

	Experiment title: X-ray Absorption Spectroscopy investigations on environmental colloids (Fe matrix)- Interaction with heavy and hazardous elements (As, Pb)	Experiment number: 20_01_015
Beamline: BM 20	Date of experiment: from: 23/02/2000 to: 28/02/2000 01/09/2000 03/09/2000	Date of report: 21/03/2001
Shifts: 24	Local contact(s): Dr. Reich, Tobias	<i>Received at ROBL:</i> 27/03/2001
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Report:

Highly mineralised, red-coloured solutions are formed by weathering of ore particles which causes acid rock drainage (ARD). Major cationic components (>1 g/l) of the ARD solution under study were Zn, Fe, Mg, Al, and Mn. Important minor components were toxic heavy metals, e.g. As, Cu, Pb, and Cd. This XAS investigation deals with the in-situ characterisation of the near-order surrounding of As in ARD solutions containing colloidal particles as well as with the determination of the particle mineralogy.

Experimental. XAFS data were recorded at the Rossendorf Beamline (ROBL) at the ESRF in Grenoble. The data were treated using the EXAFSPAK software. Theoretical back-scattering phase and amplitude functions used in data analysis were calculated using FEFF6.

Table 1: Chemical analysis of the ARD samples.

Sample	Fe [M]	As [M]	[As]/[Fe]
Raw sample	0.080	5.2×10^{-3}	0.065
5 μ m filtrate	0.070	4.8×10^{-3}	0.068
1 kD retentate	0.368	0.080	0.217
1 kD filtrate	0.054	1.4×10^{-3}	0.026
	Fe [mg/g]	As [mg/g]	
Precipitate	324	68	0.210

Results and Discussion. The Fe EXAFS data (not shown here) of the freshly formed colloids suggest that an amorphous Fe phase dominates the colloidal matrix. On the other hand, the EXAFS oscillation of the precipitate shows the presence of a more crystalline Fe phase. The data of the 5 μ m filtrate indicate an intermediate between these two stages. The Fe-Fe distance of ~ 3.60 Å suggests a relatively close relationship between the ARD samples and the jarosite. Considering the REM/EDX analysis of particle agglomerates on a Nucleopore filter [1] and the EXAFS results, we assume that the colloidal particles represent an intermediate in the precipitate formation process having a mineralogy similar to that of the precipitate, i.e., consisting of H-jarosite and amorphous Fe phases. The As K-edge XANES data, the intensive white line and the As K-edge energies of 11875 eV indicate the +5 oxidation

state of As in all ARD samples. Fig. 1 depicts the EXAFS spectra measured at the As K-edge.

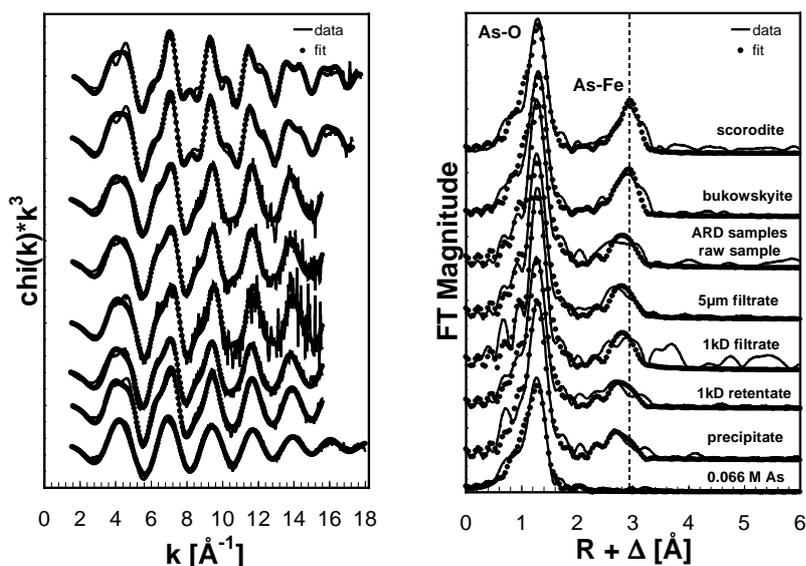


Fig. 1. Experimental EXAFS oscillations and corresponding Fourier Transforms of the model compounds and the ARD fractions at the As K-edge.

Table 2: Summary of the EXAFS structural parameters. In parenthesis XRD values [2].

Sample	Shell	N	R [Å]	σ^2 [Å ²]
Scorodite (mineral) FeAsO ₄ ·2H ₂ O	As-O	5.0 (4)	1.68 (1.68)	0.0027
	As-Fe	3.7 (4)	3.34 (3.33)	0.0048
Bukowskyite (mineral) Fe ₂ AsO ₄ SO ₄ OH·7H ₂ O	As-O	5.2	1.68	0.0025
	As-Fe	3.2	3.33	0.0042
ARD solution raw sample	As-O	4.3	1.69	0.0013
	As-Fe	2.2	3.28	0.0047
ARD solution (5 μm filtrate)	As-O	4.5	1.69	0.0017
	As-Fe	2.2	3.27	0.0046
ARD solution (1 kD filtrate)	As-O	4.4	1.68	0.0011
	As-Fe	1.9	3.26	0.0032
ARD solution (1 kD retentate)	As-O	4.7	1.69	0.0021
	As-Fe	2.5	3.29	0.0067
ARD solution, precipitate	As-O	5.0	1.68	0.0022
	As-Fe	4.5	3.28	0.0110
0.066 M As solution	As-O	5.2	1.68	0.0025

Taking the EXAFS results alone (Fig. 1, Tab. 2), one might draw the conclusion that arsenate interacts with the solid iron hydroxy sulfates in a similar way in all fractions. The pronounced As-Fe contribution at 3.28 Å (see Fig. 1) measured in the ARD raw sample and the different filtrates shows that arsenate is bound to the colloids (iron hydroxy sulfate) in a similar way to that of arsenate onto ferrihydrite, i.e., by inner-sphere surface complexation [3]. The picture is different for the precipitate. The relatively large arsenic content and the small particle surface of the precipitate make surface complexation unlikely. A better explanation is an epitaxial growth of a scorodite phase within/on the iron hydroxy sulfate. Relaxation processes of the As-Fe bond occurring in such small scorodite zones could explain the atypical As-Fe distance of 3.28 Å.

References

- [1] Zänker, H., et al., submitted to Appl. Geochem.(2001).
- [2] Hawthorne, F.C., Acta Cryst. B **32**, 2891 (1976).
- [3] Waychunas, G.A., et al., Geochim. Cosmochim. Acta **57**, 2251 (1993).