Arsenite sorption at the magnetite–water interface during aqueous precipitation of magnetite: EXAFS evidence for a new arsenite surface complex

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Received 17 August 2007; accepted in revised form 9 March 2008; available online 1 April 2008

Abstract

The interaction of aqueous As(III) with magnetite during its precipitation from aqueous solution at neutral pH has been studied as a function of initial As/Fe ratio. Arsenite is sequestered via surface adsorption and surface precipitation reactions, which in turn influence the crystal growth of magnetite. Sorption samples were characterized using EXAFS spectroscopy at the As K-edge in combination with HRTEM observations, energy dispersive X-ray analysis at the nanoscale, electron energy loss spectroscopy at the Fe L3-edge, and XRD-Rietveld analyses of reaction products. Our results show that As(III) forms predominantly tridentate hexanuclear As(III)O3 complexes (3C), where the As(III)O3 pyramids occupy vacant tetrahedral sites on {111} surfaces of magnetite particles. This is the first time such a tridentate surface complex has been observed for arsenic. This complex, with a dominant As–Fe distance of 3.53 ± 0.02 Å, occurs in all samples examined except the one with the highest As/Fe ratio (0.33). In addition, at the two highest As/Fe ratios (0.133 and 0.333) arsenite tends to form mononuclear edge-sharing As(III)O3 species (2E) within a highly soluble amorphous As(III)–Fe(III,II)-containing precipitate. At the two lowest As/Fe ratios (0.007 and 0.033), our results indicate the presence of additional As(III) species with a dominant As–Fe distance of 3.30 ± 0.02 Å, for which a possible structural model is proposed. The tridentate 3C As(III)O3 complexes on the {111} magnetite surface, together with this additional As(III) species, dramatically lower the solubility of arsenite in the anoxic model systems studied. They may thus play an important role in lowering arsenite solubility in putative magnetite-based water treatment processes, as well as in natural iron-rich anoxic media, especially during the reductive dissolution-precipitation of iron minerals in anoxic environments.

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1. INTRODUCTION

Magnetite is a common magnetic iron oxide in the lithosphere, pedosphere, and biosphere (Cornell and Schwertmann, 2003). In ambient temperature Earth surface environments, magnetite often forms via bacterial activity in aquifers, soils, and sediments. Under microaerophilic conditions, magnetotactic bacteria produce intracellular magnetite, which could serve as a potential biosignature in rocks (Thomas-Keptra et al., 2000; Golden et al., 2004). Under anoxic conditions, iron-reducing bacteria...
can induce the formation of extracellular magnetite via dissimilatory reduction of ferric-oxyhydroxides (Lovley et al., 1987; Cooper et al., 2000; Ona-Nguema et al., 2001; Ona-Nguema et al., 2002; Glasauer et al., 2003). During iron and arsenic bioreduction in anoxic media, which is thought to be responsible for arsenic contamination of groundwater in various localities, especially in Southeast Asia (e.g., Horneman et al., 2004; Polizzotto et al., 2005, 2006), neoformed, fine-grained magnetite, as well as other Fe(II)-bearing minerals (Larsen and Postma, 2001; Hansel et al., 2003; Hansel et al., 2005), can potentially influence the mobility of toxic trace elements such as arsenic via sorption and coprecipitation processes. Fine-grained magnetite is especially efficient at adsorbing As(III), the most toxic form of arsenic (Dixit and Hering, 2003), and its use for arsenic decontamination of water has been proposed based on its magnetic properties (Yavuz et al., 2006). However, little is known about the mechanism of interaction of dissolved As(III) with magnetite, especially during sorption and coprecipitation reactions. Based on X-ray absorption spectroscopy analysis, Coker et al. (2006) proposed that As(III) adsorbs onto the surface of neoformed magnetite upon dissimilatory reduction of arsenic-bearing ferricydrate; however, the structure(s) and mode(s) of adsorption of the surface complex(es) were not determined. The objectives of the present study are to investigate the fate of As(III) during aqueous precipitation of magnetite and to evaluate the effect of As(III) on magnetite nucleation and growth processes as a function of the initial As(III)/Fe ratio in the aqueous medium. The mineralogy of the samples, including size, shape, and composition of the magnetic particles, and the oxidation state of iron, was characterized by coupling high-resolution transmission electron microscopy (HRTEM), energy dispersive X-ray analysis at the nanoscale, electron energy loss spectroscopy (EELS) at the Fe L$_2$-edge, and X-ray Rietveld analysis. The local environment of arsenic was determined by extended X-ray absorption fine structure (EXAFS) spectroscopy at the As K-edge. Our results show that As(III) forms a relatively soluble amorphous surface precipitate as well as several types of surface complexes, which lower the availability of As(III) in the anoxic systems studied and significantly influence the size of magnetite crystals, they also provide insights to the behavior of arsenite during magnetite precipitation in reducing environments.

