Sorption of Arsenic to Biogenic Iron (Oxyhydr)oxides Produced in Circumneutral Environments

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Abstract. Arsenic (As) is a widespread and problematic pollutant that can be derived from natural or anthropogenic sources. Iron (oxyhydr)oxides readily sorb As and thus play critical roles in As cycling in terrestrial environments; however, little is known about the affinity and mechanism of As sorption by biogenic iron (oxyhydr)oxides formed in circumneutral environments. To investigate this, we conducted sorption isotherm and kinetics experiments to compare As(V) and As(III) sorption to synthetic 2-line ferrihydrite and iron biominerals harvested from the hyporheic zone of an uncontaminated creek. Inductively coupled plasma mass spectrometry (ICP-MS) was used to quantify both As(V) and As(III), and X-ray absorption spectroscopy (XAS) was utilized to obtain As and Fe K-edge spectra for As(V) and As(III) sorbed to environmentally collected and laboratory produced Fe(III) minerals. All environmental Fe(III) biominerals were determined to be structurally similar to 2-line ferrihydrite. However, environmental Fe(III) biominerals have a surface area normalized affinity for As(V) and for As(III) that is greater than or equivalent to synthetic 2-line ferrihydrite. Whereas the extent of sorption was similar for As(III) on all minerals, As(V) sorption to environmental Fe(III) biominerals was approximately three times higher than what was observed for synthetic 2-line ferrihydrite. Structural modeling of EXAFS spectra revealed that the same surface complexation structure was formed by As(V) and by As(III) on environmental Fe(III) biominerals and ferrihydrite. These results suggest that, despite similarities in binding mechanisms, Fe(III) biominerals may be more reactive sorbents than synthetic surrogates often used to model environmental reactivity.

1. INTRODUCTION

Arsenic (As) is a widespread and problematic pollutant that impacts the health of approximately 150 million people (Brammer and Ravenscroft, 2009). Many adverse health effects, including increased cancer rates, birth defects, neurological issues, and diabetes, are associated with chronic As exposure (Kleinert et al., 2011; Meharg and Zhao, 2012). Human exposure to As may arise from both anthropogenic and natural sources (Smedley and Kinniburgh, 2013; Muehe and Kappler, 2014), which are geographically widespread. For example, runoff of As-containing pesticides and mine drainage (Welch et al., 2000; Mandal and Suzuki, 2002) are major anthropogenic sources of As, especially in the Americas, resulting in contamination of groundwater in regions of southwestern United States and Mexico (Smedley and Kinniburgh, 2013). Natural sources of As contamination (i.e., weathering of As-bearing minerals in rocks and reductive dissolution of iron-bearing soil and sediments) present an even greater hazard to human health, and, in Southern Asia as well as South America, have developed into major societal concerns (Goldberg, 2002; Smedley and Kinniburgh, 2002). As a result, research seeking to elucidate the sources and mechanisms of As solubilization and mobilization has intensified over the last 15 years (Meharg and Zhao, 2012).

Field and laboratory studies have identified iron (oxyhydr)oxides as key sorbents that sequester As (Wilkie and Hering, 1996; Raven et al., 1998; Goldberg and Johnston, 2001; Mandal and Suzuki, 2002; Dixit and Hering, 2003; Cornell and Schwertmann, 2004; Mohan and Pittman Jr, 2007). Consequently, it is important to understand the factors controlling As interactions with these mineral surfaces. Major conditions controlling As retention on mineral surfaces include redox conditions, pH, and

concentrations of competitive ions. The effects of these conditions on surface chemical processes are well understood for many minerals (Pierce and Moore, 1982; Bowell, 1994; Fendorf et al., 1997; Giménez et al., 2007; Redman et al., 2002; Bauer and Blodau, 2006), including both crystalline and poorly ordered synthetic iron minerals (e.g., ferrihydrite (Waychunas et al., 1993; Raven et al., 1998; Jambor and Dutrizac, 1998; Jain and Loeppert, 2000; Grafe et al., 2002; Dixit and Hering, 2003; Michel et al., 2007a; Borch et al., 2009; Cismasu et al., 2011; Cismasu et al., 2012)).

Although abiotically synthesized ferrihydrite is often used as an experimental surrogate for poorly ordered Fe(III) (oxyhydr)oxide minerals that are environmentally ubiquitous (Jambor and Dutrizac, 1998), there is a growing recognition that bacteriogenic Fe minerals are common in natural waters and sediments, forming specifically at redox gradients (e.g., circumneutral Fe(II)-rich groundwater discharges into quiescent aerobic surface water) (Emerson and Weiss, 2004; Ferris, 2005; Duckworth et al., 2009; Emerson et al., 2010; Posth et al., 2010; Gault et al., 2011; Roden et al., 2012, Posth et al., 2014). These biominerals may have important structural differences (decreased crystallinity, reduced crystal domain size, and increased surface area (Ferris et al., 2000; Ferris, 2005; Hohmann et al., 2009; Posth et al., 2010; Cismasu et al., 2011)), as well as incorporated bacterial biomass and other cell-derived organic matter (Hohmann et al., 2009; Schadler et al., 2009; Muehe et al., 2013; Schmid et al., 2014; Hao et al., 2016), which may result in a sorption reactivity that differs significantly from synthetic ferrihydrite. Despite the potential importance of biogenic Fe(III) (oxyhydr)oxides to As cycling, few studies (Keim, 2011; Kleinert et al., 2011; Muehe et al., 2013; Xiu et al., 2015) have examined

sorption of As by biogenic Fe(III) (oxyhydr)oxides formed in circumneutral environments, resulting in a significant gap in our knowledge (Emerson et al., 2010).

A better understanding of As sorption onto biogenic Fe(III) biominerals that form at redox gradients in natural waters is needed to develop improved models of As transport and sequestration in the environment. Accordingly, the objectives of this study were to 1) determine the extent of As sorption to iron biominerals originally formed in aquatic environments, and 2) identify surface complexes formed by As sorbed to environmental iron biominerals.

2. MATERIALS AND METHODS

2.1. Materials

All solutions were prepared in Type I deionized water. All chemicals used were reagent grade and provided by Fisher Scientific, unless otherwise specified.

