United States
Environmental Protection
Agency

Technical Review Workgroup for Metals and Asbestos: Bioavailability Committee. Mineralogical Report. XAS Data and Linear Combination Fitting Results

Bradley W. Miller and Kirk G. Scheckel

13 August 2012

Introduction

To enhance our understanding and capabilities to protect human health and safeguard the natural environment, the application of molecular-level spectroscopic techniques that are highly sensitive and non-destructive to sample integrity would provide definitive answers to complex environmental questions. One such atomic-level technique, X-ray absorption spectroscopy (XAS), works by bombarding an element of interest with a beam of high-energy particles from a synchrotron radiation source to excite and expel outer-shell electrons of the particular element of interest. When the outer-shell electrons are expelled, they emit an energy called fluorescence that can be measured by computer-controlled detectors. The data collected by the detector yield characteristic spectra that provide information such as oxidation state, number and type of nearest neighboring atoms, coordination environment, and interatomic bond distances. XAS can be used to probe most phases of matter including crystalline or amorphous solids, liquids, and gases thus making XAS one of the most versatile research tools to fully investigate the molecular nature of a wide variety of substances. XAS is an in-situ technique meaning one can analyze samples taken directly from the field without any alterations that may skew true results. This type of research enhances our understanding of the fate and transport of toxic elements in the environment.

X-ray absorption spectroscopy (XAS) has been used in many different studies to examine contaminates such as Pb in soils (Cotter-Howells et al., 1994, 1999; Ryan et al., 2001; Scheckel and Ryan 2004). The use of XAS can determine the speciation of element and quantify via comparison to reference spectra with statistical analyses such as linear combination fitting (LCF) or principle component analysis (PCA) to predict the mineralogical identification of the element (Beauchemin et al., 2002; Scheinost et al., 2002; Scheckel and Ryan, 2004). Speciation refers to its chemical form or species. This includes its redox state and physicochemical characteristics that are relevant to bioavailability. This information can be used in conjunction with additional experiments to predict the reaction of an element of interest in the environment or human body. The speciation and bioavailability of a metal play a significant role in the risk assessment of contaminated media.

This mineralogical report contains the result of XAS analyses with LCF predictions of the As minerals present from nine samples including residential soil, orchard soil, an agricultural soil and mining wastes. XAS analyses have been performed on more than 11 reference arsenic minerals and have been included in this study. The minerals used for the LCF predictions include the As minerals most commonly found under oxidizing and reducing conditions in soil environments and at the sites where the materials were collected.

Materials/ Methods

X-Ray Absorption Spectroscopy

X-ray absorption spectroscopy data were collected on samples from nine sites at the Materials Research Collaborative Access Team 10-BM beamline, Advanced Photon Source (Argonne National Laboratory). All samples were fractured with a mortar and pestle, passed through a 250 µm sieve, pressed into a 1 cm pellet, and mounted on Kapton tape. Data was collected using a 4-element Vortex florescence detector with several layers of aluminum foil shield to suppress florescence from other elements such as iron in the samples. Arsenic concentrations < 20 mg As kg^{-1} were determined to be below the detection limit of the Vortex detector in our experiments. Three As K_{α} (11874 eV) spectra were collected in fluorescence mode at room temperature for every soil with a NaAs(V) reference sample for calibration.

Data analysis was conducted using Athena software (Ravel and Newville 2005). Each replicate scan was calibrated against the NaAs(V) reference (11874 eV), merged, normalized, and converted to k space. Linear combination fitting (LCF) was used to identify the As species in each soil samples. The LCF models were performed using the normalized, derivative, and chi(k) spectra of the soil samples and reference standards. There were 14 reference minerals included in the LCF models (Table 1). The reference minerals include a mix of synthetic and natural minerals received from the Smithsonian National Museum of Natural History. The XAS spectra of the 14 reference minerals are shown in Figure 1. The LCF models predicts the As speciation in each soil as percentages of the reference minerals.

The results of the LCF analyses generate a model with the best fit (indicated by the lowest R-factor and reduced chi square values). The pH and elemental concentration of Method 3051a extractable elements in each sample was consulted when assessing the LCF predictions of As minerals present. In some cases, the LCF model predicted mineral phases unlikely to be the present. If the LCF model predicted As minerals that were not appropriate (e.g. Yukonite was predicted but 0 mg Ca kg^{-1} soils was reported from 3051a extractions and sample pH was very acidic) then the mineral phase is very unlikely to be present. Therefore, LCF models were perform again without the predicted mineral (Yukonite in this example) and the LCF model was repeated.