2. MATERIALS AND EXPERIMENTAL DETAILS

2.1. Sample preparation

We prepared a series of magnetite samples with the following As(III)/Fe molar ratios: 0, 0.007, 0.033, 0.067, 0.133, and 0.333; these samples are referred to as MtAs0, MtAs0.007, MtAs0.033, MtAs0.067, MtAs0.133, and MtAs0.333, respectively. The synthesis was performed in a JACOMEX® glove box under N$_2$ atmosphere (<20 ppm O$_2$). All reagents were reagent grade (>99.9% purity level), and the solutions were prepared in the glove box with O$_2$-free milli-Q water. Samples were prepared by aqueous coprecipitation of Fe$^{2+}$ and Fe$^{3+}$ ions in the presence of various quantities of H$_3$AsO$_3$ ions by adding selected volumes of 1 M NaAsO$_2$ solution to serum bottles containing 5 mL of 1 M FeCl$_3$·6H$_2$O solution and 10 mL of 1 M FeCl$_2$·4H$_2$O solution. The pH was then adjusted to 7.2 by adding appropriate quantities of 1 M NaOH solution. The final ionic strength of the solutions ranged from 0.7 to 1 M. Each flask was sealed with butyl rubber stoppers and was agitated for 24 h at 25 °C. The suspension was then centrifuged, and the resulting black powder was dried under vacuum in the glove box for later X-ray diffraction (XRD) analysis, high-resolution transmission electron microscopy (HRTEM), and energy dispersive X-ray spectroscopy (EDXS) analysis. The supernatant was filtered through a 0.22 μm cellulose membrane, acidified to pH 1 with HNO$_3$, and stored in the glove box until further solution analysis.

Two reference samples were also prepared. An Fe(III)–As(III)-containing coprecipitate was synthesized as described above, with an As(III)/Fe(III) ratio of 0.5, in the absence of Fe(II) in the aqueous medium. A sample of As(III) adsorbed on magnetite, referred to as As(III)/Mt, was synthesized at the same pH as the coprecipitates studied here (pH 7.2), using sample MtAs0 as the substrate and an As/Fe ratio of 0.010. In preparing this sample, 0.5 g of magnetite powder (MtAs0) was suspended in a serum bottle with 0.1 M NaCl solution. Then, 1.0 mL of 0.0668 M NaAsO$_2$ was added, and the pH was adjusted to 7.2 by adding an appropriate quantity of 1 M NaOH solution. The final ionic strength of this solution was 0.1 M. The sample was then treated in the same way as the Fe(III)–As(III)-containing coprecipitation sample. Assuming a surface area of 103 ± 3 m$^2$ g$^{-1}$ calculated from the mean coherent dimension (MCD) value (Table 1), the As surface loading determined by analyzing the supernatant was 1.3 ± 0.1 μmol m$^{-2}$ after a reaction time of 24 h.

2.2. Aqueous phase analysis

The supernatants were filtered through a 0.22 μm membrane and acidified to pH 1 with HNO$_3$ in the glove box to avoid precipitation of iron oxides that would cause a decrease in concentration of iron and arsenic in the solution. Fe concentrations were determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES) performed on a Jobin-Yvon® IY 238 Ultratec spectrometer, and As concentrations were determined by graphite furnace atomic absorption spectrometry (GFAAS) on a Unicam® 989 QZ spectrometer. The detection limits were 0.018 and 0.03 μM for Fe and As, respectively.

2.3. Electron microprobe analysis (EMPA)

The concentration of arsenic in the solid samples was measured by electron microprobe analysis at the Centre d’Analyses par Microsonde Electronique de Paris (Université Paris 6) using an SX50 CAMBEC electron microprobe equipped with four wavelength dispersive spectrometers, operating at 20 kV and 40 nA, with a counting time of 10 s per point for measuring As. Twenty point analyses were averaged for each sample.
EXAFS evidence for a new arsenite surface complex on magnetite

2.4. X-ray diffraction (XRD)

To avoid oxidation by air, each powder sample was loaded into a glass capillary of 0.5 mm diameter, and the capillary was sealed with Super glue under an N₂ atmosphere in the glove box (O₂ ≤ 20 ppm). XRD measurements were performed with Co Ka radiation on a Panalytical X'Pert Pro MPD diffractometer mounted in Debye-Scherrer configuration using an elliptical mirror to obtain a high flux parallel incident beam and an X'Celerator detector to collect the diffracted beam. Data were recorded in the continuous-scan mode within the 5–80° range with a step of 0.0167°. Diffraction patterns of samples MtAs0.067, MtAs0.133, and MtAs0.333 were recorded in 48 h, and XRD patterns of samples MtAs0, MtAs0.007, and MtAs0.033 were recorded in 12 h and were normalized in intensity to the previously obtained diffraction patterns by multiplying the latter by a factor of 4.

X-ray powder diffraction patterns were analyzed by the Rietveld method using the XND 1.3 program (Berar, 1990). Absorption through the capillary was corrected using a factor of 4.

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Table 1

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<th>Sample</th>
<th>(Fe) initial</th>
<th>[As] initial</th>
<th>[As] solid</th>
<th>[Fe] solid</th>
<th>(A˚ F W H M)</th>
<th>(wt%)</th>
<th>MCDf</th>
<th>SA</th>
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<td>n.m.</td>
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<td>2.9</td>
<td>3.2</td>
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<tr>
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<td>316000</td>
<td>2.0</td>
<td>19.4</td>
<td>4.2</td>
<td>366</td>
<td>n.m.</td>
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<table>
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<tr>
<th>Sample</th>
<th>As(III) sorbed on</th>
<th>(A˚ F W H M)</th>
<th>(wt%)</th>
<th>MCDf</th>
<th>SA</th>
<th>g</th>
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<tbody>
<tr>
<td>MtAs0</td>
<td>2.4(1)</td>
<td>11.3(3)</td>
<td>0.82</td>
<td>n.m.</td>
<td>n.m.</td>
<td>n.m.</td>
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<tr>
<td>MtAs0.007</td>
<td>2.2(1)</td>
<td>11.3(3)</td>
<td>0.82</td>
<td>n.m.</td>
<td>n.m.</td>
<td>n.m.</td>
</tr>
<tr>
<td>MtAs0.033</td>
<td>11.2(1)</td>
<td>11.3(3)</td>
<td>0.82</td>
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<td>0.82</td>
<td>n.m.</td>
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<td>n.m.</td>
</tr>
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</table>

