

ABSTRACT

SOWERS, TYLER D. Arsenate and Arsenite Sorption to Abiogenic and Biogenic Iron (Oxyhydr)oxides Formed in Natural and Laboratory Environments (Under the direction of Dr. Owen Duckworth).

Arsenic (As) is a widespread and problematic pollutant that can be derived from natural or anthropogenic sources. Iron (oxyhydr)oxides readily sorb arsenic and thus play critical roles in arsenic cycling in terrestrial environments; however, little is known about the affinity and mechanism of As(III/V) sorption by biogenic iron (oxyhydr)oxides formed in natural 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 those harvested from circumneutral pH waters. Inductively coupled plasma mass spectrometry (ICP-MS) was used to quantify both As(V) and As(III), whereas X-ray absorption spectroscopy (XAS) was utilized to obtain As and Fe spectra for As(V) and As(III) sorbed to environmental and laboratory Fe(III) biominerals. All environmental Fe(III) biominerals were determined to be predominately composed of 2-line ferrihydrite. Results suggest that environmental Fe(III) biominerals have a surface area normalized affinity for As that is greater or equivalent to synthetic 2-line ferrihydrite. Inner sphere complexation of As(III/V) to environmental Fe(III) biomineral is suggested from the As EXAFS data. 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. We speculate these differences in relative sorption behavior are attributable to differences in the quantity of corner sharing sorption sites in synthetic and environmental oxides. This study helps to improve our understanding of the sorption reactivity of biogenic iron (oxyhydr)oxides for environmentally relevant As species (V and III) and is critical to understanding As cycling in natural systems while also having the potential to improve As remediation systems.

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Arsenate and Arsenite Sorption to Abiogenic and Biogenic Iron (Oxyhydr)oxides Formed
in Natural and Laboratory Environments

by
Tyler D Sowers

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DEDICATION

To my Mom, Connie Collins. Throughout my entire life, I have been met with challenges that would have been impossible to overcome without your tireless support and words of encouragement. You taught me the necessary values required to be a successful person and most of all, consistently reinforced there was “nothing I couldn’t accomplish that I set my mind to.” Thank you, Mom, for doing everything in your power to give me the opportunities to succeed.

BIOGRAPHY

Tyler was born in Morehead City, NC and raised in the small, rural town of Peletier. Being raised on a horse and tobacco farm inspired his interest in environmental sciences, leading to his participation in FFA sponsored soil judging competitions. Tyler then pursued a higher education by attending North Carolina State University (NCSU) to study Plant and Soil Science in 2010. He worked for Dr. Owen Duckworth in the NCSU Soil Biogeochemistry Lab for 3 of his 4 undergraduate years and gained a passion for studying the processes controlling element cycling in the environment. Tyler completed his Bachelor's of Science degree in 2014 as a NCSU valedictorian and continued working for Dr. Duckworth as a master's student. He plans to continue his education by pursuing a Ph.D. at the University of Delaware.

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Chapter 1: Literature Review

1.1 Arsenic Poisoning as a Global Issue

Arsenic (As) is a trace element that contaminates surface and ground water, negatively impacting global human health. Approximately 150 million people are exposed to unsafe concentrations of As (potentially carcinogenic at >10ppb, as defined by the World Health Organization) in drinking water (Brammer & Ravenscroft, 2009; Dixit & Hering, 2003), leading to what is being referred to as one of the largest natural mass poisonings in human history (Polizzotto, Harvey, Sutton, & Fendorf, 2005). Chronic exposure to elevated As concentrations is known to cause cancer but can also lead to other illnesses, such as birth defects, neurotoxicity, and diabetes (Meharg & Zhao, 2012). Over the past 15 years, research seeking to elucidate As sources and mobilization conditions have increased as awareness of this widespread health issue has grown.

Arsenic contamination is attributable to both anthropogenic and natural sources. Runoff of As-containing pesticides and acid mine drainage by-products resulting in non-point source pollution of surrounding water bodies have long been recognized as major anthropogenic sources of As; however, natural sources of As contamination also have recently become a major societal concern (Goldberg, 2002; P. L. Smedley & Kinniburgh, 2002). The natural release of As into groundwater has had the most impact in south and southeast Asia, where Himalayan sediments containing high As concentrations erode, and, after deposition, release As under anaerobic conditions (Polizzotto et al., 2005; Polizzotto, Kocar, Benner, Sampson, & Fendorf, 2008). Consequently, released As is cycled through aquifers, taken up by crops, and ultimately consumed by humans. Locations such as West Bengal, India, and Bangladesh are the most

affected by this issue; however, As contamination of water systems is pervasive in other regions. Other examples of affected countries include Cambodia, Taiwan, Northern China, and Mexico (P. Smedley & Kinniburgh, 2013), where natural As can be mobilized from As-containing aquifer sediments (Nickson et al., 1998; Schreiber, Gotkowitz, Simo, & Freiberg, 2003). Over-pumping can further affect As concentrations in groundwater by inducing changes in groundwater flow paths and biogeochemical conditions (Harvey et al., 2002; Klump et al., 2006). In the United States, As contamination is mainly a concern in the Southwest, primarily a result of many geogenic sources and acid-mine drainage (P. Smedley & Kinniburgh, 2013). Groundwater can become increasingly concentrated through evaporation in this region because of the largely arid climate (Ayotte, Szabo, Focazio, & Eberts, 2011; P. Smedley & Kinniburgh, 2013). Overall, it can be concluded that As contamination of groundwater is a widespread occurrence that negatively impacts human well-being.

1.2 Arsenic Biogeochemistry

Due to the widespread health effects attributable to As contamination of drinking water, it is vital to understand the environmental controls affecting As mobility. Chemical speciation partially controls As toxicity and cycling (Zavala, Gerads, Gürleyük, & Duxbury, 2008). Arsenic has two dominant species in most environments: arsenate (As(V)) and arsenite (As(III)) (Goldberg & Johnston, 2001). As(V) is thermodynamically favored in oxic systems whereas As(III) is the dominant species in reducing environments (Smith, Naidu, & Alston, 1998). Although As speciation often can be predicted by thermodynamic calculations, both species

commonly exist in at a variety of redox conditions due to the slow kinetics of As redox transformations (Goldberg & Johnston, 2001; Masscheleyn, Delaune, & Patrick Jr, 1991).