2.2. Environmental Fe(III) Biomineral Sampling and Sorbent Preparation

All environmental Fe(III) biominerals used in experiments were collected from Rocky Branch Creek near the Pullen Road Overpass (35° 46' 48" N, 8° 40' 2" W; Raleigh, North Carolina; EA Fig. S1). This site has a perennial occurrence of Fe(III) mineral-bearing biofilms at multiple locations along the stream (pH = 6.3–6.8). Submerged “fluffy” orange biofilm/mineral assemblages were sampled from the south bank of the stream via syringe and repeatedly transferred into 500 mL polypropylene bottles. All sampling was completed at the same location to reduce the effect of variable environmental conditions on Fe(III) biomineral structure and components. From here on

out, a naming convention that utilizes the date of sampling (five sampling dates in 2015–2016) is used to identify specific environmental Fe(III) biomineral samples.

In the laboratory, the mineral suspensions were transferred into 50 mL polypropylene centrifuge tubes and centrifuged for 10 minutes at ca. 10,000 g (RCF). The supernatant was decanted, and then the remaining sample was vortexed and mixed with other samples. This process was repeated to produce a pooled Fe(III) biomineral stock, which was stored in a freezer at approximately -20°C until further use. Before freezing, a 100 mg subsample (wet mass basis) was taken and allowed to dry at 80°C in an oven for approximately 24 hours to calculate a dry mass percent, which was used to apply a consistent solids loading from suspensions for all subsequent experiments.

2.3. Synthetic 2-line Ferrihydrite Synthesis

Two-line ferrihydrite was abiotically synthesized according to established procedures (Cornell and Schwertmann, 2003). Briefly, 40 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ was dissolved in 500 mL of deionized (DI) water. In order to raise pH, 330 mL of 1M KOH was added to the $\text{Fe}(\text{NO}_3)_3$ with vigorous stirring. The pH of the solution was monitored constantly during the addition of the final 20 mL of 1M KOH. Upon reaching $\text{pH} = 7.5 \pm 0.5$, the solution was centrifuged and washed with DI water. The procedure resulted in the formation of ca. 10 g of 2-line ferrihydrite. All synthesized minerals were stored in a freezer at approximately -20°C until further use.

2.4. Characterization of Fe(III) Minerals

All Fe(III) minerals were characterized to assess composition. The C content was determined by total combustion using a Perkin Elmer 2400 CHNS analyzer. The Fe content was estimated for environmental Fe(III) biomineral samples by performing a citrate-bicarbonate-dithionite (CBD) extraction (Klute, 1965). For this extraction, 100 mg subsamples (dry mass basis) were weighed followed by the addition of 20 mL of sodium citrate dihydrate (0.3 M) and 2.5 mL of sodium bicarbonate (1 M). Sample suspensions were shaken and heated to ca. 80°C in a water bath. After 1 g of sodium dithionite was added, samples were held at 80°C for 30 minutes with intermittent shaking. Samples were then centrifuged, filtered, and analyzed for aqueous Fe using a Thermo-Fisher iCE 3000 flame atomic adsorption spectrometer.

The morphology, phase, and surface properties of Fe(III) minerals were also characterized. Brunauer-Emmett-Teller (BET) analysis was conducted using a Quantachrome: Monosorb surface area analyzer to determine surface area. To determine particle phase, X-ray diffraction (XRD) was conducted by using a Rigaku (The Woodlands, TX, USA) SmartLab X-Ray Diffractometer, and Fe K-edge X-ray absorption spectroscopy (XAS) was conducted as described below. Transmission electron microscopy (TEM) was performed to elucidate morphology. Fe(III) mineral suspensions were pipetted onto a silicon nitride chip, allowed to air dry, and analyzed using a scanning transmission electron microscope (JEOL 2000FX) operated at 1 atm. In addition, ζ -potential analyses were conducted in triplicate to determine the surface charge of sorbents at pH = 7 by using a Malvern Zetasizer Nano Z (Worcestershire, UK).

2.5. Rates of Arsenic Sorption to Fe(III) Minerals

To assess the rate of arsenate and arsenite sorption to iron minerals, stock solutions (500 mg L⁻¹) were prepared from reagent grade Na₂HAs(V)O₄ • 7H₂O and NaAs(III)O₂ (Sigma Aldrich), respectively. Similarly, a suspension containing 2 g sorbent (dry mass basis) L⁻¹ in 0.01 M NaCl was prepared such that final suspension volume was 250 mL (1:125 solid:solution mass ratio). The pH of each solution was adjusted to pH = 7 via HCl and NaOH additions and monitored using a XL20 pH/conductivity meter. This pH was chosen to approximate the circumneutral conditions seen in surface waters from where environmental Fe(III) biomineral mass was collected. A magnetic stir bar was used in the reactor to agitate the suspension and aluminum foil was used as a cover to exclude stray light.

To initiate an experiment, 50 mL of 500 mg As L⁻¹ stock solution was pipetted with continuous stirring into the sorbent reactor containing either synthetic 2-line ferrihydrite or an environmental Fe(III) biomineral sample such that the initial As concentration in the reactor was 100 mg As L⁻¹. Aliquots (5 mL) were collected via syringe and filtered through 0.45 µm filters periodically over 3 days, with more samples collected near the start of the experiment. These samples were then stored in a refrigerator at 4°C until further analysis. The experiments were performed in duplicate.

Inductively coupled plasma-mass spectrometry (ICP-MS) analysis was conducted by using a Thermo X Series II for all aqueous As samples from kinetics and isotherm experiments in order to quantify total dissolved As. Prior to conducting ICP-MS analysis, all samples were diluted using 0.01 M NaCl containing 1% nitric acid and spiked with an internal calibration standard of 1 mg L⁻¹ yttrium and indium (final concentration of 10 µg L⁻¹). Samples were analyzed in collision cell mode with a 10% H₂/He gas mix to exclude

the ArCl polyatomic interference. System performance was optimized on a daily basis by analysis of a 10 ppb solution of In/Ce and system suitability was determined by periodic reanalysis of a mid-range calibration standard.