Note: All entries are given in parentheses and refer to the last digit.
2.6. XAFS data collection

XAFS data on vacuum-dried samples were recorded at the As K-edge (11,869 eV) using Si(220) double-crystal monochromator on beamline 11-2 at the Stanford Synchrotron Radiation Laboratory (SSRL). All data were collected in fluorescence detection mode using a 30 element Ge array detector. Elastic scattering and Fe fluorescence were minimized using a 3 AGeV filter. Energy resolution was around 0.4-0.5 eV, with a vertical beam width of 250 μm, which was achieved using focusing mirrors. The horizontal beam width was limited to 500 μm using vertical slits. Energy was calibrated by using a double-transmission setup in which the As K-edge spectrum of the samples and that of a soroctide, FeAsO4.2(H2O) reference sample were simultaneously recorded. The absorption maximum of the As(V)-edge was chosen at 11,872 ± 0.05 eV.

Photo-oxidation of As(III) under the X-ray beam (Ona-Nguema et al., 2005) was limited by recording all data at 10–15 K using a modified Oxford® liquid He cryostat. In order to preserve anoxic conditions, the samples were transferred from the glove box to a liquid nitrogen bath and then to the cryostat where they were placed in a He atmosphere. Between 4 and 8 EXAFS scans were accumulated for each sample in order to obtain an adequate signal-to-noise ratio at kmax = 14.5 Å-1. Samples were automatically moved 1 mm between each EXAFS scan since repeated scans on the same sample location might cause up to 7 ± 2% of As(III) to be oxidized after a 30 min EXAFS scan, which is below the EXAFS detection limit of mixed arsenic species (Cances et al., 2005).

2.7. EXAFS data analysis

EXAFS data were extracted using the XAFS program (Winter, 1997) following the procedure detailed previously (Ona-Nguema et al., 2005). Radial distribution functions around the As absorber were obtained by calculating the Fourier transform (FT) of the k2ρ(k) EXAFS functions using a Kaiser–Bessel window within the 2.7–14.5 Å-1 k-range (except for the MtAs0.333 sample within the 2.7–12.3 Å-1 k-range because of poor data quality for this sample) with a Bessel weight of 2.5. Least-squares fitting of the unfiltered k2ρ(k) functions was performed with the plane-wave formalism, using a Levenberg–Marquard minimization algorithm. Theoretical phase-shift and amplitude functions employed in this fitting procedure were calculated with the curved-wave formalism using the ab initio FEFF 8 code (Ankudinov et al., 1998). As−O and As−Fe phase-shift and amplitude functions were extracted from the toolette structure (Morin et al., 2007) using FEFF 8.

The fit quality was estimated using a reduced χ2 of the following form:

\[ \chi^2 = \frac{N_{\text{ind}}}{(N_{\text{ind}} - p)} \sum \frac{[\text{FT}]_{\text{exp}} - [\text{FT}]_{\text{calc}})^2}{n} \]

with Nind (the number of independent parameters) = (2kΔkΔR)/(π), p the number of free fit parameters, n the number of data points fitted, and [FT]exp and [FT]calc the experimental and theoretical Fourier transform magnitudes within the [0–8 Å] k-range of the k2-weighted EXAFS. The number of allowable independent parameters is 59 (Δk = 11.8 and ΔR = 8), and our fits included at most 16 variable parameters. A similar reduced χ2 was calculated for the k3ρ(k) function and is referred to as χ3.

3. RESULTS

3.1. Mineralogical composition of the samples

XRD analyses (Fig. 1) indicate that all samples except one (MtAs0.333) consist primarily of magnetite (Mt), with at least five detectable characteristic Bragg reflections ([220), (311), (400), (511), and (440)]. The exception (MtAs0.333) was a poorly defined amorphous phase with very broad lines slightly shifted with respect to the (311), (511), and (440) Bragg reflections of magnetite. Halite (NaCl) was present in all samples as a minor component, except for sample MtAs0.007, and served as an internal standard. Halite was a by-product of our magnetite synthesis procedure that used iron chloride and sodium hydroxide as starting reactants. Halite likely precipitated during vacuum drying of the final product so that no interference with magnetite nucleation and growth is expected. The capillary glass used as the sample container yielded a broad band at ~8.9°2θ.