Both As species may potentially negatively impact human health. In general, As(III), which negatively interferes with essential enzymes necessary for metabolism (Ehrlich, Newman, & Kappler, 2015), is considerably more toxic (25-60 times more so than As(V)) (Fendorf, Eick, Grossl, & Sparks, 1997; Raven, Jain, & Loeppert, 1998). The issue is exacerbated by As(III) typically having higher mobility than As(V) in water systems. As(III) release has been found to occur more than As(V) in systems containing common competitive biogeochemical factors, such as those of high ionic strength (Goldberg & Johnston, 2001; McBride, 1997). In environmental systems, As mobility is controlled by sorption and remobilization from minerals surfaces and other sorbents (Goldberg & Johnston, 2001; Korte & Fernando, 1991).

Minerals play a critical role in the biogeochemical cycling of As in the environment. Of these minerals, metal oxides (such as Fe(III), Al(III), and Mn(IV) oxides) are major mediators of As cycling through sorption and redox processes (Dixit & Hering, 2003; Ehlert, Mikutta, & Kretzschmar, 2014; Lafferty, Ginder-Vogel, Zhu, Livi, & Sparks, 2010; Manning, Fendorf, & Goldberg, 1998; Wilkie & Hering, 1996; Zhu, Pigna, Cozzolino, Caporale, & Violante, 2011). For example, it has been shown that Mn(IV) oxides can oxidize As(III) to As(V) (Ehlert et al., 2014; Lafferty et al., 2010; Ouvrard, Simonnot, & Sardin, 2002), leading to increased As sequestration (Lafferty et al., 2010) on Mn oxides or other surfaces. However, Fe(III) oxides are recognized as having the greatest impact on As sequestration.

Fe(III) (oxyhydr)oxides are of particular importance because they are environmentally ubiquitous and possess a high affinity for As (R. M. Cornell & Schwertmann, 2004; Dixit &

Hering, 2003). Examples of Fe(III) (oxyhydr)oxide phases commonly found in the environment include ferrihydrite, goethite, and hematite (Rochelle M Cornell & Schwertmann, 2003; Dixit & Hering, 2003). These Fe(III) mineral phases vary in crystallinity, structure, specific surface area, charge, and other geochemical characteristics (Rochelle M Cornell & Schwertmann, 2003; Dixit & Hering, 2003). Goethite and hematite are more crystalline phases whereas ferrihydrite is poorly crystalline (Rochelle M Cornell & Schwertmann, 2003). Less crystalline phases such as ferrihydrite are initially precipitated and then age over time to more crystalline phases (Dixit & Hering, 2003). As a result of low crystallinity, high specific surface area, and high affinity for anions, ferrihydrite (specifically, 2-line ferrihydrite) has the potential to sorb oxyanions to an extent greater than that of other more crystalline phases (R. M. Cornell & Schwertmann, 2004; Dixit & Hering, 2003), making it the most effective Fe(III) (oxyhydr)oxide sorbent readily found in the environment.

The species of As plays a critical role in determining the mechanism of sorption, which in turn affects sequestration (Dixit & Hering, 2003; Goldberg & Johnston, 2001). As(V) is sorbed primarily via ligand exchange mechanisms to Fe(III) (oxyhydr)oxide mineral surfaces, resulting in inner sphere complexation (Goldberg & Johnston, 2001). As(V)-Fe surface complexes occur predominantly as bidentate-binuclear complexes (As-Fe bond length of approximately 3.24 Å) (Fendorf et al., 1997; Goldberg & Johnston, 2001; Manning et al., 1998; Waychunas, Rea, Fuller, & Davis, 1993). However, As(III) may be sorbed via both inner and outer sphere mechanisms (Goldberg & Johnston, 2001; Manning et al., 1998). Published As extended X-ray absorption spectroscopy-fine structure (EXAFS) data for As(III)-loaded 2-line ferrihydrite shows that As(III) forms both bidentate mononuclear edge-sharing complexes (As-Fe bond length of

approximately 2.90 Å) and bidentate binuclear corner-sharing complexes (As-Fe bond length of approximately 3.35 Å) (Ona-Nguema, Morin, Juillot, Calas, & Brown, 2005). Outer sphere complexes occur when the sorbent and sorbate are separated by at least one water molecule, resulting in increased susceptibility to changing environmental conditions (Goldberg & Johnston, 2001). In particular, ionic strength effects are thought to greatly affect remobilization of As(III) bound via outer sphere complexes to Fe(III) (oxyhydr)oxide minerals (Goldberg, 2002; Goldberg & Johnston, 2001), with increased As release at higher ionic strengths. This outer sphere mechanism of sorption represents a primary reason as to why As(III) is more prone to release from metal oxide minerals than As(V) in dynamic water systems (Mandal & Suzuki, 2002; Yamaguchi et al., 2011).

The potential of Fe(III) oxide minerals to sorb, and subsequently immobilize, As is a major mediator of As cycling in natural systems; however, this immobilization is susceptible to reversal with changing redox conditions. Redox processes take a primary role in controlling Fe(III) oxide mineral surface interaction processes, as reducing conditions have been found to lead to increased As availability in water systems due to the concomitant release of As via reductive dissolution of Fe minerals and the predominance of the more environmentally mobile reduced As species (As(III)) (Borch et al., 2009; Mandal & Suzuki, 2002; E Marie Muehe et al., 2016; P. Smedley & Kinniburgh, 2013; P. L. Smedley & Kinniburgh, 2002). These redox-driven processes have been found to be driven by both abiotic and biotic factors (Borch et al., 2009; E Marie Muehe et al., 2016); however, this research has focused primarily on synthetic Fe(III) oxide minerals.

The significance of redox processes on the release of As from Fe(III) oxide minerals in natural systems is exemplified in Asia. As-bearing sulfide minerals, a by-product of the weathering of Himalayan rocks, are deposited into aqueous environments via fluvial transport, resulting in the formation of Fe (III) oxide minerals as As-bearing sulfide minerals are further weathered (Nickson et al., 1998). The newly formed Fe(III) oxide mineral continues to sequester As at high redox potentials but ultimately release As via reductive dissolution when deposited in reduced environments (Inskeep, McDermott, & Fendorf, 2001; E. Marie Muehe, Scheer, Daus, & Kappler, 2013; Nickson et al., 1998; Polizzotto et al., 2005). Release of As from environmental Fe(III) oxide minerals typically occurs through reductive dissolution processes; however, there are many different methods by which As is potentially released and is structure dependent (P. Smedley & Kinniburgh, 2013).

