

Table 1. Molar ratios and concentrations of Fe(III), citric acid, and As(V) in the initial 50-mL stock solutions used for coprecipitate formation.

| Treatment | Millimoles in Stock Solution | | | Concentration (mM) | | |
|-----------------------------------------------------|------------------------------|-------------|-------|--------------------|-------------|-------|
| | Fe(III) | Citric acid | As(V) | Fe(III) | Citric acid | As(V) |
| Fe ₁₀ As _{0.5} | 10 | 0 | 0.5 | 200 | 0 | 10 |
| Fe ₁₀ C _{0.5} As _{0.5} | 10 | 0.5 | 0.5 | 200 | 10 | 10 |
| Fe ₁₀ C _{2.5} As _{0.5} | 10 | 2.5 | 0.5 | 200 | 50 | 10 |
| Fe ₁₀ C ₅ As _{0.5} | 10 | 5 | 0.5 | 200 | 100 | 10 |

Results

Arsenic K-edge EXAFS as well as magnitude and real part of the Fourier transform of the samples analyzed are shown in Fig. 1. EXAFS fit parameters obtained from shell-fits are summarized in Table 2. The white line position at 11,875 eV in the As K-edge XANES spectra of all our samples matched those of the As(V) references (not shown), implying that a net reduction of As(V) during the experiment was negligible. Data in Table 2 reveal that citrate had no effect on the As-O bond distance, which remained constant at a mean value of 1.69 Å, which is in line with previous results [8, 10]. Citrate had also no effect on the As-Fe bond distance in the coprecipitated samples, which stayed constant within error at 3.32 Å. This value is identical to that fitted by Voegelin et al. [10] to As(V)-adsorbed Fh, and is also in agreement with the mean As-Fe distance (fitted with two As-Fe contributions) in Fh coprecipitated with As(V) at pH 4 [8].

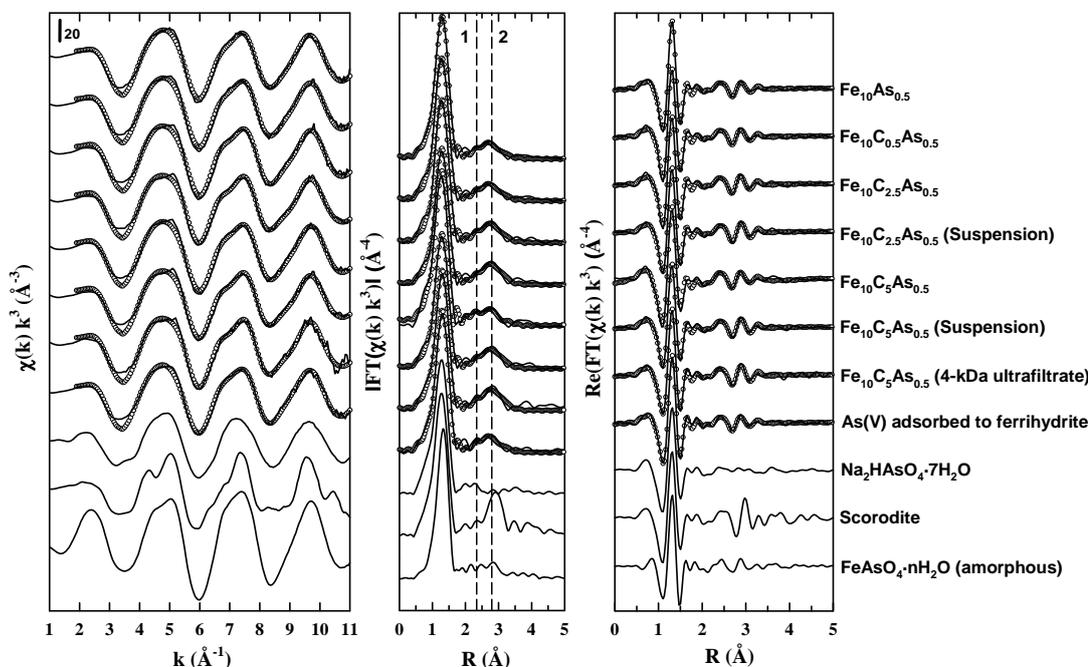


Figure 1. Arsenic K-edge EXAFS as well as magnitude and real part of the Fourier transform of the solids and suspensions analyzed. Solid lines are experimental data and open circles represent best model fits. Vertical lines indicate peaks in the Fourier transform magnitude assigned to multiple scattering within the AsO₄ tetrahedron (1) and As-Fe single scattering paths of ²C surface complexes in which As(V) shares two corners with edge-sharing Fe(O,OH)₆ octahedra (2). *R* was not corrected for phase shift.