2.6. Adsorption Isotherms

The extent of As(V) and As(III) sorption to synthetic 2-line ferrihydrite and environmental Fe(III) biominerals was quantified using approaches based on previously published methods (Dixit and Hering, 2003; Raven et al., 1998). For all isotherms, initial As concentrations ranging up to 200 mg L⁻¹ were tested. Sorbent suspensions of 2 g L⁻¹ were made for both synthetic 2-line ferrihydrite and environmental Fe(III) biominerals in 50 mL polypropylene centrifuge tubes. Arsenic stock solutions (500 mg L⁻¹) and sorbent suspensions were adjusted to pH 7.0 ± 0.1 by using HCl and NaOH, with both in an electrolyte matrix 0.1 M NaOH. Varying volumes of As stock were pipetted into sorbent suspension samples to establish a range of initial As concentrations. The resulting sample was then mixed by using a vortex genie, and pH was monitored (and readjusted as necessary to pH 7 ± 0.1) for all samples using a XL20 pH/conductivity meter. Samples were then loaded onto a MX RD Pro rotary mixer for 48 hours. Samples were checked for pH changes and were adjusted to pH 7.0 ± 0.1. After 48 hours, samples were centrifuged at ca. 10,000 g RCF for 10 minutes, pipetted into 20 mL syringes, and filtered at 0.45 µm (nylon membrane). Collected filtrate was then stored at approximately 4°C in a refrigerator for later analysis. These experiments were performed in triplicate for synthetic 2-line ferrihydrite and in duplicate for environmental Fe(III) biomineral.

The isotherm procedure was performed for both As(V) and As(III); however, to limit unwanted oxidation of As(III) to As(V) (Kim & Nriagu, 2000), As(III) experiments were performed in a glovebag with an approximately 2% O₂ atmosphere set by using a N₂ gas mixture (99% N₂, 1% O₂) and monitored intermittently using a NeoSport oxygen probe. Originally, an anoxic glovebox was used for As(III) experiments but iron in the sorbent was found to have reduced over the course of the 48 hour reaction time, suggesting the presence of Fe(III)-reducing bacteria in the environmental sample, as has previously been noted at other locations (Roden et al., 2012).

Arsenic in solution was measured by ICP-MS. By measuring the difference between the As concentrations before and after sorption (i.e., As lost from solution), the sorbed As was calculated. For series of As data at different concentrations, a preprogramed Excel spreadsheet was used to fit isotherm data to both Langmuir and Freundlich fits (Bolster and Hornberger, 2007) using non-linear optimization. For selected aqueous samples, speciation analysis was also conducted using ultra-high performance liquid chromatography-sector field-inductively coupled plasma mass spectrometry [UHPLC-SF-ICP-MS, UHPLC system: Waters ACQUITY (Milford, MA, USA); SF-ICP-MS: Thermo Element 2] to determine the concentrations of As(V) and As(III). Separation was performed by UHPLC-SF-ICP-MS using a previously described method (Milstein et al., 2003; Kim et al., 2013). Arsenic species were quantified with a standard curve constructed using solutions made from Na₂HAs(V)O₄ • 7H₂O or NaAs(III)O₂. Samples were analyzed using a Hamilton PRP-X100 liquid chromatography column (4.6 x 150 mm; 5 µm particle size). The UHPLC flow rate and mobile phase gradient are summarized in EA Table S1.

2.7. X-ray Absorption Spectroscopy

Arsenic and Fe K-edge XAS spectra were collected at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamlines 4-1, 4-3, and 11-2. Environmental samples were collected on 6/19/15 and 2/1/16, and are interpreted as being representative of all environment samples. Arsenic K-edge spectra obtained for As-loaded Fe(III) mineral samples were performed at low and high As concentrations (Fe:As ratios of 300:1 and 62.5:1, respectively). Spectra were energy calibrated by adjusting the E_0 to a metal foil (Fe K-edge and Au L-edge used for Fe and As calibration, respectively). For Fe K-edge spectra, synthetic samples were collected in transmission mode whereas environmental samples were collected in fluorescence mode using a Lytle detector. Arsenic K-edge spectra were collected at room temperature [As(V)] or in an liquid nitrogen cryostat [to prevent photooxidation of As(III)] on beamline 11-2 in fluorescence with a 100-element Ge detector. On 4-1 and 11-2, the incident beam was detuned by 35% and energy selected by using a variable-exit Si(220) double-crystal monochromator to reduce harmonics. On 4-3, rhodium-coated mirrors were used to reject harmonics and energy was selected with a Si(111) monochromator. For fluorescence measurements, spectra were collected using Soller slits and a Z-1 X-ray filter (Ge or Mn) to improve the signal-to-noise ratio. Multiple spectra were collected for each sample, with no evidence of beam damage in successive scans, and averaged to improve the signal-to-noise ratio.

Both Fe and As K-edge spectra were energy calibrated, averaged, background-subtracted, splined, and fit in R-space (Kelly et al., 2008) using the SIXPACK interface (Webb, 2005b), which makes use of the IFEFFIT code (Newville, 2001). Normalized Fe

XANES and Fe EXAFS linear combination fitting was conducted in SIXPACK for environmental Fe(III) biominerals using Fe(III) standards in order to probe Fe(III) mineral phase and structure (Kelly et al., 2008). Components found to make up less than 10% of the spectral reconstruction were removed, and fits were recalculated using remaining standards. A list of all standards (O'day et al., 2004; Harrington et al., 2012) considered in fits is shown in the electronic annex (EA Table S2), with those used in final fits shown in bold.

Structural (shell by shell) fitting analysis was also performed for As EXAFS spectra utilizing SIXPACK software. Spectra for As-bearing environmental Fe(III) biominerals and synthetic 2-line ferrihydrite were fit using SIXPACK (Webb, 2005a). Data were modeled using parameters of the EXAFS equation. Paths were generated using the mineral scorodite in Feff9 (Rehr et al., 2010). EXAFS data were fit using a common value of the parameter E_0 , which was allowed to float during optimization. The amplitude reduction factor (S_0^2) was fixed at 0.85 (Foster et al., 1998; Paktunc et al., 2003).

