



# 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.

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## 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

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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, 2003; Mohan and Pittman, 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; Howell, 1994; Fendorf et al., 1997; Redman et al., 2002; Bauer and Blodau, 2006; Giménez et al., 2007), 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, 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, 2014; Gault et al., 2011; Roden et al., 2012). 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 min 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 h 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 Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O was dissolved in 500 mL of deionized (DI) water. In order to raise pH, 330 mL of 1 M KOH was added to the Fe(NO<sub>3</sub>)<sub>3</sub> with vigorous stirring. The pH of the solution was monitored constantly during the addition of the final 20 mL of 1 M KOH. Upon reaching pH = 7.5 ± 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.

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