Except for the most As-rich sample (MtAs0.333), no shift in Mt peak positions was observed from sample to sample. Rietveld analyses of all samples except MtAs0.333 indicate that the cell parameter of the spinel phase [a ~ 8.40 Å (see Table 1)] is consistent with that of magnetite (a = 8.396Å), and it is significantly larger than that of maghemite (a = 8.347Å) (Hill et al., 1979). In contrast, the full width at half maximum (FWHM) of the observed XRD lines significantly increase with increasing As(III)/Fe ratio, except for the MtAs0.007 sample which exhibits smaller FWHM than the MtAs0 control sample. The dominant Lorentzian shape of the observed peaks and the good match to a Scherrer broadening model (H_G2 = H_G3 = H_L3 = 0 in Eq. (1); Table 1) indicate that the broadening of the XRD lines is mainly due to a decrease of the mean coherent dimension (MCD) of the magnetite crystallites in the samples studied. Surface areas calculated from these MCD values, assuming a spherical shape, vary from 90 ± 1 m2 g−1 for sample MtAs0.007 to 366 ± 25 m2 g−1 for sample MtAs0.133. Particle sizes determined by HRTEM observation of selected samples are consistent with Rietveld results and indicate that magnetite particle size decreases with increasing As(III)/Fe ratio (Table 1). In addition, TEM-determined particle sizes are consistent with this conclusion. Fifty particles of samples MtAs0 and MtAs0.007 measured using the TEM have mean diameters within the 5–15 nm range (Fig. 2a and b), whereas mean particle diameters for samples MtAs0.133 and MtAs0.333, are in the 3–5 nm range (Fig. 2c and d) and the 2–5 nm range (Fig. 2e), respectively. However, Mt crystal sizes for the samples with the lowest As(III) concentrations (MtAs0.007 and MtAs0.333) were found to be larger than that for the As-free sample (MtAs0) (Table 1). This exception to the inverse correlation between magnetite...
particle size and As(III) concentration was confirmed by preparing and analyzing several replicates of the MtAs0, MtAs0.007, and MtAs0.033 samples and is addressed in Section 4.

HRTEM observations indicate that samples MtAs0 and MtAs0.007 mainly consist of cubo-octahedral shaped magnetite particles (Fig. 2a and b, respectively) displaying well-developed \{111\} crystallographic faces. With increasing As(III) concentration, the decrease in particle size makes it difficult to unambiguously determine their morphologies (samples MtAs0.133 and MtAs0.333 (Fig. 2c, d, and e)). A thin amorphous layer was detected on some of the surfaces of As-sorbed magnetite nano-particles samples except for those with the two lowest As/Fe ratios (MtAs0 and MtAs0.007; see Fig. 2a and b). This amorphous layer was found in sample MtAs0.067 (not shown) and is thicker in samples MtAs0.133 and MtAs0.333 (Fig. 2c, d, and e).

The final concentration of dissolved iron decreased regularly with increasing initial arsenic concentration to <0.03 μM for sample MtAs0.033. For higher As concentrations, the dissolved iron concentration (e.g., 2.0 ± 0.1 μM for sample MtAs0.333) remains far below the value of the As-free sample (13270 ± 50 μM for sample MtAs0) (Table 1). This result suggests that, in addition to possible arsenic adsorption onto the magnetite particles, a fraction of arsenic and iron coprecipitated to form this amorphous layer. The composition of this coprecipitate was estimated by EDXS analysis of the amorphous layer in sample MtAs0.333 and it contains Fe and As in the As/Fe molar ratio of ~1 (Fig. 2f). EELS analysis of the amorphous layer suggests that the redox state of iron in the amorphous layer is similar to that in magnetite. Given the energy resolution

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Fig. 1. Rietveld refinement of the X-ray powder diffraction patterns of the MtAs samples. Experimental: dashed lines; calculated: solid lines.
of our EELS data, a significant change in the iron redox state should have led to a shift in the energy loss maximum of the Fe L$_3$ peak (Gloter et al., 2003), which was not observed.
3.3. EXAFS results: local environments of arsenic

Arsenic K-edge XANES data indicate that As(III) did not oxidize in any of the experiments. Indeed, XANES spectra of As(III)-sorbed samples exhibit a well-resolved edge structure with an absorption maximum at 11,871.3 eV (not shown), corresponding to As(III) (Ona-Nguema et al., 2005). Although Fe(III) can oxidize As(III) to As(V) in solution, based on equilibrium thermodynamic data (Vanysek, 1995), our XANES results indicate that no observable change in arsenic oxidation state occurred in any of the sorption samples within 24 h. This result is consistent with those recently obtained by our group for As(III) sorption onto ferric-oxihydroxides, which showed that As(III) did not oxidize in the presence of ferricydrite, goethite, or lepidocrocite even after an equilibration time of 1 week under anoxic conditions (Ona-Nguema et al., 2005). Arsenic(III) is known to oxidize rapidly under oxidic or microaerophilic conditions when Fenton reactions take place via reactive oxygen species (e.g., O$_2^\cdot$, H$_2$O$_2$, OH$^-$) formed as intermediate species during the oxidation of Fe(II) by dissolved O$_2$ (Hug and Leupin, 2003). In the present study, strict anoxic conditions prevented any As(III) oxidation by Fenton reactions.

3.3. EXAFS results: local environments of arsenic

Arsenic K-edge, unfiltered, $k^2$-weighted EXAFS data for the samples are displayed in Fig. 3a, and those for two reference compounds are shown in Fig. 3c. The corresponding Fourier transforms are shown in Fig. 3b and d. The spectra of MtAs0.033, MtAs0.067, and MtAs0.133 exhibit strong similarities, and differ from those of MtAs0.007 and MtAs0.333. Tables 2 and 3 list the results of fitting the unfiltered $k^2$*g*(k) EXAFS functions. First-neighbor contributions were fit with 2.7–3.2 oxygen atoms at 1.78 ± 0.02 Å (Table 3), corresponding to the six As–O–O paths within the AsO$_3$ pyramid (Fig. 3a and b, and Table 3). The number of multiple scattering paths was fixed at the expected value of 6. The distances fit for this contribution in our samples ranged from 3.15 to 3.22 Å, and thus they are consistent with the corresponding As–O–O multiple scattering path in the structure of tooleite (3.14 Å) (Morin et al., 2007).

