

EXAFS and XANES study of arsenic in contaminated soil

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Historical mining, processing and refinement of arsenic in purpose built calciners in Cornwall, UK, have resulted in extremely high contamination of soils with arsenic in some localized areas. The x-ray absorption spectroscopic methods XANES (x-ray absorption near-edge structure) and EXAFS (extended x-ray absorption fine structure) were used to retrieve arsenic molecular information, i.e. oxidation state and local structure around As atoms, in the soil from a calciner's residue dump near Camborne (which contained 8.82 wt% arsenic) and identify the most abundant modes of As bonding. The results show that arsenic is predominantly in pentavalent form, tetrahedrally bound to oxygen atoms in the first coordination sphere. Fe and Al atoms are found in the next neighbour coordination shells around As. The As–Fe and As–Al distances and coordination numbers strongly suggest that arsenate in the soil is present in two forms, viz. as amorphous or poorly crystalline hydrous oxides of Fe (most likely FeAsO_4) and adsorbed on aluminium (hydr)oxides or aluminosilicates such as clay. Copyright © 2005 John Wiley & Sons, Ltd.

INTRODUCTION

Polymetallic mining in southwest England took place from Roman times until the end of the 20th century. In addition to the main products copper and tin, many other metals and metalloids were recovered. Initially, arsenic, as a deleterious element in tin ore smelting, was simply allowed to escape to the atmosphere, leading to contamination of an area of nearly 700 km² with arsenic levels in agricultural soils of up to 1000 ppm or more.¹ When uses for arsenic in pigments, pesticides and glass discoloring, were discovered in the early 1800s, the metalloid was recovered and refined in purpose-built calciners. The primary arsenic-bearing ores roasted for this purpose were arsenopyrite (FeAsS) and löllingite (FeAs_2), with arsenic sublimating and condensing in the form of As_2O_3 . Through this process and by the dumping of residues, arsenic hot spots have been created in the vicinity of calciners with extremely high soil arsenic concentrations.² In this study, a hot spot near a calciner in Camborne (Cornwall) was selected for characterization of arsenic in the soil. The exact sampling location is the calciner's residue dump where the As concentration in the soil was found to be between 8 and 16 wt%.²

The potential leaching behaviour of arsenic is usually studied by sequential extraction protocols which give insight into the association with soil phases. However, such an approach only yields very crude information on the arsenic binding and gives no structural information on the surroundings of the As atoms, which is crucial to assess the potential toxicity and mobility risks.^{3,4} To this end, we applied the x-ray absorption spectroscopic methods XANES (x-ray absorption near-edge structure) and EXAFS (extended x-ray absorption fine structure) to retrieve arsenic molecular information, i.e. oxidation state and local structure around As atoms in the soil. In this way, the most abundant modes of As bonding can be identified,^{2–10} among which different crystalline and amorphous solid phases and also surface-bound or adsorbed As species on mineral particles may coexist, as shown in previous analyses of industrially polluted soils.^{2–8}

RESULTS AND DISCUSSION

A soil sample was taken from a calciner's residue dump near a calciner in Cornwall,² located ca 4 km west of the Camborne–Redruth–St. Day orefield, which ceased operation in the 1920s. The sample was taken from a depth layer of 25–30 cm below the surface, where the As concentration is much higher than in the top layer (probably because the site has been covered with a 'clean' ground layer). The soil sample was dried and sieved at 2 mm, followed by grinding in a zirconium planetary mill to a sub-micrometre particle size. Elemental analysis by inductively

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coupled plasma mass spectrometry (ICP-MS) after open acid digestion of the sample (see Experimental section for details) showed that the As concentration in the soil was 8.82 wt%. Very high levels were also found for iron (6.69 wt%), calcium (1.20 wt%) and aluminium (2.14 wt%), elements which may have potentially precipitated arsenate to insoluble secondary minerals. The sulfur content was below 0.05 wt%, excluding the existence of pyrite forms. Mineralogical studies of the soil from that particular site indicated the presence of an As–Fe oxide phase rimming silicate grains, including quartz–mica–feldspar aggregates².

