

Arsenic speciation in multiple metal environments: I. Bulk-XAFS spectroscopy of model and mixed compounds

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Abstract

X-ray absorption fine structure (XAFS) spectroscopy was employed to determine the bonding environment of As(V) in the presence of Cu(II) and Zn(II) on goethite and gibbsite. In addition, several mineral species and precipitates derived from homogeneous and heterogeneous (presence of α -Cr₂O₃) super-saturations were studied. Structural parameters were determined after resolving the broad second shells in *r*-space by differential *k*-weighting (1, 2 or 3) and *k*-ranging (2.5- vs 3.5–12.75 Å) of the raw EXAFS functions. In precipitates, AsO₄ was incorporated in the metal-hydroxides forming clinoclase-like and koettigite-like structures in the presence of Cu(II) and Zn(II), respectively. In the presence of both Cu(II) and Zn(II), the clinoclase structure formed preferentially over the koettigite structure under homogeneous oversaturated solution conditions and in the presence of eskolaite (α -Cr₂O₃). Silica promoted the formation of koettigite-like zinc-arsenate precipitates from initial As(V) and Zn(II) solution concentrations of 500 μ M. On goethite and gibbsite, 750 μ M As(V) formed mainly bidentate binuclear surface species in accordance with many previous findings even in the presence of equimolar Cu(II) and/or Zn(II) concentrations. Copper was readily identified in the second shell environment of As(V) sorbed on gibbsite, but not on goethite. We hypothesize that this complex formed on the basis of Cu(II)'s ability to form polymeric species in solution and at the mineral–water interface in agreement with previous studies. The effects of Zn(II) on the coordination environment of As(V) on gibbsite and goethite could not be ascertained with As K-edge EXAFS spectroscopy. In addition to bidentate binuclear surface complexes, As(V) formed edge-sharing complexes with Fe, Al, and Cu atoms, which we could differentiate on the basis of the inter-atomic distances, phase shifts between wavefunctions of Fourier-filtered peaks, and differences in amplitude of the absorption envelopes. The analyses showed that of all data reduction steps, data presented in *r*-space and as wavefunctions of Fourier-filtered shells offer the greatest possibility for fingerprinting and inferring the influence of co-sorbing metal cations on the As(V) sorption complex. With regards to interpretations of micro-EXAFS data by abstract factor analyses and linear least-square combination fitting, analyses of As K-edge data should not be performed on the raw $\chi(k)$ data, but rather on consistently isolated second and higher-order shell features.

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1. Introduction

Arsenic is a toxic metalloid whose chemical speciation and toxicity are dependent on the redox potential and pH. In oxidized environments, arsenate [$\text{H}_{3-n}\text{AsO}_4^{0-n} = \text{As(V)}$], the less toxic species, is prevalent, whereas in suboxic environments,

arsenite [$\text{H}_{3-n}\text{AsO}_3^{0-n} = \text{As(III)}$], the more toxic species, is dominant [1–3]. The fate of arsenic in contaminated environments is directly related to this basic differentiation of chemical species, because their symmetry (As(V)_{tetrahedral} vs As(III)_{bipyramidal}), acid/base behavior, charge and affinity to other elements such as Al, Fe, Cu, Zn, S, and C are fundamentally different [1,4]. To date, the solid phase formation of As(V) and As(III) species has been studied extensively for single ion-surface systems and specifically for the variable charged surfaces of the Fe- and Al-oxides (e.g., goethite, ferrihydrite, gibbsite, boehmite) [5–10]. Arsenate is coordinated at these

