

SYNCHROTRON-BASED SPECTROSCOPIC STUDIES OF METAL SPECIES IN SOLID PHASES: THE CASE OF ARSENIC

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The production of high-energy (1 KeV to 40 KeV) x-radiation at synchrotron laboratories around the world has enabled the spectroscopic analysis of core level electronic transitions and electronic scattering processes in trace (< 1000 ppm) metal and metalloid atoms as they are found in heterogeneous natural materials (e.g., soils, sediments, plants, and microbial mats). Environmental geochemists interested in arsenic (As) have found this information of particular interest, because the oxidation state(s) and chemical coordination of As can be studied in materials that have been difficult to study using other techniques. The primary technique used for the past 10 years has been bulk X-ray absorption fine structure spectroscopy (XAFS), but this method is becoming increasingly augmented/supplanted by microbeam XAFS and X-ray fluorescence techniques.

X-ray absorption fine structure (XAFS) spectroscopy has characteristics that make it the technique of choice for the analysis of environmentally-relevant solid materials:

- Can be “element-specific”;
- Low detection limits (relative to lab-based X-ray fluorescence and electron microprobe techniques);
- Species can be analyzed under ambient or sample-specific conditions (presence/absence of O₂, frozen, wet, or dry);
- Direct information about As oxidation state;
- Direct information about As coordination environment (number and distance of neighboring atoms) [1].

An XAFS spectrum is collected by directing a beam of X-rays (finely collimated, or just unfocused white light) on a sample. The X-ray beam can vary in size from 10 microns (μm) to 20 millimeters wide. The former technique, using very small, finely collimated and focused X-ray beams to analyze small samples, is called spectromicroscopy, and is used to analyze very small samples or to obtain spatially-resolved XAFS information from a larger sample.

Data collection for both micro- and macrobeam XAFS is similar. The energy of the X-ray beam is changed stepwise using a crystal monochromator. As the beam steps higher in energy, the attenuation of X-ray beam intensity (absorption) by the sample or the emission of X-rays from the sample (fluorescence, which is directly proportional to absorption) is recorded at each point. A background spectrum is recorded for the first 20-30 electron volts (eV). At a unique energy position (for As, this position ranges from 11867 eV to 11875 eV, depending on the As oxidation state), a rapid increase in absorption is measured, which declines to about ½ the maximum intensity. The rapid increase in absorption (Fig. 1) is attributed to the ejection of core-level electrons from the arsenic atom, and the decrease is attributed to the electron cascade resulting from the replacement of the empty core hole. The energy needed to eject an electron is quantized, leading to the element-specific absorption edge energy positions that are critical for

XAFS data collection. The NEXAFS or XANES region of the XAFS spectrum is defined as beginning just before the absorption edge and ending about 50 eV past the edge. Quantitative information about oxidation state and qualitative information about chemical speciation can be obtained from XANES data (Table 1). Depending on time constraints in data collection, As-XANES spectra can be collected from materials with as little as 2 ppm As. Routine As concentrations in samples used for XANES spectra collection are in the range of 10-100 ppm. Past the NEXAFS/XANES region, the absorption spectrum is collected for approximately 1000 eV in the extended XAFS (EXAFS) region. The EXAFS data provide quantitative information on the chemical coordination of As in the sample.

Table 1. Regions of the As-XAFS Spectrum, Dominant Processes in Each Region, and Chemical Information Obtained from Each Region.

Region	Energy Range	Inferred Electronic Process	Dominant Scattering Process	Information obtained
Pre-edge	11840-11860	background		
XANES	11860-11890	Core-hole ejection; Electronic transitions	Multiple scattering	-Valence (quant.) -Coordination environment (qual.)
EXAFS	11890-12890	Electron cascade--post core hole ejection	Single scattering	-Valence (qual.) -Coordination Environment (quant.)

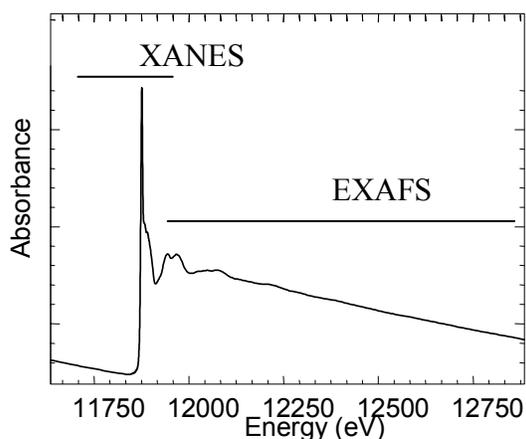


Figure 1. XAFS Spectrum of Scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$.