For As(III), published models have typically contained an As-O shell at $R \approx 1.7$ – $1.8 \text{ \AA}$, representing oxygen atoms surrounding a central As(III) atom. Arsenite is thought to be bound to the ferrihydrite surface dominantly via a bidentate mononuclear complex ($R \approx 2.9 \text{ \AA}$) and a bidentate binuclear complex ($R \approx 3.4 \text{ \AA}$) (Gao et al., 2013). We consequently constructed a three shell model to capture these features. A first shell was constructed with an As-O scattering path with N , σ^2 , and R allowed to float. To represent Fe in surface complexes, two shells with As-Fe paths were constructed. In both paths, N was fixed whereas R was allowed to float; σ^2 was allowed to float but was linked for both paths. In addition, the amplitude of each path was modified by a fraction mononuclear (f

), which was designed to allow for estimation of how much As was bound to these coordination environments (e.g., the fraction of binuclear complexes is (1-f)).

For As(V), models have typically been fit by using, in addition to an As-O first shell ($R \approx 1.7 \text{ \AA}$), a single bidentate binuclear complex ($R \approx 3.3 \text{ \AA}$) and an As-O-O multiple scattering feature (Gao et al., 2013). However, fits to our spectra were not improved by inclusion of a multiple scattering path. Therefore, we constructed a model with a first shell containing As-O and As-Fe scattering paths with N , σ^2 , and R allowed to float.

3. RESULTS

3.1. Properties of Iron Minerals

Micrographs (TEM) of environmental Fe(III) biomineral and synthetic 2-line ferrihydrite samples are shown in Fig. 1. Differences in morphology are present between environmental and synthetic samples. The environmental Fe(III) biomineral particles has a ragged morphology similar to literature reports of other Fe(III) biominerals (Posth et al., 2010), with particles sizes that range from approximately 50 to 200 nm. This morphology differs from synthetic 2-line ferrihydrite, which appears to be comprised of regular aggregates of small ball-like masses.

The composition and physical properties of Fe mineral samples are shown in Table 1. Environmental samples contained 19.7–36.1% Fe (w/w) and 8.2–11.1% C (w/w). Although there is considerable variability in the concentrations, there is neither significant correlation between Fe and C concentrations, nor are there consistent seasonal trends in the Fe or C content. There is, however, a positive correlation (data not shown; p

= 0.02) between surface area and Fe concentration, suggesting that iron (oxyhydr)oxides are the dominant contributor to surface area. Zeta potential results for Fe(III) mineral samples are all found to be negative at pH = 7. Environmental Fe(III) biominerals have a more negative charge (ranging from approximately -20 to -30 mV) than synthetic 2-line ferrihydrite (-10 mV). The mildly negative value for synthetic ferrihydrite indicates a $\text{pH}_{\text{pzc}} < 7$, which is lower than previous measurements of the point of zero charge [$\text{pH}_{\text{pzc}} = 7.0\text{--}7.5$ (Schwertmann and Fechter, 1982; Zhu et al., 2011)]. It is not clear what factors in the preparation or measurement account for this discrepancy. Surface areas (BET method) vary from $163\text{--}83 \text{ m}^2 \text{ g}^{-1}$, slightly lower than the range previously reported for natural iron minerals in a New Zealand creek (Childs et al., 1982).

The iron minerals were further characterized for mineralogy. X-ray diffraction results (EA Fig. S2) indicate that our synthetic and environmental minerals contain predominantly 2-line ferrihydrite, with quartz as the other phase observed (<10% crystalline phases). Fe K-edge X-ray absorption spectroscopy (XAS) data are presented in Fig. 2. From the normalized Fe XANES data, all spectra for Fe(III) mineral standards and Fe(III) biominerals have similar adsorption edge positions (approximately 7128 eV). For all samples, the highest FT magnitude is at $R \approx 2 \text{ \AA}$, an interatomic distance characteristic of Fe(III)-O bonding (Shannon, 1976).

Normalized Fe XANES and Fe EXAFS linear combination fitting (dashed lines in Fig. 2) were performed, with results shown in Table 2. Arsenic K-edge spectra obtained for Fe(III) mineral samples were with low and high concentrations of As (Table 3; Fe:As ratios of 300:1 and 62.5:1, respectively). Using Fe(III) XANES, all samples contain a 100% contribution from poorly ordered Fe(III) minerals (consisting of either hydrous

Fe(III) oxide or 2-line ferrihydrite), which is similar to what was seen from Fe EXAFS for EnvFe_As(III). Although the fit EnvFe_As(V) primarily contains poorly ordered Fe(III) oxides (~80–90%), the inclusion of a Fe(III) carboxylate siderophore complex (~10–20%; labeled as Fe(III)-Rhiz in Fig. 2 and Table 2) improves the Fe EXAFS LCF.

3.2. Sorption of As to Iron Minerals

The sorption of As(V) and As(III) to synthetic 2-line ferrihydrite as a function of time is shown in EA Fig. S3a and S3b, respectively. Sorbed concentration increased rapidly in the first two hours after initial As(V) or As(III) introduction into the system, with approximately 60% of the total sorption observed occurring within this time. At 48 hours, the sorbed concentration approached maximum values of approximately 1.8 $\mu\text{mol As m}^{-2}$ and 4.0 $\mu\text{mol As m}^{-2}$ for As(V) and As(III), respectively, on synthetic 2-line ferrihydrite for As(V) experiments. Similar rates of sorption were observed for As(V) sorption to environmental Fe(III) biominerals, with approximately 70% of total sorption occurring within the first two hours after initial As(V) introduction and a maximum value of 4.5 $\mu\text{mol As m}^{-2}$ reached after 48 hours. The concentration of As(III) sorbed to the environmental Fe(III) biomineral sample approached an asymptote of 6.5 $\mu\text{mol As m}^{-2}$ after 48 hours of equilibration time. We therefore used 48 hours as an equilibration time for concentration-dependent adsorption experiments for both As(V) and As(III), which is consistent with previous equilibration times used for As isotherms (Raven et al., 1998).

Sorption of As to Fe(III) biominerals and synthetic 2-line ferrihydrite as a function of dissolved As concentration is shown in Figs. 3 and 4, and EA Fig. S4. The concentration of As associated with the surface increases with increasing dissolved

concentration across the data range, with decreasing slope at high dissolved As concentrations. The data are thus consistent with an L-type isotherm (Sposito, 2008), and consequently the data were initially fit to both Freundlich and Langmuir sorption isotherm models using a preprogramed spreadsheet with a non-linear solver (Bolster and Hornberger, 2007). Based on goodness of fit, all data were modeled using the Freundlich isotherm. For all data sets, fit parameters for the Freundlich model ($S = K_f C^n$), where S is sorbed concentration, K_f is a sorption constant, C is dissolved sorbate concentration, and n is an exponential sorption constant, are shown in Table 4 and 5.