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surfaces by two hydroxyl (OH) functional groups extending from metal polyhedra (e.g., $\text{Fe}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$). This surface complex is known as the bidentate binuclear or double-corner sharing complex (${}^2\text{C}_{\text{As-Fe/Al}}$) and forms as a result of a ligand exchange reaction [5,11]. On goethite ($\alpha\text{-FeOOH}$), the bidentate binuclear sorption complex is identified by a characteristic As–Fe distance ($R_{\text{As-Fe}}$) between 3.26 and 3.32 Å and a coordination number (N) magnitude between one and two. On gibbsite ($\text{Al}(\text{OH})_3$), the bidentate binuclear complex is identified by $R_{\text{As-Al}} \sim 3.15$ Å with a similar magnitude for N as on goethite [12]. This surface complex has been corroborated by other spectroscopic evidence (Fourier transform infrared, FTIR spectroscopy) for ions with tetrahedral symmetry (e.g., PO_4), and by modeling the sorption reaction using the constant capacitance model [13–15]. A second surface complex on goethite was suggested by Fendorf et al. and Manceau in which As(V) is coordinated by two O atoms that are part of the same metal octahedron [5,16]. This surface complex, referred to as the bidentate mononuclear or edge-sharing surface complex (${}^1\text{E}_{\text{As-M, M=metal}}$) was recently analyzed by Sherman and Randall [17] who argued on the basis of density functional theory (DFT) calculations on a small $\text{Fe}_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ cluster that the ${}^1\text{E}_{\text{As-Fe}}$ complex was energetically unfavorable. Modeling extended X-ray absorption fine structure (EXAFS) data of As(V) sorbed on goethite, the authors suggested that contributions to the EXAFS spectra expressed at $R + \Delta R \sim 2.85$ Å stemmed solely from non-collinear multiple scattering (MS) in the As(V) tetrahedron in addition to the bidentate binuclear configuration of As(V) on the goethite surface. Ladeira et al. also dismissed the formation of ${}^1\text{E}_{\text{As-Al}}$ complexes based on their DFT calculations on a small $\text{Al}_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ cluster [12]. Observations of multiple scattering (MS) for ions in tetrahedral coordination have been made by Pandya [18] for chromate [Cr(VI)] and by Foster et al. and Gräfe and Spaks for As(V) [19–21]. In our own research, the MS feature for aqueous (outer-sphere), sorbed, precipitated and mineralized species ranged between 3.10 and 3.23 Å with an average coordination number (CN) of 18.9 [20]. In relation to the two proposed surface complexes (${}^1\text{E}$ and ${}^2\text{C}$), $R_{\text{As-Fe/Al, 1E}} < R_{\text{MS}} < R_{\text{As-Fe/Al, 2C}}$ suggesting that the broad second shell feature in Fourier transforms (FTs) of As(V) sorbed on Fe and Al oxides is possibly a composite of the ${}^1\text{E}$ complex, MS and the ${}^2\text{C}$ complex. As foreign metal cations are introduced to the surface, the ${}^2\text{C}$ and ${}^1\text{E}$ complexes may form on mixed edge-sharing octahedra (e.g., Fe–Cu or Fe–Zn). Indeed, the edge-sharing complex of metal cations on Fe and Al oxides is the dominant surface complex at and below monolayer coverage [20,22–26]. An unambiguous differentiation of the second shell metal in As(V) spectra is however quite difficult, with some indicators given only by the position of the imaginary part in the FT [26]. Recently, we showed that proton (H^+) promoted desorption of As(V) from 6-month old co-sorbed As(V) and Zn(II) fractions on goethite was greater in the presence of Zn(II), as opposed to its absence under the same ageing conditions) suggesting that some of the surface adsorbed As(V) was coordinated by Zn(II) [20]. Raw k^3 -weighted $\chi(k)$ spectra and FTs however could not confirm the presence or absence of Zn(II) in the second shell.

This study analyzed EXAFS data of more than 20 As sorption samples and mineral standards and discriminated among spectral analyses steps (XANES vs raw k^3 -weighted $\chi(k)$ vs FTs vs individually Fourier filtered shell contributions [$k^3 \cdot \chi(k)$]) for the greatest spectral differences upon visual inspection and upon non-linear least-square shell fitting. The analyses were performed for spectra collected on As(V) sorption complexes on goethite and gibbsite in the presence and absence of copper [Cu(II)] and or zinc [Zn(II)], on freshly precipitated Cu- and Zn-arsenate precipitates in the presence and absence of $\alpha\text{-Cr}_2\text{O}_3$ (s), on several mineral species such as scorodite (FeAsO_4), olivenite ($\text{Cu}_2[\text{AsO}_4]\text{OH}$) and adamite ($\text{Zn}_2[\text{AsO}_4]\text{OH}$), and an aqueous Na_2HAsO_4 sample. It supports an investigation into the influence of co-sorbing metals (Cr, Cu and Zn) on the solid phase speciation of arsenic (As) in a copper-chromated-arsenate (CCA) contaminated soil using *in situ* synchrotron-based, micro-focused X-ray absorption spectroscopy (μXAS). The detailed analyses presented in this paper were warranted for several reasons: (1) As(V)'s solid phase speciation in soils and sediments is greatly influenced by the presence and variety of sorbing surfaces (e.g., goethite vs gibbsite), pH, redox potential and presence of co-sorbing metals (e.g., Cu and Zn) and other ligands (e.g., PO_4) [2,20,26]. (2) The number and type of structural elements (e.g., edge-sharing vs corner-sharing complexes) comprising As(V)'s second shell ($R + \Delta R$ 2.20 Å, uncorrected for phase shifts) and possible contributions from MS remain unclear for As(V) surface complexes on Fe and Al oxides [10,16,17,27]. (3) It is unclear whether co-sorbing metals (e.g., Cu and Zn) other than Fe and or Al can be unambiguously identified in As(V)'s second shell especially when no (surface) precipitate has formed and the ions co-exist on the same surface; and (4) detailed statistical analyses (principal component analysis (PCA), target transformation (TT) and linear least-square combination fit (LLSF) analysis) of μEXAFS spectra collected from heterogeneous soil samples require a suite of known reference compounds and should be conducted at a spectral analysis step that provides the greatest measurable differences.

2. Materials and methods

2.1. Sample preparation

Table 1 lists sorption, precipitate, mineral and aqueous samples and provides a brief tabulated description on how sorption and freshly precipitated samples were prepared. Mineral species were obtained from *Excalibur*TM (Peekskill, NY). X-ray diffraction data was collected to verify the presence and purity of the minerals. The suspension density of goethite and gibbsite were adjusted such that each suspension density in solution was equal to $70 \text{ m}^2 \text{L}^{-1}$ 0.01 M NaCl. The reaction pH was held constant at 7.0 using 0.1 or 1.0 M NaOH or HCl and a pH stat. Incremental additions of 250 μM of As(V), Cu(II) and or Zn(II) were administered at minimum 0.5 h intervals or until the change in pH was equal to zero (whichever came later). The equilibration period for all samples was equal to 24 h after the final reactant was ap-

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