Results and Discussion

XAS Analyses

The As XAS spectra, both normalized and derivative data, are found in Figure 2. Analyses of the samples collected from surface soil horizons or from mining activities had strong peaks at binding energies around 11875 eV. This demonstrates that As(V) was the dominant As oxidation state in the samples. The best results of the LCF model predictions (indicated by the lowest R- factor and reduced chi square values) that most samples are dominated by arsenate sorbed to ferrihydrite or other iron minerals (Table 2a). The LCF models also predicted the concentrations of As minerals in each sample (Table 2b).

The LCF predicted that most samples contaminated with pesticides were dominated by As(V) sorbed to ferrihydrite (Table 1). Our synthetic As(V) sorbed to ferrihydrite has a strong peak around 11874.5 eV (Figure 1) which corresponds to the peaks in the samples (Figure 2). Many soils in the US are moderately to highly weathered. Therefore, these soils have higher concentrations of secondary minerals like kaolinite (alumina silicate minerals) and Fe-oxi(hydr)oxide precipitates like ferrihydrite. Most of the finely sieved reddish brown or yellowish samples appear to be dominated with Fe-minerals or Al-minerals respectively. Arsenic has a high affinity for Fe minerals. Thus, the LCF prediction that most of the samples that were contaminated with arsenical pesticides are bound to ferrihydrite was expected and is supported by previous research.

The samples collected from or affected by mining sites have more than one As species present and from less common As minerals. Generally, As mineral with arsenite have strong peak at 11871 eV, and As(III)-S bonds are formed around 11867 eV (Figure 2). Sample IKJ 583 with significant concentrations of Pb and S were predicted to have minerals with these elements, Beudantite ($PbFe^{3+}_3(AsO_4)(SO_4)(OH)_6$). Scorodite and orpiment were among the most abundant phases predicted in soils after As(V) sorbed to ferrihydrite (Table 2). The LCF model predicted that the sample Asarco-Ruston contained the mineral Lollingite ($FeAs_2$). This mineral is typically found in highly reducing environments or as an ore component.

Brief Conclusions

All of the samples were collected from oxidized environments, are dominated by the more stable As(V) phases and stable iron minerals. Only the samples from mine operations had reduced As minerals present and at concentrations less than 400 mg kg^{-1} soil. The few samples that had high concentrations of reduced As minerals, thus have the potential to be oxidized and leach As, were taken directly from or affected by mining activities.

Planned work

New As minerals, are being added to the pool of reference standards used during the LCF modeling (Table 1). These include synthetic yukonite, mimetite ($Pb_5(AsO_4)_3Cl$, an analogue of the pesticide once widely used), As(V) and As(III) adsorbed to synthetic Al minerals will be analyzed in the summer of 2012. If the new binding energies (E_0) of the synthetic minerals falls within 3 eV of the E_0 of the new reference materials, we will repeat the LCF model with the new reference minerals.

Works Cited

Beauchemin S, Hesterberg D, and Beauchemin M. 2002. Principal component analysis approach for modeling sulfur K-XANES spectra of humic acids. Soil Sci Soc Am J 66:83-91.

Cotter-Howells JD, Champness PE, Charnock JM, and Pattrick RAD. 1994. Identification of pyromorphite in mine-waste contaminated soils by ATEM and EXAFS. Eur J Soil Sci 45:393-402.

Cotter-Howells JD, Champness PE, and Charnock JM. 1999. Mineralogy of Pb–P grains in the roots of Agrostis capillaris L-by ATEM and EXAFS. Mineral Mag 63:777-89.

Prietzel, J, Botzaki, A, Tyufekchieva, N, Brettholle, M, Thieme, J, and Klysubun, W. 2011. Sulfur Speciation in Soil by S K-Edge XANES Spectroscopy: Comparison of Spectral Deconvolution and Linear Combination Fitting. Environ Sci Technol 45:2878-2886.

Ryan, JA, Zhang, PC, Hesterberg, D, Chou, J, and Sayers, DE. 2001. Formation of chloropyromorphite in a lead-contaminated soil amended with hydroxyapatite. Environ Sci Technol 35:3798-3803.

Scheckel, KG, and Ryan, JA. 2004. Spectroscopic speciation and quantification of lead in phosphate-amended soils. J Environ Qual 33:1288-1295.

Scheinost AC, Kretzschmar R, and Pfister S. 2002. Combining selective sequential extractions, X-ray absorption spectroscopy, and principal component analysis for quantitative zinc speciation in soil. Environ Sci Technol 36:5021-8.

Figures and Tables

Table 1. List of natural and synthetic As bearing minerals used for linear combination fits (LCF) using XAS normalized and derivative μ(E) spectra as well as chi(k) function to predict As phases in the soil samples. Syn = Synthetic. TBD = To Be Determined at future experiments at Advance Photon Source.