Competitive sorbates may also limit As surface sorption and facilitate the release of sequestered As. Primary environmental constituents competing with As for sorption sites on the surfaces of Fe(III) oxide minerals include phosphate, carbonate, sulfate, chloride, and silica (Darland & Inskeep, 1997; Goh & Lim, 2005; Kappler & Straub, 2005; Korte & Fernando, 1991; Zeng, Fisher, & Giammar, 2007). Of these competitive factors, phosphate is of major importance in due to its geochemical similarity to As(V) and affinity for Fe(III) (oxyhydr)oxide minerals . This similarity promotes the effective displacement of As(V) by phosphate via ligand exchange (Goh & Lim, 2005). Although phosphate is one of the most effective at As displacement from Fe(III) oxide minerals, carbonate also has been found to facilitate As(V) desorption. (Saalfield & Bostick, 2010). This is of particular importance in aquifer systems, where carbonate is often present in relatively high concentrations (Saalfield & Bostick, 2010).

However, carbonate is typically less competitive than phosphate for As(V) surface sites on Fe(III) oxide minerals (Goh & Lim, 2005). Other competitive factors of importance are sulfate and chloride. Both compete with As(III) and As(V) and possess a similar degree of competition for both As(V) and As(III) (Goh & Lim, 2005; Wilkie & Hering, 1996), whereas silica has been found to primarily influence the desorption of As(III) (Appelo, Van der Weiden, Tournassat, & Charlet, 2002; Gao, Root, Farrell, Ela, & Chorover, 2013). Competitive sorbates have variable effects on As sorption and are also greatly affected by the characteristics of Fe(III) oxide minerals. For example, mineral phases of higher crystallinity with lesser specific surface area will be more affected by competitive sorbate effects (Dixit & Hering, 2003). Understanding the variety of competitive effects that sorbates exhibit on As complexed to Fe(III) mineral oxides is critical when evaluating environmental As cycling; however, some environmental constituents can have both antagonistic and beneficial effects on As immobilization.

Organic matter, found in soil and water systems, is compositionally heterogeneous and complex, resulting in a mixed effect on environmental As sequestration when associated with metal oxide minerals. It has been observed that natural organic matter negatively influences As retention in some environmental systems due to electrostatic repulsion (Grafe, Eick, & Grossl, 2001; Liu, Fernandez, & Cai, 2011; Wang & Mulligan, 2006). Also, As redox state may be altered by organic matter, resulting in the potential reduction of As(V) to less strongly held As(III) (Redman, Macalady, & Ahmann, 2002; Wang & Mulligan, 2006). Conversely, it has also been found that organic matter complexed to metal oxide surfaces may facilitate metal bridging processes (Wang & Mulligan, 2006), resulting in As sequestration. The extent of As sorption to these organo-mineral metal oxides has been shown to be heavily dictated by the concentration

of the cationic metal (Redman et al., 2002). The range of effects that natural organic matter has on Fe(III) (oxyhydr)oxide As sorption embodies the need for further research concerning the sorption behavior of biogenic metal oxide minerals. Understanding As sorption on a molecular scale is key to understanding how As cycles in environmental systems.

1.3 Biogenic Iron Oxides

Fe(III) biominerals are formed abiotically and biotically and commonly in aqueous environments (Duckworth, Holmström, Peña, & Sposito, 2009; Emerson, Fleming, & McBeth, 2010; Roden et al., 2012; Roden, Sobolev, Glazer, & Luther, 2004). In aquatic ecosystems fed by Fe(II)-rich groundwater, Fe(III) minerals form via oxidation as they move into circumneutral oxygen-rich surface waters (Jambor & Dutrizac, 1998). The suboxic zone of this redox gradient creates a high potential for redox processes that is largely biologically mediated (Emerson et al., 2010; Jambor & Dutrizac, 1998). Fe-oxidizing bacteria (FeOB) are present in these locations where they oxidize Fe(II) minerals in order to derive chemical energy, thus creating Fe(III) minerals of heterogeneous morphologies as a by-product (Duckworth et al., 2009; Emerson et al., 2010; Roden et al., 2012). However, both biotic and abiotic formation processes can occur in similar environmental locations, typically simultaneously (R. M. Cornell & Schwertmann, 2004; Duckworth et al., 2009). In addition, Fe-reducing bacteria are also present in this redox zone; therefore, the suboxic-oxic aqueous interface establishes a redox gradient that facilitates iron cycling (Duckworth et al., 2009; Roden et al., 2012).

The high affinity of Fe(III) (oxyhydr)oxides to sorb As is well known; however, the sorption of As to biogenic Fe oxides formed in circumneutral waters has not been studied until

recently. Using the FeOB *Acidovorax* sp. BoFeN1, it was found that Fe(III) mineral aggregates were produced containing cell derived organic matter (CDOM) (Hohmann, Winkler, Morin, & Kappler, 2009; E. Marie Muehe et al., 2013; Schadler et al., 2009). Further evaluation of the biogenic Fe(III) mineral structure found differences in mineral properties compared to abiotic Fe(III) minerals, including decreased crystallinity, reduced crystal size, and increased surface area (Ferris, 2005; Ferris, Hallberg, Lyvén, & Pedersen, 2000; Hohmann et al., 2009; Posth, Huelin, Konhauser, & Kappler, 2010). These findings could potentially indicate a higher available sorption site density on biogenic Fe(III) mineral surfaces for sorbates such as As. Also, abiotic Fe(III) minerals are positively charged at circumneutral pH (where pH is less than the point of zero charge) (Rochelle M Cornell & Schwertmann, 2003); however, laboratory-produced biogenic Fe(III) minerals were found to be negatively charged due to the incorporation of CDOM (E. Marie Muehe et al., 2013; Posth et al., 2010). Because As(V) is negatively charged at circumneutral pH, As sequestration may potentially be lowered due to electrostatic repulsion. Consequentially, a full understanding of the As sorption behavior of environmental Fe(III) biominerals is needed as these differences in mineral properties are expected to impact the rate and extent of As sequestration.