The mass-normalized sorption of As(V) and As(III) is shown for environmental and synthetic samples in Figs. 3a and 3b, respectively. Variability in sorption extent was observed for both As(V) and As(III) data, with As(V) data having the highest variability per mass of sorbent. Differences in sorption behavior are reflected by differences in the Freundlich fitting parameters K_f and n (Table 4). For As(V), mass normalized sorption by environmental minerals equals or exceeds that of ferrihydrite whereas As(III) on ferrihydrite equals or exceeds those of environmental biominerals.

In Fig. 4a and EA Fig S4a, As(V) sorption isotherm data were normalized to BET surface area. Fits for environmental Fe(III) biominerals resulted in K_f and n values that were within model uncertainty. Consequently, these biominerals were fit with one Freundlich isotherm (Table 5). At dissolved As concentrations greater than 300 μM , environmental Fe(III) biominerals had a sorbed concentration of approximately 4.0 to 5.0 $\mu\text{mol As m}^{-2}$, approximately 2.5 times greater than what was observed at a similar dissolved As concentration range for synthetic 2-line ferrihydrite (sorbed As(V) concentration of approximately 1.5 to 2.0 $\mu\text{mol As m}^{-2}$).

As(III) isotherms normalized to BET surface area are presented in Fig. 4b and EA Fig. S4b. All environmental Fe(III) biominerals samples contained sorbed As concentrations that are within error of another. Interestingly, results with synthetic 2-line ferrihydrite mirrored biominerals for all dissolved As(III) concentrations. Fits for environmental Fe(III) biominerals and synthetic ferrihydrite resulted in K_f and n values that were within model uncertainty for all but one sample date; thus, all BET normalized isotherms were fit with one Freundlich model. Interestingly, at dissolved As concentrations greater than 300 μM , sorbed As concentration ranges from 7.0 to 7.5 $\mu\text{mol m}^{-2}$, which is approximately double the sorbed concentration observed for As(V) experiments.

The relative concentrations of As(III) and As(V) in As(III) sorption isotherm experiments were determined by speciation analysis using UHPLC. For As(III) isotherms, it was determined from selected samples that the aqueous As remaining in the supernatant after a 48 hour equilibration time with the sorbent was quantitatively the As(III) species (>97% in all samples tested; data not shown). Speciation was also determined for selected As(V) isotherm samples for both environmental Fe(III) biominerals and synthetic 2-line ferrihydrite, with >99% of the total As in the As(V) oxidation state.

3.3. As Binding at Iron Mineral Surfaces

Arsenic K-edge X-ray absorption spectra are shown in Fig. 5. Normalized As XANES data confirm the predominance of As(V) and As(III) in samples from As(V) and As(III) isotherms, respectively. The As(V) absorption edge occurred at approximately

11875.5 eV for all As(V)-loaded samples and the As(III) absorption edge is at approximately 11871.8 eV for all As(III)-loaded samples.

In the FTs of both As(V) and As(III) spectra, a large peak at $R = 1.6\text{--}1.8\text{ \AA}$ is the major feature, which corresponds to O surrounding As. Additional smaller peaks are seen at larger R , features which have been previously interpreted as arising from scattering from Fe or from multiple scattering phenomena. Fitting results for As EXAFS spectra are shown in Table 3. For all samples, first shell As-O coordination numbers are near their expected values for each oxyanion. EXAFS spectra of As(III) can be fit by two As-Fe distances (corresponding to two surface complexation structures) whereas As(V) is adequately fit with one As-Fe distance. For all spectra, fit parameters are generally within program estimated uncertainties of each other for As(V) or As(III) sorbed onto ferrihydrite and environmental samples. This correspondence is consistent with similarities in the beat structure of the EXAFS spectra, which appear to be invariant for each spectral set when superimposed (EA Fig. S5).

4. DISCUSSION

4.1. Mineralogy of Iron Minerals

Determining the affinity of Fe(III) biominerals for As is critical to advancing the current understanding of its cycling in environmental systems and requires a detailed understanding of their mineralogy and structure. Transmission electron micrographs (Fig. 1) indicate morphological differences between environmental Fe(III) biominerals and synthetic Fe(III) minerals. We observed our environmental Fe(III) biominerals to have ragged filamentous structures consistent to what was observed in Fe(III) microbial mats

by Chan et al. (2009), who reported that the reported biominerals were primarily attributable to common Fe(II) oxidizing organisms in the genera *Leptothrix* and *Gallionella*. Zeta potential analysis (Table 1) revealed that all Fe(III) mineral samples had negative charge at pH = 7, with environmental Fe(III) biominerals having more negative charge. This result is consistent with the incorporation of biomass and polysaccharides, which have been shown to decrease Fe(III) mineral points of zero charge (Mikutta et al., 2014), into our environmental Fe(III) minerals.

X-ray diffraction results indicate 2-line ferrihydrite as the predominant Fe(III) mineral phase present in all environmental Fe(III) biomineral samples. These results are roughly consistent with XAS linear combination fits, which suggest the predominant presence of poorly crystalline oxides in all samples with the possible presence of a minor fraction of organic iron complexes in As(V) bearing samples. Taken as whole, the mineralogy of our system agrees well to previous studies showing Fe(III) minerals produced by Fe(II) oxidizing bacteria in many environments consist predominately of a ferrihydrite-like phase (Ferris, 2005; Duckworth et al., 2009; Cismasu et al., 2011; Hohmann et al., 2011; Toner et al., 2012).

