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Using Synchrotron-based X-ray Absorption Spectrometry to Identify the Arsenic Chemical Forms in Mine Waste Materials

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Abstract. X-ray Absorption Near Edge Spectroscopy (XANES) gives arsenic form directly in the solid phase and has lower detection limits than extraction techniques. An important and common application of XANES is to use the shift of the edge position to determine the valence state. XANES speciation analysis is based on fitting linear combinations of known spectra from model compounds to determine the ratios of valence states and/or phases present. As(V)/As(III) ratios were determined for various Australian mine waste samples and dispersed mine waste samples from river/creek sediments in Vatukoula, Fiji.

Keywords: arsenic speciation, selective extraction technique, mine wastes, XANES, As(V)/As(III) ratio.

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INTRODUCTION

Arsenic speciation in the solid phase is difficult to perform directly. Traditionally arsenic species are identified using time-consuming, indirect methods that determine the identity of the compound through chemical manipulation. Thus different selective extraction techniques have been used to demonstrate classes of arsenic species in each extracted fraction, for example, using oxalic acid and sodium dithionite to release arsenic bound by metals [1]. Pre-treatment of samples may alter the chemical form of the arsenic. Inductively-Coupled Plasma Atomic Emission Spectroscopy is used to determine the total amount of arsenic in a sample acid digest but cannot distinguish particular arsenic species.

X-ray absorption spectroscopy is capable of providing detailed chemical and structural information about a specific absorbing element in situ with minor or no pre-treatments [2]. There are two regimes in X-ray Absorption Structure (XAS) Spectroscopy: X-ray Absorption Near-Edge Spectroscopy (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy; these contain diverse information about an element's local coordination and chemical state. The absorption edge energy in XANES spectra is sensitive to the oxidation state of arsenic, and the position increases with an increase in oxidation state. XANES is applicable to solution or solid-phase samples, is element and oxidation state specific, and sensitive to parts per million [3]. XANES gives chemical identity empirically by comparing sample spectra to known compounds. This paper illustrates the usefulness of the XANES technique to identify distinguishing features of arsenic species in mine wastes and dispersed sediments from various mines in Australia and Fiji.

METHOD

"Total" mine waste samples and their respective fractions were obtained via selective chemical extraction (SCE) technique based on the sequential series of 8 selective extraction reagents [1] with increasing extraction power. A modification of the 8-step sequential procedure was developed for mining waste solid-phase samples containing arsenic [4]. Eight fractions of arsenic were separated from mine waste material and dispersed creek/river sediment

by SCE [1]. The oxidation states and the ratio of arsenic species present in these samples, as well as some selected fractions (those with highest As concentrations Fraction 3 Al-As; Fraction 4 Fe-As; Fraction 5 Ca-As; & Fraction 6 Fe occluded As) were determined using XANES.

Mine Sites

Tailings were collected from four Australian mines: Gympie Gold Mine (GHT 100 yr old), the rehabilitated Jibbinbar Arsenic Mine (JAsMT), Kidston Gold Mine (the acidic (KAT) and neutral (KNT) tailings) and at the Red Dome Heap Leach (RDHL). Dispersed contaminated and upstream sediments were collected in Fiji from Vunisina Creek (8SdsVsc-02), Dakavono Creek (15SdsDvc-02) and the Nasivi River (23SdsNsr-01) upstream from Emperor Gold Mine at Vatukoula.