Remobilization of As from As-bearing Fe(III) (oxyhydr)oxides via reductive dissolution has recently been evaluated. Using the Fe-reducing bacteria *Shewanella oneidensis* strain MR-1, it was found that As(III)-bearing Fe(III) biogenic minerals produced by the FeOB *Acidovorax* sp. BoFeN1 released more As(III) than abiotic formed minerals (E. Marie Muehe et al., 2013). However, less mobilization was observed when reducing As(V)-bearing biogenic Fe(III) minerals compared to abiotic Fe(III) minerals (E. Marie Muehe et al., 2013). In a different study, it has

been shown that biogenic Fe(III) (oxyhydr)oxide formed by *Acidovorax* sp. BoFeN1 effectively immobilizes As (Hohmann et al., 2009). These As-sequestering minerals can also form in high As environments and will form different mineral phases based on As concentration (Hohmann et al., 2011; Hohmann et al., 2009). Variations in observed As sorptive behavior by biogenic Fe(III) (oxyhydr)oxides highlights the need for further research, especially in heterogeneous environmental systems, as this is expected to significantly impact arsenic environmental fate.

1.4 Motivation and Knowledge Gaps

The high affinity of Fe (oxyhydr)oxides to sorb As is well known; however, most studies have utilized abiotic laboratory samples, with only a single study using biogenic oxides produced by iron-oxidizing-nitrite reducing bacterium *Acidovorax* sp. BoFeN1. Biogenic Fe (oxyhydr)oxides have different structural properties from abiotic analogues (Ferris, 2005; Ferris et al., 2000; Hohmann et al., 2009; Posth et al., 2010). Due to significant correlation between crystal structure and sorption capacity, it could be hypothesized that biogenic Fe (oxyhydr)oxides were expected to have more sites for adsorption of arsenite and arsenate oxyanions. However, Fe (oxyhydr)oxide aggregates produced by microbes contain CDOM that causes biogenic Fe(III) mineral surfaces to be negatively charged at circumneutral pH (abiotic Fe (oxyhydr)oxides are positively charged at analogous conditions (Ferris, 2005; Hohmann et al., 2009; Posth et al., 2010)), which may result in repulsion of As(III,V) oxyanions. To investigate the net impact of these effects, mechanistic research focusing on differences in As sorption behavior to Fe(III) minerals formed in laboratory and environmental settings is required. Furthermore, because of the importance of biogenic minerals in the environment,

understanding their impact on As cycling is critical to prediction and management of As contamination. For example, exploring these knowledge gaps will not only result in increased understanding of As environmental fate, but will provide necessary information for engineering high-efficiency As removal systems. The importance of this information is exemplified by recent research suggesting that abiotic Fe(III) mineral filters used in As-removal water remediation systems are experiencing reduced efficiency due to the presence of negatively charged biogenic Fe(III) minerals (Kleinert et al., 2011; Posth et al., 2010). The proposed research strives to provide environmentally relevant findings so that As mobility may be better understood and As-free drinking water may be more available.

1.5 Structure of Thesis

The goal of this research is to determine the extent and mechanism of As loading to environmental Fe(III) (oxyhydr)oxide biominerals to improve the current understanding of As cycling in the environment. Environmental Fe(III) biominerals were compared to what is observed for laboratory-produced Fe(III) biominerals and synthetic 2-line ferrihydrite to identify similarities in As sorption behavior. In the following chapter, these Fe(III) (oxyhydr)oxide minerals were characterized to determine differences in mineral structure, crystallinity, surface area, and other properties. Also, kinetics and sorption isotherm data are presented for all Fe(III) (oxyhydr)oxide minerals to elucidate variations in the rate and extent of As sorption. Characterization and X-ray absorption spectroscopy (XAS) data are used to support observed trends in As sorption data. Chapter 3 expands on the research presented in Chapter 2 and describes ways in which the methodology could be improved based on my experiences. Also, Chapter 3 presents how this

research fits into the literature, and what new investigations would be beneficial to filling remaining knowledge gaps.

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Chapter 2: Arsenate and Arsenite Sorption to Environmental Biogenic Fe(III) Minerals

2.1 Introduction

Arsenic (As) is a widespread and problematic pollutant that impacts the health of approximately 150 million people daily (Brammer & Ravenscroft, 2009). Many adverse health effects are associated with chronic As exposure, including increased cancer rates, birth defects, neurological issues, and diabetes (Kleinert et al., 2011; Meharg & Zhao, 2012). Human exposure to As may arise from both anthropogenic and natural sources (P. Smedley & Kinniburgh, 2013), which are geographically widespread (figure 1). For example, runoff of As-containing pesticides and mine spoil drainage are major anthropogenic sources of As, especially in North and South America. However, natural sources of As contamination (i.e., weathering of arsenic minerals in rocks and reductive dissolution of iron-bearing soil and sediments) may present a hazard to human health, and in Southern Asia have developed into major societal concern (Goldberg, 2002; P. L. Smedley & Kinniburgh, 2002).

Geogenic As contamination of groundwater has had the most widespread impact in south and southeast Asia where Himalayan sediments containing high As content erode and release As under anaerobic conditions, resulting in toxic concentrations of As in irrigation and drinking water (Muehe, Scheer, Daus, & Kappler, 2013; Polizzotto, Harvey, Sutton, & Fendorf, 2005; Polizzotto, Kocar, Benner, Sampson, & Fendorf, 2008). In Bangladesh, these processes result in widespread exposure that has been described as “the greatest mass poisoning in history” (Polizzotto et al., 2008). Although south and southeast Asia are the most notable locations impacted, As contamination of groundwater is pervasive in other regions, including

regions of southwestern United States and Mexico (P. Smedley & Kinniburgh, 2013). As a result of this large-scale contamination, research seeking to elucidate the sources and mechanisms of As mobilization has intensified over the last 15 years (Meharg & Zhao, 2012).

Field studies have identified iron (oxyhydr)oxides as key sorbents that store As (R. M. Cornell & Schwertmann, 2004; Dixit & Hering, 2003; Goldberg & Johnston, 2001; Mandal & Suzuki, 2002; Mohan & Pittman Jr, 2007; Raven, Jain, & Loeppert, 1998; Wilkie & Hering, 1996). Consequently, it is important to understand the fundamental processes that control As interactions with these mineral surfaces. Major conditions controlling As retention on mineral surfaces include redox conditions, pH, competitive ions, and other biogeochemical factors. These processes are well understood for many minerals (Bauer & Blodau, 2006; Bowell, 1994; Fendorf, Eick, Grossl, & Sparks, 1997; Giménez, Martínez, de Pablo, Rovira, & Duro, 2007; Redman, Macalady, & Ahmann, 2002), including both crystalline and poorly ordered synthetic iron minerals (e.g., ferrihydrite (Borch et al., 2009; Cismasu, Michel, Stebbins, Levard, & Brown, 2012; Cismasu, Michel, Tcaciuc, Tyliszczak, & Brown Jr, 2011; Jambor & Dutrizac, 1998; F. Michel et al., 2007; Waychunas, Rea, Fuller, & Davis, 1993)).