Arsenic K-edge XANES was used to probe directly the average As valence in the soil sample, by its effect on the energy position of the As K-edge.^{2,7,9,11} With increasing oxidation state, the K-edge is shifted to higher energies. For a given type of ligand, a linear relation between the edge shift and the valence state was established.^{12,13} For As, the relation can be calibrated with XANES spectra of reference compounds with well-defined oxidation states. For this purpose we measured As XANES spectra of the following As compounds and minerals: metallic As, trivalent As compounds [realgar (AsS), orpiment (As₂S₃), NaAsO₂ and arsenolite (As₂O₃)], pentavalent organoarsenic compounds {monomethylarsenic acid (MMAA) [CH₃AsO(OH)₂] and dimethylarsenic acid (DMAA) [(CH₃)₂AsO(OH)₂]} and pentavalent As minerals {scorodite (FeAsO₄·2H₂O) and pharmacosiderite [KFe₄(AsO₄)₃(OH)₄·6–7H₂O]}.

The normalized As XANES spectra of the soil and reference samples are shown in Fig. 1. The relative K-shell contribution is obtained from the measured absorption spectra by removing the extrapolated best-fit linear function determined in the pre-edge region (–250 to –70 eV) and normalizing to a unit As K-edge jump. Zero energy is taken at the first inflection point in the As metal edge at 11 866.7 eV (i.e. the first maximum in the derivative spectrum), which marks the 1s ionization threshold. The vertical dashed line in Fig. 1 is plotted at the peak position above the edge in the spectra of As(V) minerals to facilitate the comparison of edge shifts. From the plots it is evident that the edge position in the soil sample coincides with those of the As(V) minerals scorodite and pharmacosiderite, which clearly indicates that arsenic in soil is predominantly in pentavalent form.

In addition to K-edge position, the shape of the K-edge is characteristic for the local symmetry of the investigated atom and can be used as a fingerprint in the identification of its local structure.^{3,8,9,12,13} The edge profile of the soil sample is very similar to those of the two reference As(V) minerals scorodite and pharmacosiderite, where As atoms are tetrahedrally coordinated to four oxygen atoms, which suggests a similar local symmetry for the As atom in the soil.

A more detailed insight into the local structure around As atoms in the soil can be obtained from the As K-edge EXAFS analysis. We performed EXAFS analysis using the exact As atomic absorption background^{14,15} to separate the EXAFS signal from the absorption spectrum. The *k*³-weighted EXAFS spectra of the soil sample and the reference As(V) mineral scorodite are shown in Fig. 2. From the Fourier transforms (Fig. 3), some idea of the As atom neighbourhood can already be obtained, even before a detailed quantitative

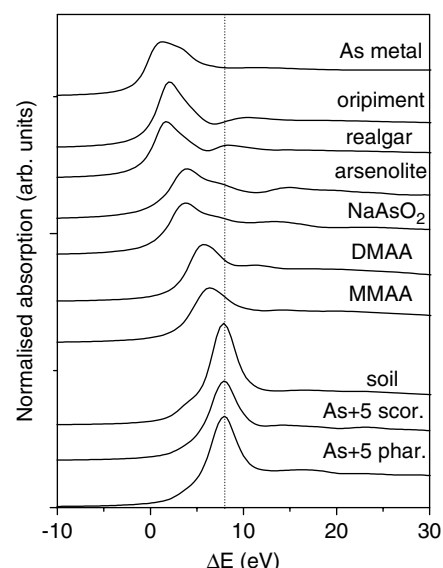


Figure 1. Normalized As K-edge profiles for the soil sample and reference As compounds and minerals. The energy scale is relative to the As K-edge in As metal (11 866.7 eV). The spectra are displaced vertically for clarity. The vertical dashed line is plotted at the peak position above the edge in the spectra of As(V) minerals to facilitate the comparison of edge shifts.

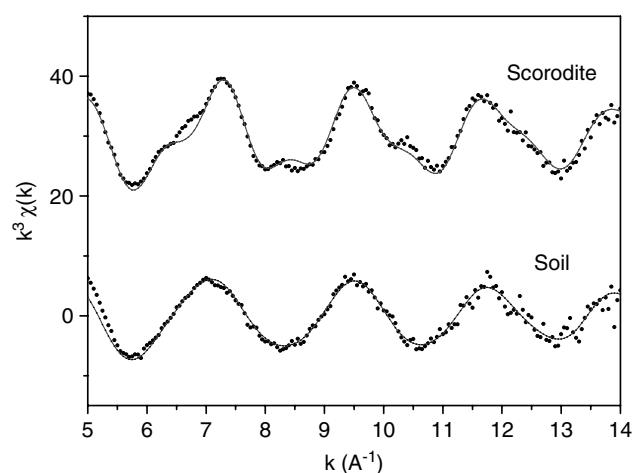


Figure 2. The *k*³-weighted As EXAFS spectra of the soil and reference scorodite sample. Experiment, dots; EXAFS model, solid line.

analysis is performed. In the spectrum of scorodite, the most likely candidate for the As carrier in the soil, two distinct peaks represent the contributions of the first two shells of neighbours around the As atom.¹⁶ In the spectrum of the soil sample, only the first peak of the nearest coordination shell is similar to that in the mineral, while the characteristic strong peak of the second shell is absent, clearly showing that As in the soil is predominantly not in the form of crystalline scorodite.