As-XANES Analysis

Determination of As valence state(s) by XAFS is possible because the resolution of the crystal monochromators used to vary the X-ray energy is on the order of 1 eV, and the transitions between the nominal valence states of As (“absorption edges”) are on the order of 2-3 eV. If multiple species of As are present, the XAFS spectrum will show a superposition of two or more absorption edges (Figure 1). The relative magnitude of each species’ edge is related to the amount of that species present in the sample, and is estimated by fitting the sample spectrum to a library of model

compound spectra until a best fit is obtained. Within the same oxidation state, the shapes of XANES spectra vary as a function of chemical species.

Almost any chemical species will serve as an adequate representative for quantitative determination of oxidation state by the least-squares method. However, determination of chemical speciation by XANES alone is limited by the need for an

extensive library of model compounds, but even more importantly, by the inherent similarity of XANES spectra of As species in similar (but not identical) chemical environments. Figure 2 shows that the XANES spectra of crystalline scorodite ($\text{FeAs(V)O}_4 \cdot 2\text{H}_2\text{O}$) is almost indistinguishable from that of As(V) sorbed onto amorphous iron oxide (or hematite, which is not shown). However, the XANES spectrum of As(V) sorbed onto Mn oxide is readily distinguished from As(V) sorbed onto Fe oxide. These factors must be taken into consideration when drawing conclusions about chemical coordination based on XANES data alone.

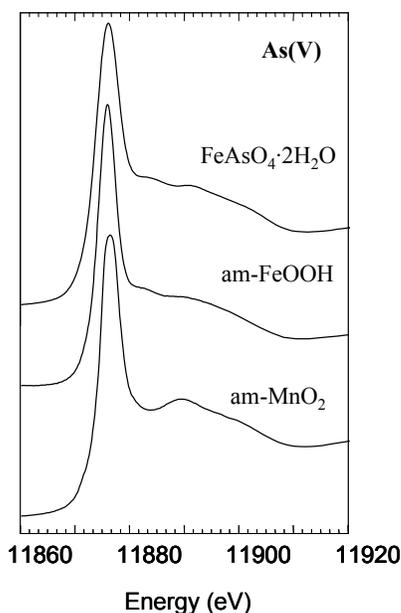


Figure 2. Comparison of As(V)-XANES spectra of different chemical species

As-EXAFS Analysis

The determination of As chemical species is more complicated than measurement of valence state(s), and also demands a more concentrated sample (typically 300 - > 1000 ppm), or significantly more time for data collection. The raw EXAFS spectrum (Fig 1) is converted from energy space to momentum space (k) using Planck's relation [2] and the spectrum amplified by k^3 (Fig. 3a). The spectroscopic process that gives rise to the EXAFS spectrum is scattering between each As (absorber) atom in the sample and nearby elements called backscatterers. Although the scattering process affects all atoms, only scattering within a 7 Å diameter typically affects the EXAFS spectrum. The interaction between multiple absorber-backscatterer pairs of atoms appears in the EXAFS

spectrum as a superposition of sinusoidal oscillations that can be separated in angstrom space using a Fourier transformation (Fig. 3b). For visual analysis, the position of FT peaks must be corrected for atomic phase shift; this results in an approximate +0.5 eV shift in peak position for arsenic samples when the primary scattering atom is oxygen. In quantitative analysis the shift is determined by more accurate methods.

EXAFS spectra are useful for quantitative analysis of chemical speciation even when XANES are not because EXAFS spectra are more sensitive to changes in the positions of nearby atoms, even of the same type. For example, the EXAFS spectra and Fourier transforms of As in scorodite, X-ray amorphous ferric arsenate, and As(V) sorbed on goethite are all easily distinguished (Fig. 3b).