Model Arsenic Compounds

Standard arsenic model compounds were used to identify suspected arsenic chemical forms in the mine waste materials, and in their sequentially extracted fractions. The model inorganic arsenic compounds used in this study (Table 1) were classified as either As(-I), As(III) or As(V) compounds, according to their formal oxidation states. The synthetic arsenic compounds (Table 1) calcium arsenite, aluminium arsenate, calcium arsenate and iron arsenate were prepared by precipitation reactions of suitable soluble salts using standard methodologies. The arsenopyrite used was a mineralogical sample from Jibbinbar analysed to show % arsenic present. Crystalline reagent grade sodium arsenite tetrahydrate, $\text{NaAsO}_2 \cdot 4\text{H}_2\text{O}$ and disodium orthoarsenate heptahydrate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (BDH, Australia), arsenic(III) sulfide and arsenic(V) sulfide, (Aldrich Chemical Company, Inc., WI, USA) were also used as model compounds. They were all diluted to about 1000mg As/kg using the “neutral” (<10ppm As) 23SdsNsr-01 upstream sediment of Nasivi River by adding 5g of each model compound with 5g of 23SdsNsr-01 prior to grinding to fine powder (<75 μm) in a zirconia tema swing mill (N.V. Tema, Germany) and stored in clear capped clean 5mL clear plastic vials prior to analysis. At the synchrotron facility, approximately 2g of the model compounds/sand mixtures and samples were evenly loaded into 1mm thick aluminium holders. Both sides of the holder were encapsulated with X-ray transparent Kapton tape. The valency and individual quantity of arsenic present in each mine waste sample were calculated after scanning using XANES.

TABLE 1. Model arsenic compounds used and their class

As(-I)	As(III)	As(V)
Arsenopyrite, FeAsS	Arsenic sulfide, As_2S_3	Aluminum arsenate, $\text{AlAsO}_4 \cdot 8\text{H}_2\text{O}$
	Calcium arsenite, CaAsO_3H	Arsenic sulfide, As_2S_5
	Sodium arsenite, $\text{NaAsO}_2 \cdot 4\text{H}_2\text{O}$	Calcium arsenic, $\text{Ca}_3(\text{AsO}_4)_2$
		Iron arsenate, FeAsO_4
		Sodium arsenate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$

Spectroscopic Technique/XANES Data Analysis

Arsenic K-edge XAFS spectra were collected at the Australian National Beamline Facility (ANBF BL-20B) Photon Factory, Tsukuba Science City, Japan over the energy range 11840–11940eV (ring conditions: 2.5GeV, 300-400mA). BL-20B was equipped with a channel-cut Si (111) monochromator which was detuned 50% to reject harmonics. The monochromator step size was reduced to 0.25eV per step in the XANES region (11845-11895eV) to collect high-resolution spectra. XAFS data for the above-mentioned samples and model compounds were collected at ambient temperature and pressure in fluorescence, with the simultaneous collection of an As reference foil for energy calibration (the first peak of the first derivative of the spectrum of elemental As was assumed to be 11867.0eV). A 10-element germanium fluorescence detector was used to collect the data. The detection limit for adequate speciation was approximately 6mg/kg arsenic (see Fig. 1).

Data analysis was processed using the EXAFSPAK suite of programs [5]. XANES spectra of model compounds and samples were background subtracted and normalised to edge jump (normalised to the absorbance value of the spline at 11885eV). The XANES analysis consisted of fitting linear combination of model spectra to sample spectra using the program DATFIT [5]. The precision of this fit procedure was determined to be ~10% based on analyses of control mixtures of model compounds.

RESULTS

The results are tabulated (see Tables 2 & 3) and shown in Figs. 1 and 2 below.

TABLE 2. The XANES fitting analysis of the oxidation states and ratio of arsenic species identified

(a) Original mine waste samples from various Australian mine sites

Sample Description	Total [As] (mg/kg)	As(III) sulfide	Fe arsenate	Arseno- pyrite	Al arsenate	Ca arsenate	Ca arsenite	Fit Residual
GHT	750		~ 100%					0.006%
KAT	1200	9.30%	60.70%		32.10%			0.002%
KNT	320	7.30%	27.30%	63.50%				0.01%
RDHL	520		~ 100%					0.02%
JAsMT	2600		15.90%		54.40%	27.50%		0.001%