4.2 Sorption of As to Fe Minerals

It is instructive to compare of mass-normalized sorption data to previous studies. We observed that the As(III) sorbed concentration to synthetic 2-line ferrihydrite at pH = 7 was approximately 1100 $\mu\text{mol g}^{-1}$ (Fig. 4). This value is somewhat less the ca. 1500 $\mu\text{mol g}^{-1}$ observed by Dixit and Hering (2003) at their highest concentrations, but is higher than the maximum value of 513 $\mu\text{mol g}^{-1}$ reported by Pierce and Moore (1982) at

pH = 7. Our maximum As(V) sorbed concentration (ca. 400 $\mu\text{mol g}^{-1}$) is lower than the maximum pH = 7 value of approximately 1100 $\mu\text{mol g}^{-1}$ reported by Dixit and Hering (2003), but agrees well with the pH = 7 maximum of 454 $\mu\text{mol g}^{-1}$ reported by Pierce and Moore (1982). The observed difference in As sorption may be due to differences in experimental setup or mineral properties in individual studies. For biogenic minerals, these results are consistent with a field study that found biogenic Fe(III) (oxyhydr)oxides formed in a contaminated mining environment to have a large affinity for As (Keim, 2011). It should also be noted that biogenic oxides have been shown to have a lower affinity for As(V) than iron-based commercial filter material and to reduce efficiency of these filters (Kleinert et al, 2011) .

For both As(V) and As(III), surface area normalization effectively accounted for the variation in reactivity of environmental Fe(III) biominerals. This outcome is perhaps non-intuitive because the structure and morphology of biominerals can vary temporally, as formation process may be controlled by environmental factors, such as groundwater flow rates, temperature, aquatic chemical conditions, and microbial community composition. In our data, this variability manifests itself in a range of compositions (including iron and carbon) and surface areas for samples collected at different times. The fact that normalization by surface area effectively accounts for this variability suggests that the area of exposed Fe surfaces is the dominating factor in controlling sorption of biogenic (oxyhydr)oxides, as it typically is for abiotic minerals of the same phase (Goldberg and Johnston, 2000; Dixit and Hering, 2003; Sherman and Randall, 2003).

Surface area normalization of As(V) and As(III) isotherm data resulted in different trends in the data sets for each species. All tested environmental Fe(III)

biominerals were observed to sequester similar concentrations of As(V) (approximately 4.0 to 5.0 $\mu\text{mol As m}^{-2}$), such that all environmental Fe(III) biomineral data were fit accurately to the same sorption model ($E = 0.979$). As(III) sorption data showed a similar trend, although to a greater sorption extent, among environmental Fe(III) biominerals; however, both environmental Fe(III) biomineral and synthetic 2-line ferrihydrite sorption data converged effectively to one model ($E = 0.972$). This result is different than what was observed for the As(V) data, as environmental Fe(III) biominerals were found to sorb As(V) to approximately three times the extent that was observed for synthetic 2-line ferrihydrite.

4.3 Surface Binding of As to Fe Mineral Surfaces

For model fits for all As samples, first shell coordination numbers (Table 3) were near those expected for sorbed arsenate and arsenite. In addition, As-O interatomic distances ($R = 1.76\text{--}1.77$ and $1.67\text{--}1.68$ Å; Table 3) are consistent with known bond distances for As(III) and As(V), respectively. These results, coupled with XANES spectra, suggest that As on the surface remains in its initial oxidation state (section 3.3). This speciation behavior is consistent with the aqueous speciation data that indicated that dissolved As also remains in its initial oxidation state (section 3.2). Furthermore, As K-edge EXAFS spectra for both As(V) and As(III) (cf. overlain spectra in EA Fig. S5) show that the beat structure of spectra are similar for all samples, suggesting that binding structure is the same for each As species for synthetic and environmental samples, and is invariant with concentration for environmental samples. Possible reasons for the difference in the extent in As(V) sorption, despite the similarity in the structure of the

binding environment for synthetic and biogenic minerals (as determined by EXAFS), are discussed in section 4.4.

Previous studies employing As K-edge EXAFS have shown As(III) to bind to synthetic 2-line ferrihydrite primarily through two bidentate inner-sphere complexation structures. Based on this structural model, our fits (Table 3 and Fig. 5) yield a mononuclear species with an As-Fe interatomic distance of $R = 2.88\text{--}2.90$ Å and a binuclear species with an As-Fe distance of $R = 3.38\text{--}3.39$ Å. These results are within error of previous EXAFS derived interatomic distances; however, coordination numbers from these studies (Ona-Nguema et al, 2005; Voegelin et al., 2007; Gao et al., 2013) suggest a prevalence of mononuclear surface structures whereas our results suggest a near even distribution of monodentate and bidentate complexes ($f = 0.5 \pm 0.2$ for all samples).

Previous EXAFS studies performed at similar As/Fe molar ratios, 0.016 As/Fe, have shown that As(V) sorbs predominately through an inner-sphere corner sharing bidentate binuclear complex (Waychunas et al., 1993; Gao et al., 2013), although outer sphere complexes have been identified on hematite (Catalano et al., 2008). In a scenario where all As(V) is sorbed as bidentate binuclear complexes, $N = 2$ whereas the coordination number would approach 0 for a predominantly outer-sphere complexes. Our modeled coordination numbers ($N = 1\text{--}2 \pm 3$) are poorly constrained, and do not allow for discrimination of the distribution of inner- and outer-sphere complexes. We note that other approaches (e.g., surface complexation modeling) also are unable to definitively distinguish between outer-sphere and bidentate binuclear complexes (Fukushi and Sverjensky, 2007). We thus assert that our results are consistent with the presence of bidentate binuclear complexes but do not preclude the presence of outer-sphere species.

4.4 Why do environmental Fe(III) biominerals sorb more As(V) than synthetic minerals?

Although all As(III) sorption data converged when normalized to surface area for all minerals tested, environmental Fe(III) minerals sorbed approximately three times As(V) at their maximum loading as compared to the synthetic ferrihydrite. We emphasize that EXAFS spectroscopy yields no detectable difference in As surface complexation structure for different Fe minerals (Table 3 and EA Fig. 5A). Although we lack direct evidence of the factors that drive changes in the extent of As(V) binding, we speculate that either changes in the nature of surface sites or in the nature of surface complexation structures are primary factors.