The EXAFS spectra of samples MtAs0.007, MtAs0.033, MtAs0.067, and MtAs0.133 exhibit sharp second-neighbor contributions, as well as significant contributions from neighbors at longer distances (Fig. 3b). Second-neighbor contributions for samples MtAs0.033, MtAs0.067, and MtAs0.133 are similar (Fig. 3b), but they differ from those for sample MtAs0.007.

For sample MtAs0.007, two As–Fe pair correlations at 3.30 ± 0.02 and 3.49 ± 0.02 Å were observed (Fig. 3a and b, and Table 3). In contrast, for samples MtAs0.033, MtAs0.067, and MtAs0.133, the fits yielded a well-defined As–Fe pair correlation at 3.53 ± 0.02 Å and an additional one at 3.73 ± 0.02 Å (Fig. 3a and b, and Table 3). In sample MtAs0.333, the weak second-neighbor contribution was fit by 0.3 Fe atoms at 2.97 ± 0.03 Å (Fig. 3b and Table 3). This As–Fe distance is similar to that found for the XRD amorphous Fe(III)–As(III) coprecipitate model compound, although for this latter compound, an additional As–Fe pair correlation was fit at 3.37 ± 0.02 Å (Fig. 3d and Table 3).

Interestingly, the As–Fe pair correlations at 3.53 ± 0.02 and 3.73 ± 0.02 Å in samples MtAs0.033, MtAs0.067, and MtAs0.133 are, within estimated error, similar to those observed in the As(III)/magnetite sorption sample (Fig. 3d and Table 3). This similarity extends to more distant features in the FT at 4–7 Å, which are significant for all samples except the most concentrated one (sample MtAs0.333). Analysis of these long-distance contributions is detailed for sample MtAs0.067 in Fig. 4 and Table 2, and shows that they are due to multiple scattering. Arsenic K-EXAFS data of this sample are consistent with a 3C tridentate hexanuclear As(III) surface complexes where the AsO$_3$ pyramid occupies a tetrahedral vacancy on the [111] surface of magnetite. The geometry of this proposed surface complex is displayed in Fig. 5a and b. Feff8 calculations show that major photoelectron multiple scattering paths expected from the proposed geometry compare well with the experimental data. Indeed, in addition to the As–Fe pair correlations at 3.53 ± 0.02 and 3.72 ± 0.02 Å, the fit result yields two main multiple scattering paths: As–O–Fe at 5.53 ± 0.05 Å and As–Fe–Fe–Fe at 6.97 ± 0.5 Å, and a minor single scattering As–Fe pair at 6.00 ± 0.5 Å, all of which are consistent with the proposed 3C complex. Although the number of neighbors that can be determined from these longer distance contributions has lower precision than the number of closer Fe neighbors, these longer distances have good precision (±0.05 Å); therefore, they can be used to propose this intermediate-range structure model. Contributions from all of these long paths are clearly observed in the FT's of the EXAFS spectra of the As(III)/Mt sorption sample (Fig. 3d), and most of them are observed in the FT's of samples MtAs0.033 and MtAs0.007 (Fig. 3b). They are much less intense in the FT of sample MtAs0.133 (Fig. 3b).

4. DISCUSSION

4.1. Molecular-level speciation of arsenic(III) at the magnetite–water interface

Our results indicate the formation of tridentate hexanuclear corner-sharing (3C) As(III)O$_3$ complexes on the [111] facets of magnetite under the experimental conditions of this study. Such a surface complex, referred to as species (i) in Table 3 and in the following text, is displayed in Fig. 5a and b. It occurs in samples MtAs0.007, MtAs0.033, MtAs0.067, and MtAs0.133 as well as in the As(III)/Mt sorption sample. The dominant As–Fe pair correlation at 3.53 ± 0.02 Å, which is characteristic of the proposed 3C complex on the magnetite surface, is similar to the single As–Fe pair correlation at 3.50 ± 0.05 Å recently observed by Coker et al. (2006) in their As(III)/Mt sorption sample, as well as in their Mt sample resulting from the bioreduc-
tion of As-doped ferrihydrite. Such a similar distance that differs from those generally observed for As(III) sorption complexes on other iron oxides, i.e. 2.9 and 3.4 Å for $^2E$ and $^2C$ complexes, respectively (Ona-Nguema et al., 2005).
EXAFS evidence for a new arsenite surface complex on magnetite