Coordination numbers of second-shell Fe correspond well to our As(V)-adsorbed Fh reference and suggest that the binding mode of coprecipitated As(V) is not significantly different from adsorbed As(V). All data are in accordance with a bidentate binuclear As(V) surface complex (²C) in which As(V) binds to the corners of two adjacent edge-sharing Fe(O,OH)₆ octahedra. Implementation of a bidentate mononuclear ¹E surface complex in our shell-fit scheme yielded negative coordination numbers for an As-Fe path with a mean half path length of about 2.85 Å, which implies the absence of ¹E complexes in agreement with Waychunas et al. [6]. In addition, coordination numbers of the As-Fe path (Table 2) were significantly greater than those for As(V) on goethite (0.8 - 1.1 ± 0.7; [11]) and do not support the exclusive formation of a monodentate As(V) complex on Fh. It follows that during rapid coprecipitation of As(V) with Fh in the presence or absence of citrate, no energetically less favorable innersphere surface complexes (¹E) are formed, even when the molar concentration of citrate exceeds that of As(V) ten-fold. Our results suggest that under the experimental conditions used in this study (pH 4.3 - 6.6, *I* ~ 0.45 M) low molecular weight polyhydroxycarboxylates do not change the surface speciation of As(V) on poorly crystalline Fe(III)-(hydr)oxides.

Table 2. EXAFS shell-fit parameters determined from the As K-edge EXAFS spectra. The passive amplitude reduction factor, S_0^2 , was set to 1 for all samples. Bold values: parameter fixed in the fit. Errors are given as standard errors.

| Sample | ΔE_0 (eV) ^a | Path | CN ^b | σ^2 (Å ²) ^c | R ^d (Å) | R-factor ^e | Red χ^2 ^f |
|------------------------------------------------------------------|--------------------------------|--------------------|-----------------|-------------------------------------------|--------------------|-----------------------|---------------------------|
| As(V) adsorbed to ferrihydrite | 12.8 +/- 1.1 | As-O | 4.00 | 0.0023 +/- 0.0003 | 1.69 +/- 0.00 | 0.011 | 32 |
| | | As-Fe | 2.14 +/- 0.65 | 0.0120 | 3.30 +/- 0.02 | | |
| | | MS1-3 ^g | | | | | |
| Fe ₁₀ As _{0.5} | 13.5 +/- 1.3 | As-O | 4.00 | 0.0023 +/- 0.0003 | 1.69 +/- 0.01 | 0.015 | 65 |
| | | As-Fe | 2.09 +/- 0.78 | 0.0120 | 3.32 +/- 0.03 | | |
| | | MS1-3 ^g | | | | | |
| Fe ₁₀ C _{0.5} As _{0.5} | 13.2 +/- 1.5 | As-O | 4.00 | 0.0023 +/- 0.0004 | 1.69 +/- 0.01 | 0.019 | 110 |
| | | As-Fe | 2.31 +/- 0.87 | 0.0120 | 3.31 +/- 0.03 | | |
| | | MS1-3 ^g | | | | | |
| Fe ₁₀ C _{2.5} As _{0.5} | 13.4 +/- 1.5 | As-O | 4.00 | 0.0023 +/- 0.0004 | 1.69 +/- 0.01 | 0.019 | 96 |
| | | As-Fe | 2.74 +/- 0.87 | 0.0120 | 3.30 +/- 0.02 | | |
| | | MS1-3 ^g | | | | | |
| Fe ₁₀ C _{2.5} As _{0.5} (Suspension) | 12.7 +/- 1.3 | As-O | 4.00 | 0.0027 +/- 0.0003 | 1.69 +/- 0.01 | 0.015 | 149 |
| | | As-Fe | 3.06 +/- 0.76 | 0.0120 | 3.32 +/- 0.02 | | |
| | | MS1-3 ^g | | | | | |
| Fe ₁₀ C ₅ As _{0.5} | 12.5 +/- 1.1 | As-O | 4.00 | 0.0022 +/- 0.0004 | 1.69 +/- 0.01 | 0.024 | 162 |
| | | As-Fe | 2.44 +/- 0.84 | 0.0120 | 3.30 +/- 0.03 | | |
| | | MS1-3 ^g | | | | | |

^a energy shift parameter

^b CN = coordination number (path degeneracy)

^c Debye-Waller parameter; the value for the As-Fe path was fixed to that of arsenate adsorbed to ferrihydrite [10]

^d R = half path length uncorrected for phase shift. The half path length of the Fe-O path was identical within error for all samples. Hence, its value was fixed to the one determined from a simultaneous fit of all spectra.

^{e, f} R-factor = $\frac{\sum_i (\text{data}_i - \text{fit}_i)^2}{\sum_i \text{data}_i}$ and reduced $\chi^2 = \frac{N_{\text{idp}}}{N_{\text{pts}}} \sum_i \left(\frac{\text{data}_i - \text{fit}_i}{\varepsilon_i} \right)^2 (N_{\text{idp}} - N_{\text{var}})^{-1}$. N_{idp} , N_{pts} , and N_{var} are,

respectively, the number of independent points in the model fit, the total number of data points, and the number of variables in the fit. ε_i is the uncertainty of the i^{th} data point [12]. Fit range: 0.9-3.6 Å; $N_{\text{idp}} = 15$, $N_{\text{var}} = 5$.

^g Multiple scattering paths: MS1 = triangular As-O-O MS path, path degeneracy = 12, $R = 1.8165 \times R_{\text{As-O}}$, $\sigma^2 = \sigma_{\text{As-O}}^2$; MS2 = collinear As-O-As-O MS path, path degeneracy = 4, $R = 2 \times R_{\text{As-O}}$, $\sigma^2 = 4 \times \sigma_{\text{As-O}}^2$; MS3 = non-collinear As-O-As-O MS path, path degeneracy = 12, $R = 2 \times R_{\text{As-O}}$, $\sigma^2 = 2 \times \sigma_{\text{As-O}}^2$.

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