A non-linear, least-squares routine is used to fit the sample EXAFS spectrum with a spectrum generated from a mixture of theoretical absorber-backscatterer pairs specified by the analyst. A necessary simplification is that atoms of the same identity at similar distance are grouped into "shells". For example, As(III) is surrounded by a shell of 3 oxygen atoms/hydroxyl molecules with an average radial distance of 1.77-1.81 Å from the central As(III) atom. In contrast, As(V) is surrounded by a shell of 4 oxygen atoms/hydroxyl molecules with an average distance of 1.69-1.71 Å from the central As(V) atom. A comparison of the quantitative fits to the spectra shown in Fig. 3 is given

in Table 2, and demonstrates that EXAFS analysis can distinguish between As(V) in the 3 coordination environments.

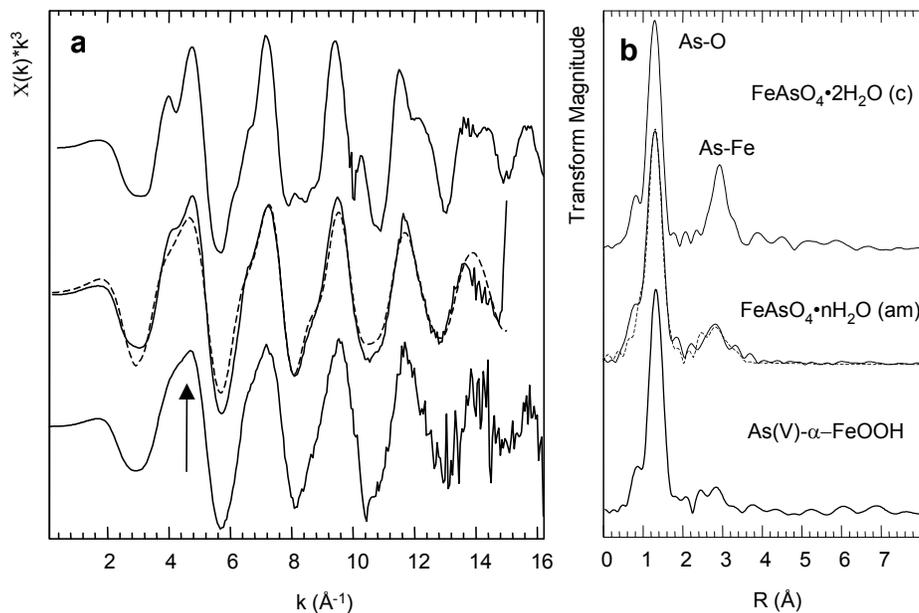


Figure 3. (a) k^3 -weighted EXAFS spectra and Fourier transforms (b) comparing As(V) coordination in increasingly ordered systems. The non-linear, least squares fit to amorphous ferric arsenate is plotted as the dotted line.

Table 2. Comparison of non-linear, least-squares refinement of Arsenic (V) species in crystalline scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), X-ray amorphous ferric arsenate, and As(V) sorbed to goethite. EXAFS analysis can distinguish between these forms even when XANES analysis cannot.

Sample	1 st Shell	Radial distance	2 nd and higher Shells	Radial Distance
Scorodite (XRD data*)	4.0 O	1.68 Å	4 Fe 1 As	3.35 Å 4.21 Å
Scorodite	6.4 ± 1 O	1.68 ± 1 Å	4 Fe 1 As	3.36 ± 0.01 Å 4.20 ± 0.06 Å
“amorphous” Ferric Arsenate	5.5 ± 1 O	1.69 ± 1 Å	1.6 Fe 0.4 Fe	3.33 ± 0.01 Å 3.63 ± 0.01 Å
As(V)- α -FeOOH	5.1 ± 1 O	1.69 ± 1 Å	2.9 ± 1 Fe 1.5 ± 1 Fe	3.30 ± 0.03 Å 3.50 ± 0.03 Å

* values generated from crystal structure report [3]. Error of structure refinement not given.

References

- [1] Brown, G. E., Jr. (1990) *Annual Review of Earth and Planetary Science* **18**, 387-447.
- [2] Sayers, D. E. & Bunker, B. A. (1988) in *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*, eds. Koningsberger, D. C. & Prins, R. (John Wiley and Sons, New York).
- [3] Hawthorne, F. C. (1976) *Acta Crystallographica B* **32**, 2891-2992.