Although ferrihydrite is often used as an experimental surrogate for poorly ordered Fe(III) hydroxide minerals that are environmentally ubiquitous, there is a growing recognition that bacteriogenic Fe minerals are common in natural waters and sediments (Duckworth, Holmström, Peña, & Sposito, 2009; Emerson, Fleming, & McBeth, 2010; Emerson & Weiss, 2004; Ferris, 2005; Gault et al., 2011; Posth, Huelin, Konhauser, & Kappler, 2010), forming specifically at redox gradients (e.g., circumneutral Fe(II)-rich groundwater discharges into quiescent aerobic surface water as shown in figure 2) (Duckworth et al., 2009; Emerson et al.,

2010; Emerson & Weiss, 2004; Roden et al., 2012). These biominerals may have important structural differences (decreased crystallinity, reduced crystal size, and increased surface area) (Cismasu et al., 2011; Ferris, 2005; Ferris, Hallberg, Lyvén, & Pedersen, 2000; Hohmann, Winkler, Morin, & Kappler, 2009; Posth et al., 2010)), as well as incorporated bacterial biomass and other cell-derived organic matter (Hohmann et al., 2009; Muehe et al., 2013; Schadler et al., 2009), which may result in a sorption reactivity that differs significantly from synthetic ferrihydrite. Despite the potential importance of biogenic Fe(III) oxides to As cycling, few studies (Kleinert et al., 2011; Muehe et al., 2013) have studied the sorption of biogenic Fe(III) oxides formed in circumneutral environments, resulting in a significant gap in our knowledge (Emerson et al., 2010).

A better understanding of As sorption extent onto biogenic Fe(III) (oxyhydr)oxides that form at redox gradients in natural waters is needed to develop improved models of As transport in the environment. The objectives of this study address this knowledge gap by: 1) determining the extent of arsenic sorption to iron (oxyhydr)oxides originally formed in natural environments and by bacterial cultures ; and 2) identify arsenic sorption mechanism differences to iron (oxyhydr)oxide biominerals. The findings of this research are meant to not only further our understanding of iron cycling in terrestrial ecosystems, but may also lead to the improvement of arsenic remediation systems.

2.2 Materials and Methods

2.2.1 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; figure 3). This site was chosen for sampling for its proximity to North Carolina State University's campus and perennial occurrence of environmental Fe(III) oxides. "Fluffy" orange biofilm/mineral assemblages were sampled 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.

In the laboratory, the mineral suspensions were transferred into 50 mL polypropylene centrifuge tubes and centrifuged for 10 minutes at ca. 10000 *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 dry mass to samples for all subsequent experiments.

2.2.2 Laboratory Fe(III) Biomineral Sorbent Preparation

Diffusion gradient chambers (DGC) were used to produce Fe(III) biominerals in the laboratory (Kikuchi et al., 2014). The DGCs (figure 4) consist of two chambers that are

connected via a permeable membrane (Kikuchi, Makita, Takai, Yamaguchi, & Takahashi, 2014).

An anoxic chamber that contains a source of Fe(II) (FeS) is connected by a permeable membrane to a suboxic chamber containing iron-oxidizing bacteria (FeOB). The anoxic chamber is mixed via stir bar, facilitating the transfer of Fe(II) across the permeable membrane and to the suboxic chamber where it is then oxidized biogenically by FeOB, resulting in the formation of biogenic Fe(III) (oxyhydr)oxides in approximately 4-9 days (Kim & Nriagu, 2000).

Before setting up a DGC, a FeS suspension was prepared for use in the anoxic chamber. In a one liter flask, 11.6 g of FeSO₄ was added 250 mL of DI held at 50°C with continuous stirring, immediately followed by the addition of 9.9 g NaS. The resulting solution was then stirred for approximately 5 minutes, removed from heat and agitation, and allowed to gravitationally settle. After the FeS suspension had settled for approximately 2 hours, the mineral was washed with DI water and stored in the fumehood until further use. Similarly, a low nutrient medium for the suboxic chamber of the DGC was prepared by adding 0.75 g NH₄Cl, 0.15 g MgSO₄·7H₂O, 0.075 g CaCl₂·2H₂O, 0.0375 g K₂HPO₄, 0.315 g NaHCO₃, and 1 µL of trace mineral and vitamin supplement to 750 mL of DI. Liquid cultures of *Rhizobium leguminosarum*, a Fe oxidizing bacteria, were grown in TY media. After allowing four days for growth, these cultures were centrifuged and decanted to make a bacteria pellet. 30 mL of the low nutrient medium was then added to the pellet and used as a stock when inoculating the suboxic chamber of the DGC. This stock was frozen at approximately -20°C until further use.

To prepare the DGC to produce Fe(III) biominerals, a polycarbonate track-etched 0.2 µm membrane was placed between the two chambers and then fastened with screws.

Approximately 100 mL of FeS suspension was placed in one of the chambers of the DGC and

purged with N₂ until anoxic conditions were met. Next, the other chamber received approximately 100 mL of low nutrient media and was purged with N₂:CO₂ (80:20) gas until oxygen concentration of the solution was about 30 μM. *Rhizobium leguminosarum* stock was pipetted into the suboxic chamber such that optical density at 600 nm was 2.6. Both chambers were capped and the chamber was placed on a magnetic stir plate and allowed to stir for about 10 days. Generated biomineral was then collected via syringe, centrifuged, and stored at approximately -20°C until further use.

2.2.3 Synthetic 2-line Ferrihydrite Synthesis

Two-line ferrihydrite was abiotically synthesized according to established procedures (R. M. Cornell & Schwertmann, 2004). Briefly, 40 g of Fe(NO₃)₃ · 9 H₂O was dissolved in 500 mL of deionized (DI) water. In order to raise pH, 330 mL of 1M KOH was added to the Fe(NO₃)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 pH = 7-8, the solution was centrifuged and washed with DI water. The procedure resulted in the formation of 10 g of 2-line ferrihydrite. All synthesized minerals were stored in a freezer at approximately -20°C until further use.