Table 2

<table>
<thead>
<tr>
<th>Scattering paths</th>
<th>EXAFS MtAs0.067</th>
<th>³C As(III) complex on the [111] face of magnetite</th>
<th>Tetrahedral Fe on the [111] face of magnetite⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R (Å) N</td>
<td>R (Å) N</td>
<td>R (Å) N</td>
</tr>
<tr>
<td>O</td>
<td>1.79 3 As–O</td>
<td>1.79 3 As–O</td>
<td>1.89 4 Fe–O</td>
</tr>
<tr>
<td>A</td>
<td>3.53 4.6 As–Fe–O</td>
<td>3.52 6 As–Fe–O</td>
<td>3.48 6 Fe–Fe–O</td>
</tr>
<tr>
<td>B</td>
<td>3.72 1.9 As–Fe–O</td>
<td>3.72 1 As–Fe–O</td>
<td>3.63 1 Fe–Fe–O</td>
</tr>
<tr>
<td>C</td>
<td>5.53 1.8 As–O–Fe–O</td>
<td>5.48 8 As–O–Fe–O</td>
<td>5.45 8 Fe–Fe–O</td>
</tr>
<tr>
<td>D</td>
<td>6.00 1.8 As–Fe–O</td>
<td>6.00 3 As–Fe–O</td>
<td>5.93 3 Fe–Fe–O</td>
</tr>
<tr>
<td>E</td>
<td>6.98 1.1 As–Fe–O–Fe–O</td>
<td>6.94 3 As–Fe–O–Fe–O</td>
<td>6.88 3 Fe–Fe–O–Fe</td>
</tr>
<tr>
<td>G</td>
<td>6.99 1.8 As–O–Fe–O–Fe–O</td>
<td>6.96 3 As–O–Fe–O–Fe–O</td>
<td>6.75 3 Fe–Fe–O–Fe–O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Dominant single and multiple scattering paths (O, A, B, C, D, E, F, G) were identified by a Feff8 calculation based on the structural model drawn in Fig. 5a and b. In this model, the position of the As atom and of its first-neighbor oxygen atoms has been adjusted by trial and error to approach the optimum geometry of the AsO₃ pyramid (As–O = 1.79 Å and O–As–O = 100° in As₂O₅) and to satisfy the observed As–Fe distance of 3.53 Å. The corresponding displacement of oxygen atoms belonging to Fe octahedra leads to a relaxation of the Fe–O distance of only 1%. The relative contributions to the EXAFS of the dominant single and multiple scattering paths corresponding to the proposed ³C surface complex are displayed in Fig. 4 for sample MtAs0.067.

Note: R (Å), interatomic distances; N, number of neighbors; errors on R and N values, estimated from the fit of the tooeleite As K-edge EXAFS data (not shown), are ±0.02 and ±0.05 below R = 4 Å, ±0.05 and ±1.0 above R = 4 Å.

⁶ Scattering paths shown in Fig. 5.

²⁷ Feff calculation based on the crystal structure from Hill et al. (1979), assuming a central Fe atom in tetrahedral site lying on the half of a crystal sliced along a (111) plane terminated by octahedral sites.

and references therein), suggests that the dominant speciation of arsenite in the As(III)/Mt samples prepared by Coker et al. corresponds to the ³C surface complex we have proposed. Finally, the formation of this complex on the [111] surfaces of our fine particle magnetite is consistent with the octahedral termination of this surface, as recently proposed by Petitto et al. (2006) from single crystals surface X-ray diffraction analyses.

A second species, referred to as (ii), is characterized by a single As–Fe pair at 2.98 ± 0.03 Å that can be interpreted as a bidentate mononuclear edge-sharing surface complex (²E). This dominant species in the most concentrated MtAs0.333 sample is likely related to the abundant amorphous surface precipitate coating magnetite particles that was observed by HRTEM in the same sample (Fig. 2e). HRTEM observations of our other samples indicated that species (ii) forms for initial As/Fe ratio of 0.067 and above and that its abundance increases with increasing initial arsenite concentration. The absence of the As–Fe pair correlation at 3.37 ± 0.02 Å in the MtAs0.333 sample, which is observed in the amorphous As(III)–Fe(III) model compound, suggests that the local structures of these amorphous compounds differ significantly. Such a difference could be related to the presence of both Fe(II) and Fe(III) in the amorphous coating and of only Fe(III) in the model compound.

A third species, referred to as species (iii) in Table 3 and in the following text, forms at low initial As concentration and is characterized by As–Fe distances of 3.30 and 4.51 Å, which are clearly observed in the FT’s of sample MtAs0.007 and are observed to a lesser extent in the FT of sample MtAs0.033. No suitable geometry for a surface complex matching these distances was found on the [111] surface of magnetite. Although the structural interpretation of such As–Fe distances is not unique, bidentate binuclear ²C complexes (e.g., on {100} facets or steps of the magnetite particles) could account for such distances. The {100} surface of magnetite exhibits rows of FeO₆ octahedra with singly coordinated oxygens pointing outwards on either oxygen surface termination chosen. Such a ²C complex would yield two As–Fe distances of 3.3 Å, which correspond to the binding of As(III) to singly coordinated oxygen atoms of two adjacent FeO₆ octahedra, and two As–Fe distances of 4.5 Å corresponding to the distance between As and the next tetrahedral Fe sites. According to such a model, the decreasing amount of species (iii) with increasing initial As(III) concentration could indicate that the number of available sites for this species (i.e., (100) facets or steps) decreases with increasing As/Fe ratio. Unfortunately this hypothesis cannot be verified by HRTEM analysis because the morphology of our fine magnetite particles cannot be unambiguously determined when increasing As(III) concentration. Other structural models could also be proposed to explain the set of distances characterizing species (iii), including the formation of As-bearing solid phases other than magnetite during the precipitation process at low As/Fe ratio. However, our HRTEM observations were unsuccessful in revealing the occurrence of such minor phases in samples MtAs0.007 and MtAs0.033.
4.2. Influence of As(III) on the magnetite nucleation and growth process

Magnetite is often synthesized by aqueous precipitation of Fe\(^{3+}\) and Fe\(^{2+}\) ions (Mann et al., 1989; Tronc et al., 1992; Jolivet et al., 1994; Cornell and Schwertmann, 2003). Ionic strength and pH are known to control magnetite particle size (Vayssieres et al., 1998; Jolivet et al., 2004; Sun and Zeng, 2002; Fairev et al., 2004) and crystal morphology (Devouard et al., 1998; Fairev et al., 2005), and the effect of these solution variables on particle size has been modeled by Jolivet et al. (2004). The formation of magnetite is also influenced by other ions in solution, such as phosphate (Mann et al., 1989) and sucrose (Tamura et al., 1979). Based on these past studies, the formation of surface species (i), (ii), and (iii) is thus expected to influence the growth of magnetite.