Quantitative EXAFS analysis, performed with the University of Washington UWXAFS program code¹⁷ and the FEFF6 code for *ab initio* calculation of the scattering paths,¹⁸ was used to determine the structural parameters of the local As neighbourhood: the radii and Debye–Waller factors of

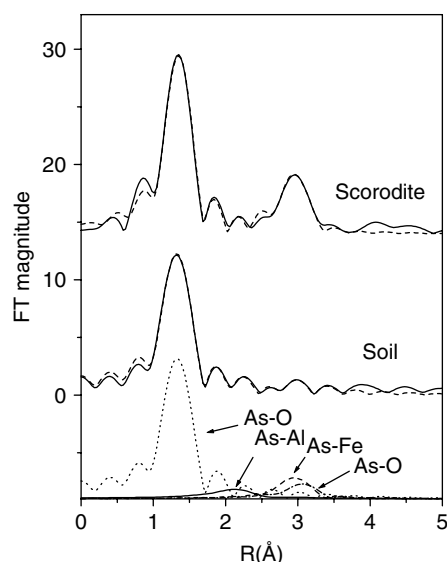


Figure 3. Fourier transform of the k^3 -weighted As EXAFS spectra of the soil and reference scorodite sample, calculated in the k range 5–14 Å⁻¹. Experiment, solid line; EXAFS model, dashed line. Bottom: FT magnitude of consecutive neighbour shell contributions in the EXAFS model of the soil sample.

nearest neighbour shells, together with chemical species and average number of atoms in the shell. For the reference scorodite spectrum an FEFF model was constructed from the crystallographic data.¹⁶ In scorodite, As(V) is coordinated to four oxygen atoms at a distance of 1.68 Å in the first coordination shell, and the second coordination shell is composed of four Fe atoms located at distances from 3.35 to 3.38 Å and two oxygen atoms, one at 3.24 Å and the other, belonging to an OH group, at 3.35 Å. The FEFF model, comprising all single scattering paths and all significant multiple scattering paths up to 3.4 Å, yields a very good fit in the k range 5–14 Å⁻¹ for the R region from 1.1 to 3.3 Å (Figs 2 and 3). Six variable parameters were used in the fit: the amplitude reduction factor (S_0^2), the zero-energy shift ΔE_0 , the interatomic distances $R_{\text{As-O}}$ and $R_{\text{As-Fe}}$ and the corresponding Debye–Waller factors ($\sigma^2_{\text{As-O}}$ and $\sigma^2_{\text{As-Fe}}$). The shell coordination numbers were fixed at their crystallographic values. Best-fit values of the structural parameters, listed in Table 1, are in good agreement with previous EXAFS results for scorodite.^{3,7} The contribution of oxygen atoms in the second coordination shell was found to be negligibly small owing to a large static disorder (large Debye–Waller factors) and therefore excluded from the model.

In modelling the EXAFS spectrum of the soil sample, the amplitude reduction factor was kept fixed at the value obtained for scorodite ($S_0^2 = 0.78$). A very good fit (Figs 2 and 3) was obtained with the structural parameters listed in Table 1. Four oxygen atoms were identified in the first coordination shell at a short distance of 1.687 Å and with a small Debye–Waller factor, characteristic for a tight As(V)–O bond, as in scorodite. In the second coordination shell, iron atoms are clearly identified at a distance of 3.34 Å, similar to the finding for scorodite. This is not surprising, taking into account the elemental analysis data, which show that As and Fe concentrations in the soil are strongly correlated.

Table 1. Parameters of the nearest coordination shells around As atoms in the soil sample and reference mineral scorodite: average number of neighbour atoms (N), distance (R) and Debye–Waller factor (σ^2)^a

As neighbour	N	R (Å)	σ^2 (Å ²)	R -factor
<i>Soil sample with 8.82 wt% As</i>				
O	4.2(2)	1.687(1)	0.0018(3)	0.0011
Al	1.7(4)	2.54(2)	0.009(5)	
Fe	1.6(8)	3.34(2)	0.006(3)	0.0085
O	4(1)	3.48(3)	0.004(2)	
<i>Reference mineral scorodite (FeAsO₄ · 2H₂O)</i>				
O	4	1.693(1)	0.0013(1)	0.0066
Fe	4	3.345(4)	0.006(1)	0.0048

^a Uncertainty of the last digit is given in parentheses. Best fit is obtained with the amplitude reduction factor $S_0^2 = 0.78 \pm 0.05$ and the zero-energy shift $\Delta E_0 = -4 \pm 1$ eV. The goodness-of-fit parameter, R -factor,¹⁷ obtained in the separate fit of the first and second coordination shells, is given in the last column.