Firstly, As(V) has been shown to sorb predominately through corner sharing sites whereas As(III) sorbs through both corner and edge sharing complexes (Gao et al., 2013). Although lower surface areas were measured for the environmental Fe(III) biomineral samples, we expect that the environmental Fe(III) biominerals generally have smaller domain sizes compared to synthetic 2-line ferrihydrite (Cismasu et al., 2011). Based on the small domain size, we speculate that the environmental Fe(III) biominerals may contain more sites for corner sharing complexes. Alternately, it is possible that environmental minerals may sorb more outer-sphere complexes. The close association of organic matter may result in physicochemical changes to the interfacial region (e.g., change to the ordering, and thus activity of water) that may facilitate accumulation of outer-sphere complexes (Dzombak and Morel, 1990; Fukushi and Sverjenski, 2007). However, to further explore these explanations, careful determination of domain size

(e.g., paired distribution function analysis or high resolution TEM) (Michel et al., 2007b) is needed to better elucidate the drivers of the differences in sorption reactivity of As species on environmental biominerals. Finally, because our environmental biominerals contain 8.2–11.1% carbon, it is possible that As-Fe-organic ternary complexes (Sharma et al., 2010; Mikutta and Kretzschmar, 2011) may also contribute to As binding to biominerals. Although our XAS data does not support the presence of these species, spectroscopic data may not be adequately sensitive to preclude the presence of a fraction of ternary complexes.

5. CONCLUSIONS

Our results suggest that environmental Fe(III) biominerals are chemically and mineralogically similar to synthetic ferrihydrite. Although we observed variability in composition and As-sorption reactivity (on a per mass basis), surface area normalization effectively accounts for the variability of environmental biominerals. In terms of reactivity, the environmental Fe(III) biominerals sorb As(III) to the same extent as synthetic ferrihydrite. However, despite their structural similarity, environmental Fe minerals sorb approximately three times more As(V) (on a surface area basis) than ferrihydrite. Interestingly, analysis of K-edge As EXAFS does not reveal significant differences in the binding mechanism for As(III) or As(V) on the different minerals.

The results have significant implications for the transport of As. In anoxic groundwater, both As and Fe are typically found in their reduced states [As(III) and Fe(II)] (Smedley and Kinniburgh, 2013). Upon gradual aeration, redox gradients that promote formation of Fe(III) biominerals may develop (Emerson et al., 2010). Our results

suggest As(III) would be retained preferentially [as compared to As(V)] by these Fe(III) deposits at circumneutral pH; however, if As(V) is produced by oxidation, its retention is more favorable than would be predicted based on the reactivity of synthetic ferrihydrite. Biominerals may thus be important regulators of transport where contaminated groundwater discharges into slow moving waters (particularly because imbedding of minerals in biofilms may reduce colloidal transport of Fe minerals) or possibly near the roots of plants with aerenchyma (including rice) (Mandal and Suzuki, 2002; Meharg and Zhao, 2012; Smedley and Kinniburgh, 2013). In addition, our results suggest that biominerals may be useful in treatment of contaminated water by designed remediation systems with controlled aeration. Future work could seek to quantify how the observed structural properties and reactivity of biominerals manifest themselves in terms of contaminant desorption and long-term sequestration potential.

Electronic Annex. Supplementary data associated with this article can be found in the online version, at doi:XXXX

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Table 1. Composition and properties of synthetic 2-line ferrihydrite and environmental Fe(III) biominerals. Unless specified, reported values have an error estimated at approximately 10%.

Sorbate	Sample	Surface Area (m ² g ⁻¹)	Fe (% w/w)	C (%w/w)	ζ-potential (mV)
As(V)	Synthetic	210	50	---	-10 ± 8
	Env_6/19/15	132	36.1	8.2	-32 ± 5
	Env_8/22/15	83	19.7	10.4	-31 ± 5
	Env_1/8/16	156	35.3	9.7	-32 ± 4
As(III)	Synthetic	210	50	---	-10 ± 8
	Env_9/11/15	86	28.7	11.1	-21 ± 5
	Env_1/8/16	159	35.3	8.7	-32 ± 4
	Env_2/12/16	163	33.9	9.5	-22 ± 8

Table 2. Linear combination fitting results for biomineral samples using X-ray absorption spectroscopy data collected at the Stanford Synchrotron Radiation Lightsource. Linear combination fitting was performed in SIXPACK and normalized to 100%, with raw fits summing to $100 \pm 1\%$ and $100 \pm 30\%$ for XANES and EXAFS spectra, respectively.

Sample	Standard	% contribution	R-factor
XANES Spectra Linear Combination Fits			
EnvFe_High As(V)	Hydrous Fe(III) oxide	100 ± 1	0.00014
EnvFe_Low As(V)	Hydrous Fe(III) oxide	100 ± 1	0.00067
EnvFe_High As(III)	Ferrihydrite	100 ± 2	0.00042
EnvFe_Low As(III)	Ferrihydrite	100 ± 1	0.00002
EXAFS Spectra Linear Combination Fits			
EnvFe_High As(V)	Fe(III)-Rhiz	10 ± 2	0.024
	Hydrous Fe(III) oxide	40 ± 10	
	Ferrihydrite	50 ± 20	
EnvFe_Low As(V)	Fe(III)-Rhiz	18 ± 4	0.013
	Hydrous Fe(III) oxide	50 ± 10	
	Ferrihydrite	36 ± 8	
EnvFe_High As(III)	Hydrous Fe(III) Oxide	49 ± 10	0.050
	Ferrihydrite	50 ± 10	
EnvFe_Low As(III)	Hydrous Fe(III) Oxide	62 ± 9	0.027
	Ferrihydrite	40 ± 10	

Table 3. Coordination numbers, interatomic distances, and Debye-Waller factors for As sorbed to iron minerals.