2.2.4 Characterization of Fe(III) Minerals

All Fe(III) (oxyhydr)oxides were characterized to assess compositional and physical properties. Percent 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 (0.3M) and 2.5 mL of sodium bicarbonate (1M). Sample suspensions were shaken and heated to 75-80°C in a water bath. 1 g of sodium dithionite was then applied and stirred thoroughly for 1 minute. Samples were kept at 75-80°C for the next 30 minutes with intermittent shaking. After the reaction had completed, samples were centrifuged, filtered, and analyzed for aqueous Fe using a Thermo-Fisher iCE 3000 flame atomic adsorption spectrometer. The resulting aqueous Fe data was used to calculate percent Fe for all samples.

Other mineral characterization analyses were also conducted. CHN analysis was performed to determine sample C and N content. All mineral samples were submitted to the NCSU Environmental and Agricultural Testing Service (EATS) lab for CHN analysis. Brunauer-Emmett-Teller (BET) analysis was conducted using a Quantachrome: Monosorb surface area analyzer to determine external surface area. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were performed to elucidate mineral structure and morphology, respectively. Both techniques were conducted at the NCSU Analytical Instrumentation Facility (AIF).

2.2.5 Rates of Arsenic Sorption to Fe(III) Minerals

To assess the rate of arsenate sorption to iron (oxyhydr)oxides, a stock solution (500 mg/L As(V)) was prepared using reagent grade $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$. Similarly, a suspension containing 2 g sorbent (dry mass basis)/L in 0.01 M NaCl was prepared in a 250 ml flask. The pH of each solution was adjusted to 7 via HCl and NaOH additions and monitored using a XL20 pH/conductivity meter. This pH was chosen to approximate the circumneutral conditions (pH = 6.5-7.5) seen in surface waters from where the environmental Fe(III) biomineral mass was

collected. A magnetic stir bar was placed in the 250 mL flask to agitate the suspension and aluminum foil was used as a cover to exclude stray light.

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

Inductively coupled plasma mass spectrometry (ICP-MS) analysis was conducted at Research Triangle Institute (RTI International) 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 ppb).

2.2.6 Adsorption Isotherms

The extent of As(V) and As(III) sorption to synthetic 2-line ferrihydrite and environmental Fe(III) biomineral were tested. A 0.01 M NaCl solution was used to make As stock solutions and sorbent suspensions. As(V) and As(III) stock solutions (500 mg L⁻¹) were prepared using reagent grade Na₂HAsO₄ · 7H₂O and NaAsO₂, respectively. 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) biomineral in 50 mL polypropylene centrifuge tubes. As stock solutions and sorbent suspensions were adjusted to

approximately pH 7 by using HCl and NaOH. Varying volumes of As stock solution (500 mg L^{-1}) 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 approximately pH = 7) for all samples using a XL20 pH/conductivity meter. Samples were then loaded onto a MX RD Pro rotary mixer for 48 hours (Dixit & Hering, 2003; Raven et al., 1998). Samples were checked for pH changes. After 48 hours, samples were centrifuged at ca. $10000 g$ RCF for 10 minutes, pipetted into 20 mL syringes, and filtered at $0.45 \mu\text{m}$. 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 previous isotherm procedure was performed for both As(V) and As(III); however, to limit unwanted oxidation As(III) oxidation to As(V) (Kim & Nriagu, 2000), As(III) experiments were performed in a glovebag at approximately 2% O_2 content using a N_2 gas mixture (99% N_2 , 1% O_2) 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 previous been noted (Roden et al., 2012)).

Isotherms were conducted using biominerals produced in diffusion gradient chambers (DGC). Limited experimentation was performed using DGC-produced biomineral due to a low production rate. The experimental procedure remained similar to earlier isotherms using synthetic 2-line ferrihydrite and environmental Fe(III) biomineral, except for sample sorbent preparation. Due to low masses of sorbent, a stock sorbent suspension was made using 0.01 M

NaCl as a matrix. The Fe concentration of this stock was then determined by flame atomic adsorption spectroscopy and found to be approximately 1200 mg Fe L⁻¹. From this Fe concentration, sorbent stock was transferred, while being well-mixed, into each isotherm sample such that the Fe concentration was comparable to isotherms conducted for other sorbents tested.

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 isotherm fitting tool was used to fit isotherm data to both Langmuir and Freundlich fits (Carl H Bolster & George M Hornberger, 2007) using non-linear optimization. For selected samples, speciation analysis was also conducted at RTI using ultra-high performance liquid chromatography (UHPLC) to determine the concentrations of As(V) and As(III) in aqueous samples. In no case was As transformed from its initial state.

2.2.7 X-ray Absorption Spectroscopy

Fe K-edge spectra were collected at Stanford synchrotron radiation Lightsource (SSRL) on beamlines 4-1, 4-3, and 11-2. Spectra were energy calibrated by adjusting the E₀ to a metal foil (Fe or Au). Synthetic samples were collected in transmission mode whereas environmental samples were collected in fluorescence mode using a Lytle detector. On 4-1 and 11-2, the incident beam was detuned to 30% 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. 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. As 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. 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. As K-edge spectra obtained for As-loaded Fe(III) mineral samples were performed at low and high (Fe:As ratios of 300:1 and 62.5:1, respectively).

Both Fe and As K-edge spectra were energy calibrated, averaged, background-subtracted, splined, and fit in *R*-space (Kelly, Hesterberg, & Ravel, 2008) using the SIXPACK interface (S. M. Webb, 2005), which makes use of the IFEFFIT code (Ravel & Newville, 2005). Normalized Fe XANES and Fe EXAFS linear combination fitting was conducted in SIXPACK for DGC-produced biomineral and environmental Fe(III) biomineral using Fe(III) standards in order to probe Fe(III) mineral phase and structure. Components found to make up less than 10% of the sample were removed, and fits were recalculated using remaining standards. A list of all standards (Harrington et al., 2012; O'day, Rivera, Root, & Carroll, 2004) considered in fits is shown in table 1, 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. As-bearing environmental Fe(III) biomineral and synthetic 2-line ferrihydrite samples were fit using SIXPACK (S. Webb, 2005), which makes use of the IFEFFIT engine (Newville, 2001). Data were modeled using parameters of the EXAFS equation. Paths were generated using the mineral scorodite in Feff9 (Rehr, Kas, Vila, Prange, & Jorissen, 2010). EXAFS data were fit using a common value of the parameter $E0$, which was allowed to float

during optimization. The amplitude reduction factor (S_0^2) was fixed at 0.85 (Foster, Brown, Tingle, & Parks, 1998).

