

DIRECT AND IN-SITU SPECIATION OF ARSENIC IN MICROBIAL MATS AND SEDIMENTS USING X-RAY ABSORPTION SPECTROSCOPY

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The mobility and toxicity of arsenic (As) is related to its speciation (defined as oxidation state and coordination environment). The speciation of arsenic in natural solids (such as sediments) and mixed solids/liquids (such as microbial mats) is usually determined via indirect methods requiring significant sample preparation that may result in alteration or redistribution of As species. We have employed X-ray absorption spectroscopy (XAS) (which includes X-ray absorption near edge spectroscopy [XANES] and extended X-ray absorption fine structure spectroscopy [EXAFS]) to determine As species in ore material from the Lava Cap gold mine and in tailings and microbial mats from nearby Lost Lake. Two tailings dams existed downgradient from the Lava Cap mine; the older, upgradient dam failed in Dec. 1998, causing an estimated 20,000 yd³ of tailings to be deposited in the feeder creek to Lost Lake and in the lake itself (see abstract by R. Ashley, et al. [this conference]). We examined mine tailings that were exposed to air since the dam failure (“dry tailings”) and mine tailings that were released by the dam failure, and submerged in Lost Lake (“submerged tailings”). We also sampled an extensive, Fe-stained microbial mat that develops seasonally in a drainage produced from seepage below the intact tailings dam that created Lost Lake. At this site, seepage from below the tailings dam has influenced water quality for many years (Table 1).

Table 1. Representative Analyses of Dam Seepage Water, Showing Seasonal Variation in Water Chemistry.

Date	pH	C*	As(III)	As(V)	Filtered As	Particulate As	Fe(III)	Fe(II)
		μS	μg/l			μg/l		μg/l
3/24/99	7.84	372	3.1	437	471	239	7.6	< 2.4
8/24/99	8.12	362	6.1	1334	987	98	4.1	4.4
Analysis Method			----HG-CT-AAS----		-----ICP-MS-----		-----Ferrozine-----	

*conductivity, measured in microsiemens (μS)

XAS Analysis of Ore and Tailings. XAS analysis of Lava Cap ore shows that As is associated with arsenopyrite (FeAsS) and arsenian pyrite (FeS₂), in which it has a nominal valence of 0 (edge position coincident with native As). Sulfide minerals are in general very insoluble, so if As remains in these minerals, it should be less mobile than oxidized forms. Simulated *in vitro* digestion studies also suggest that arsenic in sulfide minerals has low bioavailability [1]. However, we find evidence that a significant amount of the As is converted to oxidized forms both types of tailings. We find two species of As in dry and submerged tailings: Reduced As in pyrite and/or arsenopyrite (10-20% in dry tailings, and 70-100% in submerged tailings), and oxidized As [As(V) in dry tailings or As(III) in submerged tailings] that is adsorbed onto mineral surfaces.

Submerged tailings sampled from the same site twice over a one year period showed evidence for progressive oxidation of reduced As to As(III) (Fig. 1).

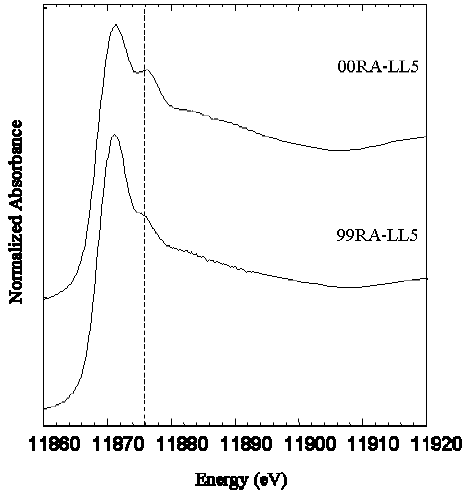


Figure 1. As-XANES spectra of samples collected in 1999 and 2000 from the same site (LL5). The higher energy shoulder is indicative of As(V) and is of greater relative magnitude in the year 2000 sample.

Arsenic-EXAFS spectra of dry and submerged tailings suggest that the process of As oxidation/mobilization is more rapid when tailings are exposed to air for extended periods of time. Figure 2 shows EXAFS spectra (a) and Fourier transforms (b) of model compounds and tailings. The dry tailings sample has a higher proportion of oxidized As (as As(V), although the fit is not shown) than do the submerged tailings. Also, the submerged tailings EXAFS spectrum is very similar to the spectrum of the arsenopyrite model compound.