(b) Sequentially extracted fraction

Sample Description	Total [As] (mg/kg)	As(III) sulfide	Fe arsenate	Arseno- pyrite	Al arsenate	Ca arsenate	Ca arsenite	Fit Residual
KAT Desorption Fr. 4 (Fe-As) incl.	1100		63.70%	16%	13.20%	9.10%		0.001%
KAT Desorption Fr. 5 (Ca-As) incl.	1100		72.40%	11.90%	3.10%	14.30%		0.003%
KAT Desorption Fr. 6 (Fe Occl.-As) incl.	610	12.80%	78.90%		8.50%			0.002%
JAsMT Desorption Fr. 3 (Al-As) incl.	2500		78.70%	23.40%				0.003%
JAsMT Desorption Fr. 4 (Fe-As) incl.	2000		67.30%			35.40%		0.002%
JAsMT Desorption Fr. 5 (Ca-As) incl.	860	2.20%	59.70%		22.70%	19.20%		0.002%

TABLE 3. The XANES fitting analysis of arsenic species identified and determined on dispersed mine waste samples from creek sediments together with their sequentially extracted fraction in Vatukoula, Fiji

Sample Description	Total [As] (mg/kg)	As(III) sulfide	Fe arsenate	Arseno- pyrite	Al arsenate	Ca arsenate	Ca arsenite	Fit Residual
8SdsVsc-02	300		40.60%	7.80%	56.30%			0.0008%
8SdsVsc-02 Desorption Fr. 4 (Fe-As) incl.	190	3.30%	84.20%	12.70%				0.0009%
8SdsVsc-02 Desorption Fr. 5 (Ca-As) incl.	120	8.30%	87%	4.60%				0.0010%
15SdsDvc-02	690	5.20%	89.40%	6.30%				0.0004%
15SdsDvc-02 Desorption Fr. 4 (Fe-As) incl.	520		~ 100%					0.0010%
15SdsDvc-02 Desorption Fr. 5 (Ca-As) incl.	380		75.40%		9.20%	17.80%		0.0010%
23SdsNsr-01	10		16.70%		69.40%		21.30%	0.0070%

DISCUSSION AND CONCLUSIONS

XANES analysis indicates that As(V) comprising the arsenates of iron, aluminium, and calcium is the dominant oxidation state in most mine waste samples, including the ones that were dispersed as creek sediments. Mixed oxidation states; supposedly As(V) (comprising the arsenates of iron, aluminium, and calcium), As(III) (consisting of arsenic sulfide), and As(-I) (comprising of arsenopyrite only) were observed to be present in most of the total mine waste samples and their respective selective extraction fractions. The XANES analysis technique is a direct measurement of the composition of mine waste components in relation to the oxidation states and chemical forms (species) of arsenic that may be present in original sample and selected fractions. Thus, the usefulness of the XANES technique to measure arsenic speciation in the solid phase of mine wastes has been demonstrated.