For As(III), models have typically contained an As-O shell at $R = 1.7\text{--}1.8 \text{ \AA}$, representing an arsenite molecule. Arsenite is thought to be bound to the ferrihydrite surface dominantly via a bidentate mononuclear complex ($R = 2.9 \text{ \AA}$) and a bidentate binuclear complex ($R = 3.4 \text{ \AA}$) (Gao, Root, Farrell, Ela, & Chorover, 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 factor (f or $(1-f)$), which was designed to allow for estimation of how much As was bound to these coordination environments.

For As(V), models have typically been fit by using, in addition to a As-O first shell ($R = 1.7 \text{ \AA}$), a single bidentate binuclear complex ($R = 3.3 \text{ \AA}$) and an As-O-O multiple scattering feature (Gao, Root, Farrell, Ela, & Chorover, 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 an As-O scattering path with N , σ^2 , and R allowed to float and a shell with an As-Fe path with $N = 2$, and R and σ^2 allowed to float.

2.3 Results

Elemental analysis, transmission electron microscopy (TEM), and surface area analysis were performed to determine mineral morphology and crystalline phase. The composition of

samples is shown in table 2. TEM images of environmental Fe(III) biomineral and synthetic 2-line ferrihydrite samples are shown in figures 5a and 5b, respectively. Differences in morphology are present between environmental and synthetic samples. Environmental Fe(III) biomineral has a ragged morphology similar to literature reports of other Fe(III) biominerals (Posth et al., 2010), which differs from the morphology observed for synthetic 2-line ferrihydrite. Surface areas of environmental sample collected at different dates vary by a factor of two (table 2). Our synthetic ferrihydrite had a surface area of $210 \text{ m}^2 \text{ g}^{-1}$, which is within the range reported in the literature (Rochelle M Cornell & Schwertmann, 2003). Similarly, iron contents vary by roughly a factor of two whereas carbon contents are relatively constant at ca. 8–10%.

The iron oxides were further characterized for mineralogy. X-ray diffraction results (figure 6) indicate that our synthetic and environmental minerals were predominantly 2-line ferrihydrite (<10% crystalline phases). The DGC-produced material was not analyzed because we were unable to produce adequate mass for XRD. Fe K-edge X-ray absorption spectroscopy (XAS) data are presented in figure 10. Normalized X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra are shown left to right, respectively. From the normalized Fe XANES data, all spectra for Fe(III) mineral standards and Fe(III) biominerals were observed to have similar adsorption edge positions (approximately 7128 eV). The highest FT magnitude at ca. 2 \AA , an interatomic distance characteristic of Fe(III)-O bonding (Shannon, 1976), for our standards was also seen for all biomineral samples. As(V)-loaded and As(III)-loaded environmental Fe(III) biomineral (labeled EnvFe(III)_Sorbed As(V) and EnvFe(III)_Sorbed As(III), respectively) EXAFS (\AA^{-1}) spectra and FT magnitude plots corresponded

best to our 2-line ferrihydrite standards; however, signal differences were observed between the environmental Fe(III) biominerals. EnvFe(III)_Sorbed As(III) was observed to have a more destructive signal, seen in the k -spacing from 6 to 9 Å⁻¹ whereas EnvFe(III)_Sorbed As(V) shows a higher degree of ordering that is evident by higher amplitude in this region. Although these differences were observed, comparing both in R -space at approximately 3.3 Å (shoulder known to be representative of Fe-Fe bonding) suggests that they both are closest in signal to our 2-line ferrihydrite standard. DGC biomineral spectra were observed to have a signal suggestive of a higher degree of second-shell ordering than environmental Fe(III) biominerals. This is clearly seen by the increased FT magnitude at 3.3 Å relative to environmental Fe(III) biomineral spectra.

Normalized Fe XANES and Fe EXAFS linear combination fitting were performed to probe the percentage of Fe(III) mineral phases found in environmental Fe(III) and DGC-produced biominerals. Fe XANES and Fe EXAFS were found to mostly agree in terms of spectral components, with results for each are shown in tables 3 and 4, respectively. DGC-produced mineral was best fit with a combination of Fe(III) phosphate, lepidocrocite and 2-line ferrihydrite. Lepidocrocite was the dominant mineral phase in the fit (55% using Fe EXAFS LCF). EnvFe(III)_Sorbed As(V) and EnvFe(III) Sorbed As(III) were both fit with a dominant 2-line ferrihydrite fraction (75% and 100%, respectively, using Fe EXAFS LCF). However, EnvFe(III)_Sorbed As(V) was best fit with a combination of lepidocrocite, ferrihydrite, and an Fe(III)-carboxylate complex. All LCFs are represented by dashed lines overlaying samples in figure 10.

The sorption of As(V) and As(III) to synthetic 2-line ferrihydrite as a function of time is shown in figure 7a and 7b, 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 0.13 mg As m⁻² and 0.30 mg 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) biomineral, with approximately 70% of total observed sorption occurring within the first two hours after initial As(V) introduction and a maximum value of 0.34 mg As m⁻² reached after 48 hours. As(III) sorbed concentration to environmental Fe(III) biomineral reached an asymptote of 0.48 mg 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). This value is consistent with previous equilibration times used for As isotherms (Raven et al., 1998).

Sorption of As to Fe(III) biomineral and synthetic 2-line ferrihydrite as a function of initial dissolved As concentration are shown in figures 8 and 9. The concentration of As associated with the surface increases with increasing dissolved concentration throughout 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 (Carl H. Bolster & George M. Hornberger, 2007). Based on goodness of fit, all data was 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 and model efficiencies are shown in table 5.

The mass-normalized sorption of As(V) at varying concentrations (0 to 100 mg L⁻¹) is shown for five sorbents in figure 8a. Samples include three environmental Fe(III) biominerals (Env_6/19/15, Env_8/22/15, and Env_1/8/16) collected at different dates, DGC-produced biomineral (DGC) sample, and synthetic 2-line ferrihydrite sample. Maximum sorbed concentration for all environmental Fe(III) biominerals is greater than synthetic 2-line ferrihydrite; however, there is significant variation in sorption capacity among the biomineral samples. Env_6/19/15 and Env_1/8/16 have a maximum sorption concentration (approximately 45 to 50 g As kg⁻¹ sorbent) that is two times Env_8/22/15. Differences in sorption behavior are emphasized by differences in the Freundlich fitting parameters K_f and n (table 5).