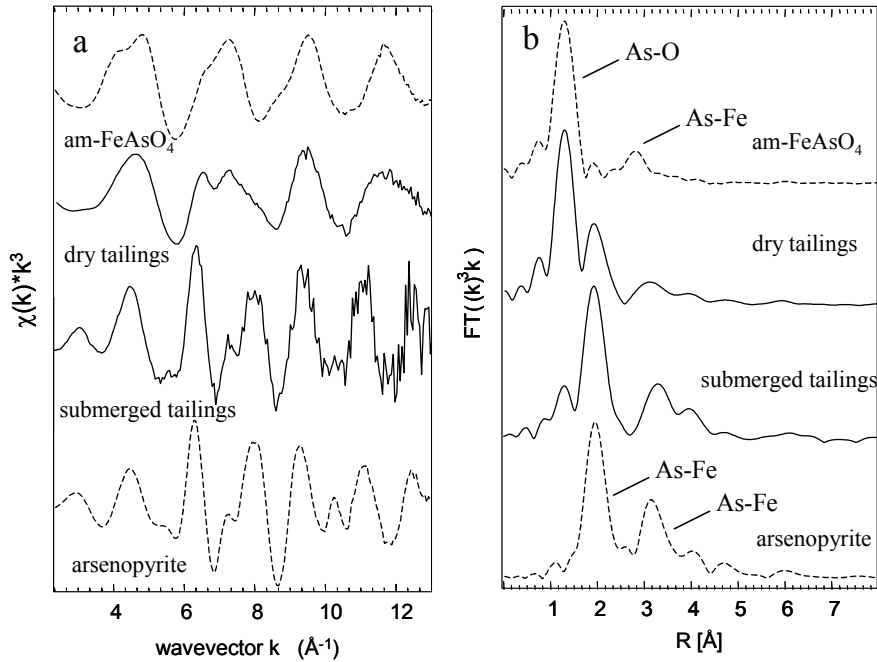


Figure 2. Arsenic EXAFS spectra (a) and Fourier transforms (b) of model compounds (X-ray amorphous ferric arsenate and arsenopyrite, dotted lines) and tailings samples.

XAS Analysis of Microbial Mats. Fluorescence microscopy (not shown) and scanning electron micrographs (Fig. 3 a and b) demonstrate that the Fe-accumulating mat sampled below the intact tailings dam is primarily composed of several types of sheath-forming bacteria, with the predominant species being *L. ochracea*. According to van Veen et al. [2] this Fe-storing sheathed bacterium is the most widespread of the nutrient-poor-loving (oligotrophic) species in the *Sphaerotilus-Leptothrix* genus. This genus is composed of gram-negative, obligately aerobic heterotrophs, many of which have the ability to induce the oxidation of reduced Mn and/or Fe species.

The amount of As in the oven-dried *Leptothrix* mat was 5140 mg/kg (as determined by ICP-AES after digestion in aqua regia). This amount is far in excess of the arsenic concentrations measured in the water at this site (see Table 1). Arsenic (V) was the only species detected in the mat by XAFS, even though As(III) is the predominant species in the waters in contact with the mat (Table 1).

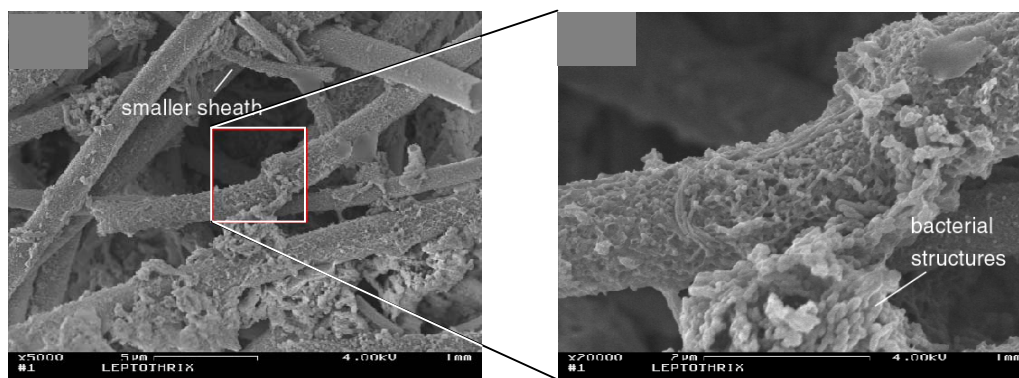


Figure 3. Scanning electron micrographs of the air-dried *Leptothrix* microbial mat, showing at least two sheath morphologies and variable sheath encrustation (a), and what appears to be a colony of non-sheath forming bacteria. Individual *Leptothrix* bacteria live within the sheaths and are not visible. Scale bar: 5 μm (a) and 2 μm (right).