	[As] (mg g ⁻¹)	As-O			N [§]	As-Fe mononuclear			N [§]	As-Fe binuclear	
		N	R (Å)	σ^2 (Å ²) [†]		R (Å)	σ^2 (Å ²) [†]	f		R (Å)	σ^2 (Å ²) [†]
As(III)-ferrihydrite	24	2.8 ± 0.4	1.76 ± 0.01	0.003 ± 0.002	1	2.88 ± 0.03	0.003 ± 0.002	0.6 ± 0.1	2	3.39 ± 0.03	0.003 ± 0.003
Low As(III)_EnvFe(III)	8	2.8 ± 0.5	1.76 ± 0.01	0.004 ± 0.002	1	2.90 ± 0.05	0.005 ± 0.003	0.4 ± 0.2	2	3.38 ± 0.03	0.005 ± 0.003
High As(III)_EnvFe(III)	24	2.6 ± 0.4	1.77 ± 0.01	0.003 ± 0.002	1	2.88 ± 0.03	0.005 ± 0.003	0.5 ± 0.2	2	3.38 ± 0.03	0.005 ± 0.003
As(III)- ferrihydrite [‡]	15	3.39	1.78	0.004	0.8	2.92	0.008	N/A	0.83	3.43	0.008
As(III)- ferrihydrite h [¶]	40	2.8	1.76	0.005	0.6	2.92	0.008	N/A	0.8	3.40	0.008
As(III)- ferrihydrite [§]	27	3.07	1.79	0.0046	N/A	N/A	N/A	N/A	2	3.38	0.0100

$S_0^2 = 0.85$ (Foster et al., 1998; Paktunc et al., 2003); [§]fixed coordination numbers; [†]linked parameters; [‡]Gao et al. (2013); [¶]Ona-Nguema et al. (2005); [§]Voegelin et al. (2007).

	[As] (mg/g)	As-O			As-Fe binuclear		
		N	R (Å)	σ^2 (Å ²) [†]	N	R (Å)	σ^2 (Å ²) [†]
As(V)-ferrihydrite	24	3.2 ± 0.6	1.68 ± 0.01	0.001 ± 0.002	1 ± 3	3.31 ± 0.05	0.01 ± 0.01
Low As(V)_EnvFe(III)	8	3.7 ± 0.7	1.68 ± 0.01	0.001 ± 0.001	1 ± 3	3.30 ± 0.05	0.01 ± 0.01
High As(V)_EnvFe(III)	24	3.5 ± 0.7	1.67 ± 0.01	0.001 ± 0.001	2 ± 3	3.29 ± 0.05	0.01 ± 0.01
As(V)-ferrihydrite [¥]	15	4	1.68	0.0029	1.3	3.27	0.0042
As(V)-ferrihydrite [€]	24	4	1.67	0.002	1.8	3.3	0.01
As(V)-ferrihydrite [#]	12.5	3.79	1.663	0.0035	2.57	3.26	0.011
As(V)-ferrihydrite ⁺	24	4.0	1.69	0.0029	2.0	3.27	0.0061
As(V)-ferrihydrite [§]	27	4.05	1.69	0.0026	2	3.31	0.0103

$S_0^2 = 0.85$ (Foster et al., 1998; Paktunc et al., 2003); [†]linked parameters; [¥]Gao et al. (2013), pH = 9; [€]Sherman and Randall (2003); [#]Waychunas et al. (1993); ⁺Das et al. (2014); [§]Voegelin et al. (2007).

Table 4. Freundlich parameters used to model As(V) and As(III) sorption to synthetic 2-line ferrihydrite and environmental Fe(III) biomineral samples normalized to mass. K_f = sorption constant; n = exponential constant; E = model efficiency.

	Data Set	K_f ($\mu\text{mol As g}^{-1}$)	n	E
As(V)	Synthetic	170 ± 10	0.17 ± 0.03	0.919
	Env_6/19/15	250 ± 10	0.21 ± 0.02	0.984
	Env_8/22/15	190 ± 9	0.17 ± 0.01	0.992
	Env_1/8/16	320 ± 10	0.18 ± 0.02	0.974
As(III)	Synthetic	400 ± 10	0.33 ± 0.02	0.944
	Env_9/11/15	190 ± 10	0.31 ± 0.03	0.933
	Env_1/8/16	360 ± 10	0.36 ± 0.02	0.976
	Env_2/1/16	370 ± 10	0.32 ± 0.02	0.962

Table 5. Freundlich parameters used to model As(V) and As(III) sorption to synthetic 2-line ferrihydrite and environmental Fe(III) biomineral samples normalized to surface area. K_f = sorption constant; n = exponential constant; E = model efficiency.

	Data Set	K_f ($\mu\text{mol As m}^{-2}$)	n	E
As(V)	Synthetic	0.80 ± 0.1	0.18 ± 0.02	0.915
	Env_6/19/15	2.0 ± 0.3	0.21 ± 0.02	0.984
	Env_8/22/15	2.4 ± 0.1	0.16 ± 0.01	0.992
	Env_1/8/16	2.4 ± 0.3	0.15 ± 0.01	0.983
	Combined Env.	2.0 ± 0.3	0.19 ± 0.03	0.979
As(III)	Synthetic	1.9 ± 0.3	0.33 ± 0.04	0.954
	Env_9/11/15	2.4 ± 0.3	0.31 ± 0.03	0.933
	Env_1/8/16	2.4 ± 0.1	0.36 ± 0.03	0.976
	Env_2/1/16	1.9 ± 0.4	0.40 ± 0.04	0.976
	All Combined	2.3 ± 0.3	0.31 ± 0.04	0.972

Figures.

Figure 1. TEM images of environmental Fe(III) mineral (A) and synthetic 2-line ferrihydrite (B) samples. The environmental Fe(III) mineral is morphologically consistent with those produced by iron-oxidizing bacteria.

Figure 2. Fe K-edge (A) XANES and (B) EXAFS spectra for Fe(III) mineral standards and samples. Linear combination fitting was performed for each sample of the three differing formation settings and is represented with an overlain dashed line, with fit parameters shown in Table 3.

Figure 3. Mass-normalized sorption of (A) As(V) and (B) As(III) sorption to environmental Fe(III) and synthetic 2-line ferrihydrite. All data was modeled using a Freundlich sorption isotherm model, with fit parameters shown in Table 4.

Figure 4. Surface area normalized sorption of (A) As(V) and (B) As(III) to environmental Fe(III) biominerals and synthetic 2-line ferrihydrite. All data was modeled using a Freundlich sorption isotherm model, with fit parameters shown in Table 5.

Figure 5. As K-edge (A) XANES, (B) EXAFS spectra, and (C) FT magnitude plots Fe(III) standards and minerals used in sorption isotherm experiments. Fits to the data based on structural models are represented with an overlain dashed line with fit parameters shown in Table 3.

Figure 1

Fig 1.

Figure 2

Fig. 2.

Figure 3

Fig 3.

Figure 4

Fig 4.

Figure 5

Fig. 5.