Mineral	Chemical Elements	As Species	Edge (E_0)
Arsenopyrite	FeAsS	As (III)	11865.84
Orpiment Cryst	As2S3	As(III)S	11866.67
Realgar	As4S4	As(III)S	11866.89
Lollingite	FeAs2	As(III)	11867.49
Mackinawite	Fe(Ni)S0.9	As(III)	11867.59
Fougerite	$(Fe^{2+},Mg)_6Fe^{3+}{}_2(OH)18\bullet 4H_2OAs_3$	As(III)O	11868.42
Arsenolite NMNH 94146	As_2O_3	As(III)	11868.48
As(III) Ferrihydrite	$FeOOH\bullet 0.4(H_2O)$ As(3)	As(III)O	11868.68
Beudantite NMNH B13898	$PbFe^{3+}{}_3\ (AsO_4)(SO_4)(OH)_6$	As(V)O	11872.66
Scorodite	$Fe^{3+}AsO_4\ \bullet 2H_2O$	As(V)O	11873.11
Sodium Arsenate	NaAs	As(V)O	11874.00
As(V) Ferrihydrite	$FeOOH\bullet 0.4(H_2O)$ As(5)	As(V)O	11874.61
Yukonite NMNH 6481	$Ca_7Fe^{3+}{}_{12}\ (AsO_4)_{10}(OH)_{20}\ \bullet 15H_2O$	As(V)O	11875.69
Yukonite (syn)	$Ca_7Fe^{3+}{}_{12}\ (AsO_4)_{10}(OH)_{20}\ \bullet 15H_2O$	As(V)O	TBD
As(V) AlOH (syn)	(AsO_4) - AlOH	As(V)O	TBD
As(V) Kaolinite (syn)	$(AsO_4)Al_2(Si_2O_5)(OH)_4$	As(V)O	TBD
As(V) Montmorillonite (syn)	$(AsO_3)(Na,Ca)_{0.33}(Al,Mg)_2\ (Si_4O_{10})(OH)_2\cdot nH_2O$	As(V)O	TBD
As(III) AlOH (syn)	(AsO_3) - AlOH	As(III)O	TBD
As(III) Kaolinite (syn)	$(AsO_3)Al_2(Si_2O_5)(OH)_4$	As(III)O	TBD
As(III) Montmorillonite (syn)	$(AsO_3)(Na,Ca)_{0.33}(Al,Mg)_2\ (Si_4O_{10})(OH)_2\cdot nH_2O$	As(III)O	TBD
Mimetite (syn)	$Pb_5(AsO_4)_3Cl$	As(V)O	TBD
Hydroxlmimetite (syn)	$Pb_5(AsO_4)_3OH$	As(V)O	TBD

Table 2. Results of linear combination fitting (LCF) models with arsenic source, concentration (3051a extractable), and linear combination fitting (LCF) models. A) Predictions of mineral present (%); B) concentrations of mineral present (mg kg^{-1}).

						LCF Analyses %			
Soil Name	**As Source**	**RBA As**	**As mg/kg***	**R-factor**	**Reduced chi**	**Beudantite**	**As(V) Ferrihydrite**	**Scorodite**	**Lollingite**
Asarco-Ruston	Smelter	Mouse	162	0.0170	0.0220	-	76%	-	24%
Barber Orchard MS1	Pesticide	Mouse	283	0.0355	0.0442	-	100%	-	-
Barber Orchard MS4	Pesticide	Mouse	353	0.0253	0.0302	-	100%	-	-
Barber Orchard MS5	Pesticide	Mouse	391	0.0414	0.0526	-	100%	-	-
Barber Orchard MS8	Pesticide	Mouse	375	0.0335	0.0398	-	100%	-	-
HI-Hilo	Pesticide	Mouse	641	0.0119	0.0172	-	64%	36%	-
HSJ 583	Mining	Swine	249	0.0119	0.0176	-	61%	39%	-
IKJ 583	Mining	Swine	3913	0.0095	0.0145	8%	67%	25%	-
Mohr Orchard	Pesticide	Mouse	332	0.0048	0.0071	-	100%	-	-

						LCF Analyses mg/kg			
Soil Name	**As Source**	**RBA As**	**As mg/kg***	**R-factor**	**Reduced chi**	**Beudantite**	**As(V) Ferrihydrite**	**Scorodite**	**Lollingite**
Asarco-Ruston	Smelter	Mouse	162	0.0170	0.0220	-	123.63	-	38.76
Barber Orchard MS1	Pesticide	Mouse	283	0.0355	0.0442	-	282.81	-	-
Barber Orchard MS4	Pesticide	Mouse	353	0.0253	0.0302	-	352.65	-	-
Barber Orchard MS5	Pesticide	Mouse	391	0.0414	0.0526	-	390.85	-	-
Barber Orchard MS8	Pesticide	Mouse	375	0.0335	0.0398	-	375.27	-	-
HI-Hilo	Pesticide	Mouse	641	0.0119	0.0172	-	409.89	231.13	-
HSJ 583	Mining	Swine	249	0.0119	0.0176	-	152.71	96.58	-
IKJ 583	Mining	Swine	3913	0.0095	0.0145	331.43	2610.05	971.71	-
Mohr Orchard	Pesticide	Mouse	332	0.0048	0.0071	-	331.64	-	-

Figure 1**.** XAS scans of standards used for linear combination fit models. A) Normalized data and B) smoothed derivative of normalized XAS data used for linear combination fits models. Three vertical lines are at 11867, 11871 and 11875 eV.