Extended X-ray absorption fine structure (EXAFS) spectra of the *Leptothrix* microbial mat material is compared with the spectrum of a synthetic sample of arsenic sorbed on Fe-oxyhydroxide in Fig. 4a. Phase-uncorrected Fourier transforms (solid lines; add 0.5 \AA for true distances) and the non-linear least squares fits (dotted lines) are plotted in Fig. 4b. The mat EXAFS spectrum and Fourier transform are qualitatively and quantitatively very similar to those of the model As(V) sorption sample. The fits verify that As in this mat is adsorbed to Fe-oxyhydroxide. The predominant sorption complex is a bidentate species composed of 1.5 ± 1.0 Fe atoms at an average distance of $3.30 \pm 0.02 \text{ \AA}$ (see model in Fig. 4 b). A minor component of $< 0.5 \pm 1.0$ Fe atoms at $2.81\text{-}2.89 \pm 0.02 \text{ \AA}$ could also be fit to the data. This component may represent a monodentate, edge-sharing sorption complex, as has previously been suggested [3]. Similar results were obtained from microbial mats sampled from another site near Lost Lake.

Conclusions. The fate of arsenic associated with tailings and microbial mats is not well understood. A typical assumption is that in the presence of oxygen, arsenopyrite and

arsenian pyrite will weather to form Fe-oxyhydroxide with sorbed As, effectively limiting its mobility if oxic conditions are maintained. Precise mechanisms for this process have not been determined, but EXAFS analysis generally confirms this hypothesis in tailings exposed to air since the dam failure. Of particular interest at the Lost Lake site is the fate of As in submerged tailings, in which conditions are generally anoxic. Processes of As mobilization are not well understood under these conditions. EXAFS analysis indicates minimal oxidation of reduced As from submerged tailings since the dam failure.

The As-rich *Leptothrix* microbial mat has the potential to release arsenic (accumulated during the dry season) during winter storm events, when the mat is usually washed away. Arsenic(V) in the mats is sorbed (adsorbed and/or coprecipitated) to Fe-oxyhydroxides, which suggests that changes in stream chemistry variables such as (pH, total dissolved solids, or redox state) could result in the partial mobilization of this pool of arsenic via desorption of As or dissolution (with or without concomitant reduction) of Fe-oxyhydroxides. The EXAFS spectral signature of As(V) sorbed to biogenic Fe-oxyhydroxide is indistinguishable from As(V) sorbed to synthetic Fe-oxyhydroxide, and indicates contributions from bidentate corner-sharing and possibly from monodentate edge-sharing sorbed As(V).

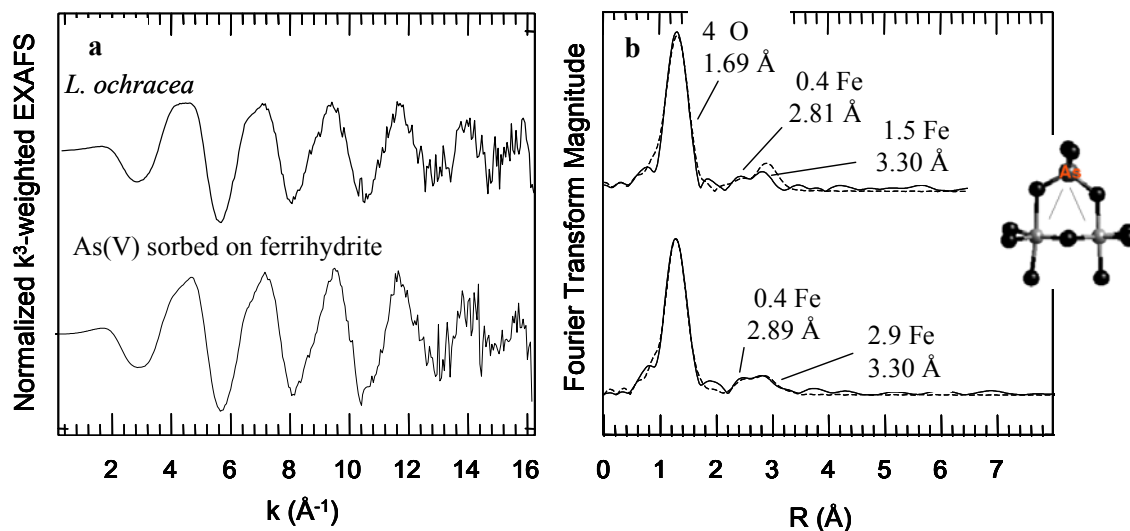


Figure 4. EXAFS spectra (a) and Fourier Transforms (b) of *Leptothrix* microbial mat material compared to a model compound of As(V) sorbed on ferrihydrite.

References

1. Davis, A., Ruby, M. V., Bloom, M., Schoof, R., Freeman, R., and Bergstrom, P. D. (1996) Mineralogic Constraints on the bioavailability of arsenic in smelter-impacted soils. *Env. Sci. Technol.* **30**, 392-399.
2. van Vleen W L, Mulder E G, Deinema M H. (1978) The *Sphaerotilus-Leptothrix* group of bacteria. *Microbio Rev* **42**, 329-56.
3. Manceau A. (1995) The mechanism of anion adsorption on iron oxides: Evidence for the binding of arsenate tetrahedral on free Fe(O,OH)₆ edges. *Geochim Cosmochim Acta* **59**, 3647-53.