### Table 3

Results of shell-by-shell fitting of unfiltered EXAFS data for the MtAs samples, the As(III) sorbed on magnetite sample, and the amorphous As(III)–Fe(II) co-precipitate

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\sigma) (Å)</th>
<th>(N)</th>
<th>(\Delta\varepsilon_0) (eV)</th>
<th>CHI(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MtAs0.007</td>
<td>3.22</td>
<td>6.0(1) As–O–O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MtAs0.033</td>
<td>3.18</td>
<td>5.0(1) As–O–O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MtAs0.067</td>
<td>3.15</td>
<td>6.0(1) As–O–O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MtAs0.133</td>
<td>3.12</td>
<td>6.0(1) As–O–O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MtAs0.333</td>
<td>3.11</td>
<td>6.0(1) As–O–O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As(III) adsorbed on MtAs0</td>
<td>3.10</td>
<td>6.0(1) As–O–O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(III)–As(III) co-precipitate</td>
<td>3.07</td>
<td>6.0(1) As–O–O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The fits indicate three groups of distances that are interpreted as corresponding to three types of surface complexes: (i) a tridentate complex on the {111} face, (ii) a tridentate complex in amorphous As(III)–Fe(II,III) precipitate, and (iii) a third species (see text).

**Note:** \(\Delta\varepsilon_0\): difference between the user-defined threshold energy and the experimentally determined threshold energy, in electron volts; CHI\(^2\): goodness-of-fit (see text). During the fitting procedure, all parameter values indicated by (—) were linked to the parameter value placed above in the table and those followed by (f) were fixed. Errors on \(\sigma\) and \(N\) values, estimated from the fit of the tooeelite As K-edge EXAFS data (not shown), are ±0.02 and ±1.0 above \(R = 4\) Å; ±0.05 and ±1.0 above \(R = 4\) Å. Errors on \(\sigma\) and \(\Delta\varepsilon_0\) values are ±0.01 and ±3, respectively.
the nucleation and growth of magnetite in the present study, as discussed below. Cubo-octahedral magnetite particles are the most common shapes observed in our HRTEM images of sample MtAs0, which slightly differ from the morphology of nano-magnetite prepared by Faivre et al. (2005) via coprecipitation of ferrous and ferric ions in aqueous solution. Indeed, Faivre et al. observed magnetite nano-particles with more regularly shaped \{111\} facets than in the present study. This difference may be due to the fact that the supersaturation was higher in the present study than in Faivre et al. (2005). The cubo-octahedral shape of the arsenite-free sample (MtAs0) is preserved at low arsenite concentration (sample MtAs0.007), whereas at higher As(III) concentrations, the particle morphologies become more and more irregular.

The XRD and HRTEM results also show that the particle size of the single-domain magnetite varies as a function of the initial arsenic concentration in the precipitation medium (Table 1). Foreign solutes are known to inhibit the growth of small crystals. For instance, Rose and co-workers (Rose et al., 1996, 1997) found that the presence of sulfate (SO$_4$/Fe = 0.5) had little effect on the outcome of the Fe-oxide synthesis, while a small quantity of phosphate (PO$_4$/Fe = 0.05) can modify the mineralogy as well as the size and structure of the Fe-oxide particles. In addition, Vayssetieres et al. (1998) and Jolivet et al. (2002) have studied the effect of ionic strength ($I$) and pH on the formation of magnetite particles, showing that average particle size decreases from 12.5 nm at pH 8.5 and $I = 0.5$ M to 1.6 nm at pH 12 and $I = 3$ M. In the present study, the only variable affecting particle size is the As(III) concentration in the medium, since the reaction pH and the ionic strength are similar for all samples (pH 7.2, $I = 1.5$ M). Surprisingly, at low concentration, the presence of arsenite favors an increase in size of the magnetite particles. Indeed, the mean particle size in sample MtAs0.007 (13.0 nm) and in sample MtAs0.033 (12.3 nm) is slightly larger than that in the As-free sample MtAs0 (11.3 nm) (Table 1). In contrast, higher arsenic concentrations tend to result in a decrease of the mean size of the magnetite particles: from 12.3 nm for sample MtAs0.033 to 3.2 nm for sample MtAs0.133.

Such an effect could be explained by the hypothesis that the adsorption of As(III) on iron-(hydr)oxide nuclei (species (iii) and (i)) inhibits their further growth and dissolu-

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**Fig. 4.** As K-edge unfiltered EXAFS data recorded at 10 K for sample MtAs0.067 with different fit solutions: (a) $k^3$-weighed $\chi(k)$ EXAFS, and (b) its corresponding Fourier transforms (FT), including the magnitude and imaginary part of the FT. Experimental and calculated curves are displayed as dashed and solid lines, respectively. Form top to bottom, the first fit includes three scattering paths described in Table 2, and each successive fit includes one more scattering path than the previous. The values of the reduced $\chi^2$ and $\chi^2_{FT}$ values (see text) significantly decrease when adding the shells corresponding to the 3C tridentate As(III) complexes on the \{111\} face of magnetite (Table 2). The slight mismatch between the experimental and calculated EXAFS functions at low $k$ values is due to single and multiple scattering by oxygen atoms at long distance. These paths were not included in the fit because of their very small contribution to the EXAFS, by comparison with the large number of fitting parameters required to fit them.
occurrence, giving As–Fe distances from (A) to (G) that are listed in Table 2. FeO₆ octahedra and FeO₄ tetrahedra are represented as shaded polyhedra. The AsO₃ pyramid is represented by a sphere corresponding to the As atom and by gray lines symbolizing the As–O bonds.