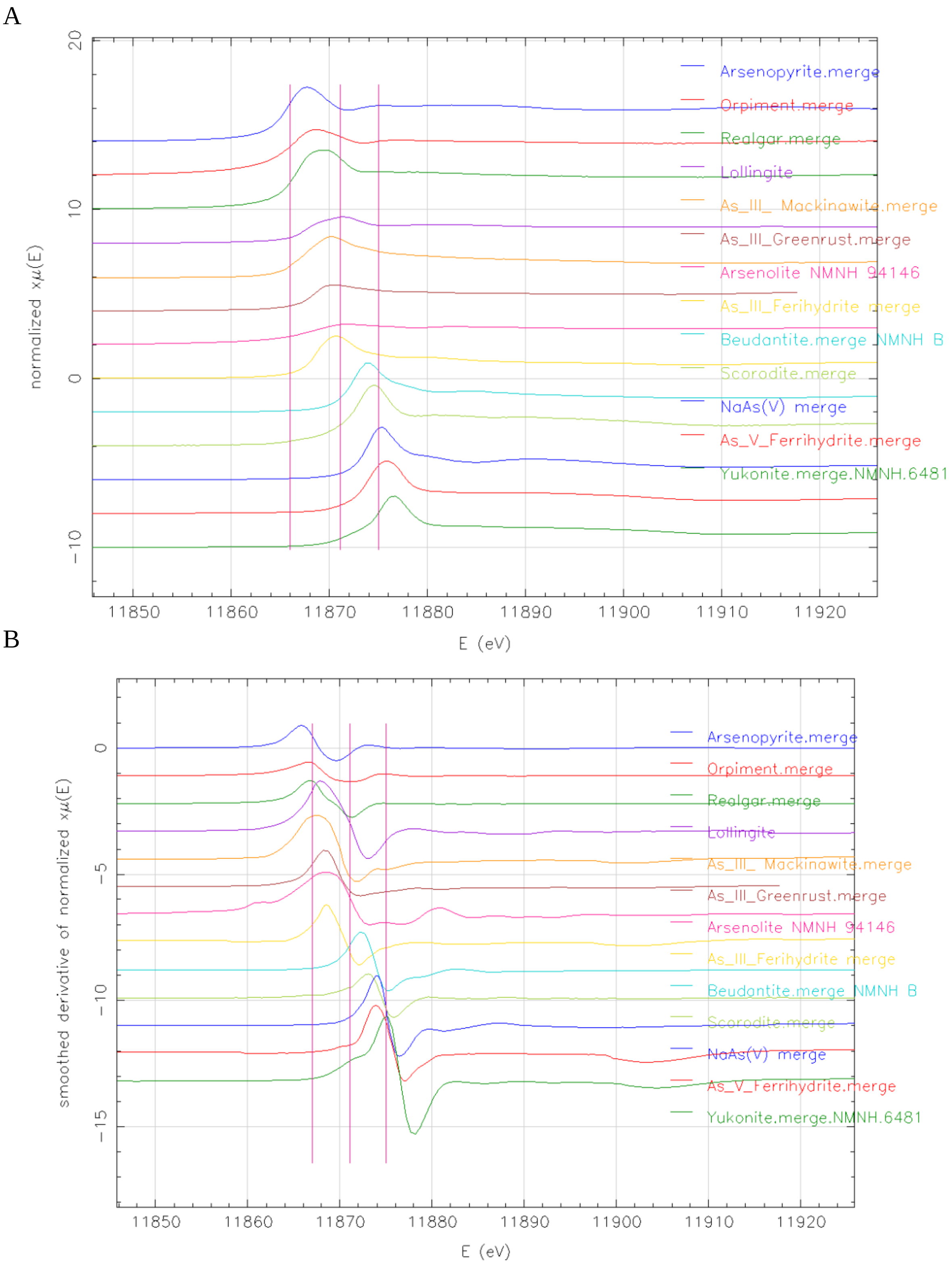

Figure 2**.** A) Normalized XAS data of soils used for linear combination fit models. B) Smoothed derivative of normalized XAS data of standards used for linear combination fits models. Three vertical lines are at 11867, 11871 and 11875 eV.

A