together and thus inter-elemental reactions and complex formations play a major role for mobility and toxicity of arsenic. There are controversies whether the As-S species occurring under reduced conditions are thioarsenites[1-4] or thioarsenates[4-7]. The recent study focused on obtaining X-ray Absorption Spectroscopy (XAS) data for thioarsenate standards already identified as such by XRD[5], indispensable for all further studies.

*Experimental.* The solid thioarsenate salts (mono-, di-, and tetrathioarsenate; pellets with 8.9 mg total As in 300 mg Boronitrite), and liquid and flash-frozen thioarsenate solutions (10 mM, pH $\approx$ 12) were subject to XAS experiments at the Rossendorf Beamline (BM20) in Grenoble, France. XAS spectra were collected at the As K-edge (11867 eV) at room temperature (liquids) and at 15 K (He-Cryostat; solids and flash-frozen samples) in absorption (Oxford ionization chamber) and fluorescence mode (Canberra 13-element Ge-Detector). The spectra were averaged, dead-time corrected, background subtracted and normalized using *SixPack*[8]. EXAFS shell fitting was performed using FEFF 7.02 and WinXAS 3.1[9].

*Results.* The As-O and As-S coordination numbers (Tab. 1) confirmed the structure as the expected mono- ($AsO_3S^{3-}$), di- ($AsO_2S_2^{3-}$), and tetrathioarsenates ($AsS_4^{3-}$). The As-O bond distances of 1.69 to 1.70 Å are comparable with those stated for arsenates (e.g. scrondiotite 1.60 Å[10]), and are easily distinguishable from those for arsenite at 1.78 Å. The As-S distances with 2.13 to 2.18 Å were clearly shorter than those published for arsenite-sulfide minerals with 2.24 to 2.34 Å[10]. As expected, no As-O bonding was determined in tetrathioarsenate, which is fully coordinated with S. As the extent of sulfide-groups increases, the position of the absorption edge shifts systematically and linearly towards lower energies compared to that of arsenate. The structural data for the individual solid and liquid samples, measured at room temperature or at 15 K, did not show obvious differences, suggesting that the aqueous complexes have similar structures as the XRD-identified solids and are stable in solution.

**Table 1: As-K edge energies and EXAFS fit results of thioarsenate standards**

| **Thioarsenate samples** | **$E_0$ [eV]** | **O coordination** | | | **S coordination** | | | **$\Delta E_0$ [eV]** | **$\chi^2_{res}$ %** |
|---|---|---|---|---|---|---|---|---|---|
| | | **CN** | **R[Å]** | **$\sigma^2$[Å$^2$]** | **CN** | **R[Å]** | **$\sigma^2$ [Å$^2$]** | | |
| Mono- (liquid, 15K) | 11871.0 | 2.9 | 1.70 | 0.0007 | 0.9 | 2.17 | 0.0001 | 6.0 | 23.9 |
| Mono- (liquid, RT) | 11871.0 | 2.8 | 1.70 | 0.0025 | 0.7 | 2.13 | 0.0013 | 4.8 | 23.4 |
| Mono- (solid) | 11871.0 | 2.6 | 1.70 | 0.0016 | 0.7 | 2.14 | 0.0014 | 6.2 | 20.2 |
| Di- (liquid, 15K) | 11870.0 | 2.0 | 1.70 | 0.0015 | 1.7 | 2.15 | 0.0007 | 6.4 | 22.3 |
| Di- (solid) | 11870.0 | 1.6 | 1.70 | 0.0007 | 1.9 | 2.17 | 0.0022 | 8.2 | 17.7 |
| Tetra- (liquid, 15K) | 11869.5 | | | | 4.5 | 2.18 | 0.0029 | 9.8 | 25.3 |
| Tetra- (liquid, RT) | 11869.0 | | | | 4.1 | 2.18 | 0.0030 | 8.8 | 15.0 |
| Tetrathioarsenate (solid) | 11869.5 | | | | 3.9 | 2.17 | 0.0025 | 7.8 | 16.9 |
| CN: coordination number, error ± 25 %, R: Radial distance, error ±0.01 Å, $\sigma^2$: Debye-Waller factor, error ±0.0005 Å$^2$ | | | | | | | | | |

*References.*

(1) Wood, S.et al. *Geochem. Trans.* **2002**, *3*, 31.
(2) Wilkin, R. T.et al. *Geochem. Trans.* **2003**, *4*, 1.
(3) Beak, D. G.et al. *Environ. Sci. Technol.* **2008**, *42*, 1643.
(4) Helz, G. R.et al. *Geochim. Cosmochim. Acta* **2008**, 72, 4457.
(5) Wallschlager, D.et al. *Anal. Chem.* **2007**, *79*, 3873.
(6) Stauder, S.et al. *Environ. Sci. Technol.* **2005**, *39*, 5933.
(7) Planer-Friedrich, B.et al. *Environ. Sci. Technol.* **2007**, *41*, 5245.
(8) Webb, S. M. *Phys. Scr.* **2005**, *T115*, 1011.
(9) Ressler, T. *J. Synchrot. Radiat.* **1998**, *5*, 118.
(10) Foster, A. L. *In:* Welch, A. H. & Stollenwerk, K. G., Eds.; Kluwer Academic Publishers: Boston, 2003; 27.