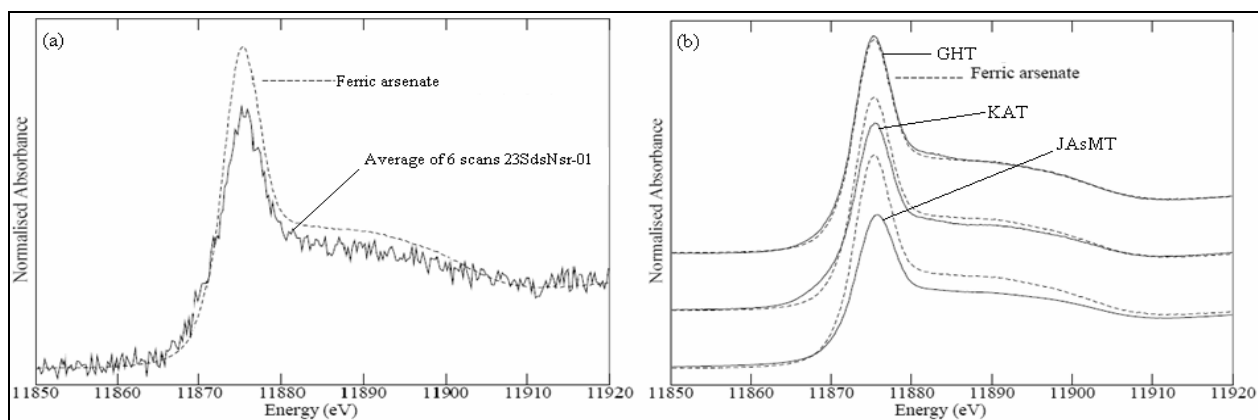


FIGURE 1. Comparison of sample spectra and the model ferric arsenate compound spectrum: (a) average spectra of 23SdsNsr-01 upstream sediment of Nasivi River, Fiji revealing a low level of arsenic, compared with ferric arsenate model spectrum; and (b) GHT with almost 100 % ferric arsenate showing good fit to the model spectrum, KAT - about 61 % ferric arsenate and JAsMT - approx. 16 % ferric arsenate. Table 2 gives the % composition of arsenic species in these samples.

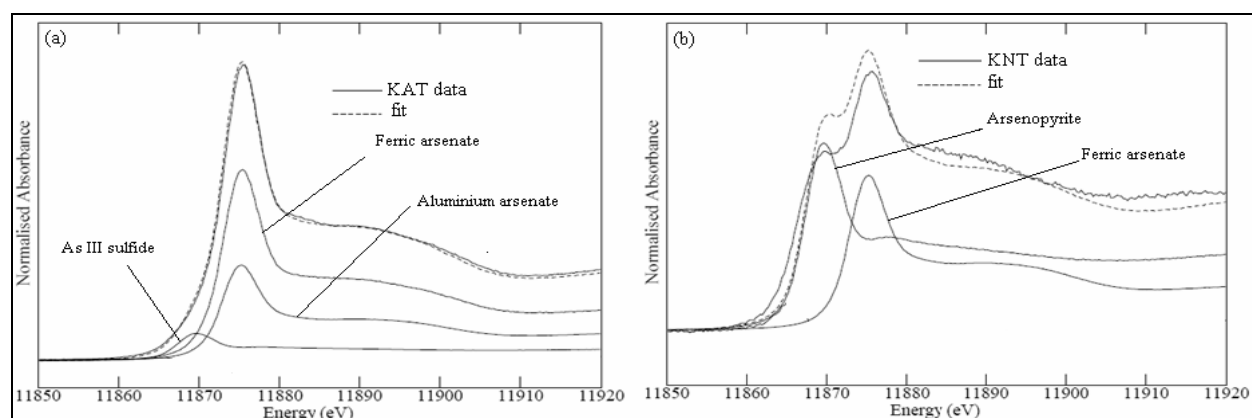


FIGURE 2. The data and fitted model spectra (normalized vs % composition) for two types of tailings collected from the Kidston Gold Mine: (a) KAT - acid tailings, mainly As V arsenates; and (b) KNT - neutral tailings showing the presence of As(-I) and As(III) in the neutral tailings together with ferric arsenate. Table 2 gives the ratio of arsenic species present in these two samples.

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REFERENCES

1. Chunguo, C. and Zihui, L., Chemical speciation and distribution of arsenic in water, suspended solids and sediments of Xiangjiang River, China. *The Science of the Total Environment*, 1988. 77: p. 69-82.
2. Bertsch, P.M. and Hunter, D.B., Elucidating fundamental mechanisms in soil and environmental chemistry: The role of advanced analytical spectroscopic and microscopic methods. *Soil Sc. Soc. Am. Spec. Publ.*, 1998. 55: p. 103-122.
3. Cutler, J.N., Jiang, D.T., and Remple, G., Chemical Speciation of Arsenic in Uranium Mine Tailings by X-ray Absorption Spectroscopy. *Can. J. Anal. Sci. Spectrosc.*, 2001. 46(4): p. 130-135.
4. Noller, B.N., Parry, D., and Eapaea, M.P., Arsenic dispersion and retention at mine sites in the Northern Territory Australia. in *8th International Conference on the Biogeochemistry of Trace Elements (ICOBTE)*. 2005. Adelaide, Australia. pp 668-669.
5. George, G.N. and Pickering, I.J., EXAFSPAK: A Suite of Computer Programs for Analysis of X-ray Absorption Spectra. 2000, Stanford Synchrotron Radiation Laboratory: Stanford, CA.