However, the number of Fe neighbours of an As atom is significantly lower than in the crystal structure of scorodite. This suggests that as a result of weathering secondary arsenic compounds have been formed by (co)precipitation of arsenate leading to amorphous or poorly crystalline FeAsO₄.

Additionally, we found two Al atoms at a distance of 2.54 Å and about four oxygen atoms at 3.48 Å. A possibility for the occurrence of the mineral phase mansfieldite (AlAsO₄ · 2H₂O) should be excluded because the As(V)–Al distance in this mineral is 3.15 Å.⁸ However, the As–Al distances of 2.54 Å match very well the distances reported for bidentate mononuclear complexes in arsenate adsorption studies at the aluminium oxide–water interface.⁹ The presence of Si atoms instead of Al at the same distance cannot be completely excluded by the fit, owing to similar backscattering amplitudes and phase shifts of the two elements in EXAFS spectra; however, the model with Al atoms gives a slightly better fit. The presence of As, Ca or Fe atoms as possible candidates for the As coordination at a distance of about 2.5 Å can be excluded by the fit. Also, there is no evidence for the organic As ligands in XANES and EXAFS spectra, so the presence of organoarsenic compounds in the soil may be excluded. This suggests that arsenate is partially adsorbed on aluminium (hydr)oxides or aluminosilicates such as clay.

CONCLUSION

EXAFS and XANES results for the soil sample from a dump site near a former calciner used for the production of As₂O₃ (soil As content 8.82 wt%) shows that arsenic is predominantly in pentavalent form, tightly (tetrahedrally) bound to oxygen atoms in the first coordination sphere. Coordination parameters of next neighbour coordination shells around As strongly suggest that arsenate is present in two forms: (i) in the form of amorphous or poorly crystalline hydrous oxides of Fe (most likely FeAsO₄) and (ii) adsorbed

on aluminium (hydr)oxides or aluminosilicates such as clay. This is in agreement with previous reports about the speciation of arsenic in industrially polluted soils.

Since arsenic is present in pentavalent form, it has a strong interaction with mineral surfaces; however, the fact that arsenic is mostly seen in association with amorphous phases or adsorbed species means that it represents a higher environmental risk than when present in a crystalline state. The results therefore implicate the potential leaching behaviour of arsenic and may be helpful in the management of such highly polluted sites.

EXPERIMENTAL

Total elemental concentrations were determined with a Hewlett-Packard 4500 PLUS ICP-MS system after open acid digestion with HClO_4 and HF of the soil sample in a Teflon beaker on a hot-plate.¹⁹

Arsenic K-edge absorption spectra (EXAFS and XANES) of the soil sample and reference As compounds and minerals were recorded at the BM29 beamline of ESRF in Grenoble (France) and at the X1 station of HASYLAB at DESY (Hamburg, Germany). An Si(311) double-crystal monochromator was used at both beamlines with about 2 eV resolution at the As K-edge (11 866.7 eV). The higher order harmonics were effectively eliminated by detuning of the monochromator crystals to 60% of the rocking curve maximum, using the beam-stabilization feedback control. The absorption spectra were obtained in transmission mode. The intensity of the x-ray beam was measured by three consecutive ionization chambers. At the BM29 station the chambers were filled with Ar–He gas mixture containing 14, 47 and 47% of Ar at 2 bar. At the X1 station the first ionization chamber was filled with Ar–N₂ mixture (50:50) and the second and third with Ar–Kr mixture (90:10) at ambient pressure.

Powder samples were prepared on multiple layers of adhesive tape and inserted between the first and the second ionization chambers. Stacking of layers to achieve an attenuation of ~ 1 above the As K-edge improved the homogeneity of the samples. The absorption spectra were measured within the interval -250 to 900 eV relative to the edge. In the XANES region equidistant energy steps of 0.5 eV were used, whereas for the EXAFS region equidistant k steps ($\Delta k \approx 0.03 \text{ \AA}^{-1}$) were adopted, with an integration time of 2 s

per step. The exact energy calibration was established with a simultaneous absorption measurement on metallic As placed between the second and the third ionization chambers.

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