The final concentration of dissolved arsenite in our magnetite synthesis experiments was found to regularly increase with increasing initial arsenite concentration (Table 1). However, more than 99.7% of the initial arsenic pool is sorbed by the solid phase for all samples, except for the most concentrated one (MtAs0.333). For this sample, in which As(III) is dominantly hosted by an amorphous surface precipitate (species (ii)), only 71.8% of the initial arsenic pool is sorbed by the solid phase. Such values of arsenic uptake can be interpreted by invoking both adsorption and precipitation, with the later process becoming dominant at the highest arsenite concentration (sample MtAs0.333). Apparent arsenite surface coverage, estimated from surface area values and from dissolved arsenic concentrations, is 0.8 ± 0.1 μmol m⁻² for the most dilute sample (MtAs0.007), and it reaches a maximum value of 4.0 ± 0.2 μmol m⁻² for all other samples (Table 1). This maximum value is slightly higher than the value of 3.7 μmol m⁻² (i.e. a site density of 2.31 sites nm⁻²) generally reported for arsenite sorption on iron oxides, including magnetite (e.g., Dixit and Hering, 2003). Such a high maximum surface coverage (4.0 ± 0.2 μmol m⁻²) observed in our samples is, however, consistent with adsorption complexes of As(III) at the surface of magnetite particles. Indeed this maximum value is lower than the theoretical maximum site density (5.3 μmol m⁻² or 3.2 sites nm⁻²) of tetrahedral vacancies on the {111} magnetite surface with octahedral Fe terminations, which are the dominant sorption sites (³C surface complex); it is also lower than the theoretical maximum density of sites available for ²C complexes on the {100} magnetite surface (4.7 μmol m⁻² or 2.8 sites nm⁻²). However, this high apparent surface coverage could also be explained by the presence of the amorphous precipitate coating magnetite particles observed by HRTEM in samples with As/Fe ratios of 0.067 and above.

4.3. Implications for As(III) solubility at the magnetite–water interface

The final concentration of dissolved arsenite in our magnetite synthesis experiments was found to regularly increase with increasing initial arsenite concentration (Table 1). However, more than 99.7% of the initial arsenic pool is sorbed by the solid phase for all samples, except for the most concentrated one (MtAs0.333). For this sample, in which As(III) is dominantly hosted by an amorphous surface precipitate (species (ii)), only 71.8% of the initial arsenic pool is sorbed by the solid phase. Such values of arsenic uptake can be interpreted by invoking both adsorption and precipitation, with the later process becoming dominant at the highest arsenite concentration (sample MtAs0.333). Apparent arsenite surface coverage, estimated from surface area values and from dissolved arsenic concentrations, is 0.8 ± 0.1 μmol m⁻² for the most dilute sample (MtAs0.007), and it reaches a maximum value of 4.0 ± 0.2 μmol m⁻² for all other samples (Table 1). This maximum value is slightly higher than the value of 3.7 μmol m⁻² (i.e. a site density of 2.31 sites nm⁻²) generally reported for arsenite sorption on iron oxides, including magnetite (e.g., Dixit and Hering, 2003). Such a high maximum surface coverage (4.0 ± 0.2 μmol m⁻²) observed in our samples is, however, consistent with adsorption complexes of As(III) at the surface of magnetite particles. Indeed this maximum value is lower than the theoretical maximum site density (5.3 μmol m⁻² or 3.2 sites nm⁻²) of tetrahedral vacancies on the {111} magnetite surface with octahedral Fe terminations, which are the dominant sorption sites (³C surface complex); it is also lower than the theoretical maximum density of sites available for ²C complexes on the {100} magnetite surface (4.7 μmol m⁻² or 2.8 sites nm⁻²). However, this high apparent surface coverage could also be explained by the presence of the amorphous precipitate coating magnetite particles observed by HRTEM in samples with As/Fe ratios of 0.067 and above.

Finally, the high solubility of this amorphous surface precipitate, as shown by the elevated final dissolved arsenic concentrations in the synthesis experiments for samples MtAs0.133 and MtAs0.333 (Table 1), suggests that it may not represent a relevant species in natural systems unless the As(III) contamination levels of anoxic ground-water exceed the observed maximum of about 5000 μg/L, i.e., 66.67 μM (Smedley and Kinniburgh, 2002). In contrast, our results indicate that the ³C As(III)O₃ surface complex...
(species (i)), together with species (iii), plays a key role in lowering arsenite solubility in our experiments. Such species may thus play an important role in lowering the concentration of dissolved arsenite in putative magnetite-based water treatment processes (Yavuz et al., 2006), as well as in natural iron-rich anoxic media, especially during the reductive dissolution-precipitation of iron minerals in natural anoxic environments.

ACKNOWLEDGMENTS

The authors are indebted to the SSRL staff, especially John R. Bargar, Joe Rogers, and Samuel Webb as well as the SSRL Biotechnology Group, for their technical assistance during the XAS experiments. The three anonymous referees are acknowledged for their constructive comments that improved the quality of the manuscript. This work was supported by the ECCO/ECDYN CNRS/INSU Program, by ACI/FNS Grant #3033, by SESAME Idf Grant #1775 and by NSF-EMSI Grant CHE-0431425 (Stanford INSU Program, by ACI/FNS Grant #3033, by SESAME IdF contribution # 2322.

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*Associate editor: Robert H. Byrne*