In figure 8b, As(V) sorption isotherm data (taken from figure 8a) was normalized to BET surface area. Fits for environmental Fe(III) biominerals resulted in K_f and n values that were similar (and, in all but one case, within model uncertainty). Consequently, these biominerals were fit with one Freundlich isotherm within uncertainties (table 5). At dissolved As concentrations greater than 20 mg L⁻¹, environmental Fe(III) biomineral had a sorbed concentration of approximately 0.30 to 0.35 mg As m⁻². This is approximately 2.5 times greater than what was observed at a similar dissolved As concentration range for synthetic 2-line ferrihydrite (sorbed As concentration of approximately 0.10 to 0.15 mg As m⁻²).

Mass-normalized As(III) isotherm data is presented in figure 9a. As(III) sorption to four sorbate samples across dissolved As concentrations of 0 to 40 mg L⁻¹ were tested. These samples include three environmental Fe(III) biomineral (Env_9/11/15, Env_1/8/16, and

Env_2/1/16) and one synthetic 2-line ferrihydrite. Environmental samples obtained at differing dates are compared in figure 9a. Env_1/8/16 and Env_2/1/16 shared similar sorbed As concentrations across all dissolved As concentrations, with sorbed As concentration equaling 80 g As kg⁻¹ at the highest dissolved As concentrations. Also, K_f and n values for both samples were similar (table 5). Both Env_1/18/16 and Env_2/1/16 sorbed approximately 2.5 times the sorbed As concentration of Env_9/11/15. As(III) sorption isotherm data for environmental Fe(III) biominerals and synthetic 2-line ferrihydrite is also compared in figure 9a. Env_9/11/15 sorbed approximately 2.5 times less As(III) than synthetic 2-line ferrihydrite; however, Env_1/8/16 and Env_2/1/16 was observed to sorb similar As concentrations to synthetic 2-line ferrihydrite across all dissolved As concentrations.

As(III) isotherms normalized to BET surface area are presented in figure 9b. Similar to 7b, all environmental Fe(III) biominerals shared similar sorbed As concentrations per m². However, the sorbed As concentration per m² for environmental Fe(III) biominerals and synthetic 2-line ferrihydrite was similar for all dissolved As(III) concentrations. Fits for environmental Fe(III) biominerals and synthetic ferrihydrite resulted in K_f and n values that were similar and, in all but one case, within model uncertainty; thus, all BET normalized isotherms fit with one Freundlich model. Interestingly, at dissolved As concentrations greater than 20 mg As L⁻¹, sorbed As concentration ranges from 0.5 to 0.6 mg As 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) biomineral and synthetic 2-line ferrihydrite, with >99% of the total As as As(V) .

In figure 11, As K-edge X-ray absorption spectroscopy data are presented. Normalized As XANES data confirms 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, thus oxidation state was not observed to change during As loading onto environmental Fe(III) biomineral.

In the FTs of both As(III) and As(V) spectra, a large peak at $R = 1.6-1.7 \text{ \AA}$ is the major feature, which corresponds to As-O bonding. 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 6. EXAFS spectra of As(III) can be fit by two surface complexation structures whereas As(V) is adequately fit with one complex. For all spectra, fit parameters are generally within program estimated uncertainties of each other for As(III) or As(V) sorbed onto ferrihydrite and environmental samples. This correspondence is consistent with similarities in the beat structure of the EXAFS (figure 12), which appears to be invariant for each spectral set when superimposed. For As(III), $f = 0.6 \pm 0.3$ for all samples, suggesting a near even mix of mononuclear and binuclear complexes.

2.4 Discussion

2.4.1 Mineralogy of Iron Minerals

Determining the affinity of Fe(III) biominerals for common environmental As species (arsenate and arsenite) is critical to advancing the current understanding of As cycling in environmental systems, and requires a detailed understanding of their mineralogy and structure. TEM images (figure 5) indicate morphological differences between environmental Fe(III) biomineral, with the presence of ragged structures for the environmental Fe(III) biomineral. Environmental Fe(III) images compare well to what has been observed in the literature. TEM images of Fe(III) biominerals have been shown to have filamentous structures similar to what we observe in our sample (Chan, Fakra, Edwards, Emerson, & Banfield, 2009), which was reported to be produced by iron oxidizing bacteria related to the genera *Gallionella*, which are commonly found at suboxic redox gradients (Emerson et al., 2010).

Variation in mineral morphology may impact sorbate complexation. X-ray diffraction results confirmed the presence of 2-line ferrihydrite as the predominant Fe(III) mineral phase present in all environmental Fe(III) biomineral samples. This analysis roughly agrees with XAS analysis. EXAFS LCF suggest mixtures of 2-line ferrihydrite, lepidocrocite, and Fe_Rhiz (an Fe-organic complex) for EnvFe_As(V); however, 2-line ferrihydrite made up approximately 75% of the composition. EnvFe_As(III) was found to fit well to a 100% synthetic 2-line ferrihydrite standard. XANES LCF suggested that lepidocrocite was a predominant component of EnvFe_As(V) but this conflicts with what was observed from the XRD and EXAFS LCF data. However, because the spectra region has few diagnostic features, LCF of the Fe K-edge XANES

region is less definitive than XRD and EXAFS analyses, which agree well with each other; therefore, all samples were concluded to consist of predominately 2-line ferrihydrite. This conclusion relates well to previous studies showing Fe(III) oxides produced by Fe(II) oxidizing bacteria in many environments have a predominate ferrihydrite phase (Duckworth et al., 2009; Ferris, 2005; Hohmann et al., 2011; Toner et al., 2012). In contrast, XANES and EXAFS LCF analysis of DGC-produced biomineral suggests the presence of crystalline phases, suggesting that laboratory-produced biominerals from DGC may be a poor model of environmental Fe(III) biomineral.

2.4.2 Sorption of As to Fe Minerals

The sorption of As(V) and As(III) to Fe(III) minerals has been extensively studied. In previous studies, As sorption percent has been reported to be 55% and 35% for As(V) and As(III), respectively (Dixit & Hering, 2003; Raven et al., 1998). Our synthetic 2-line ferrihydrite As sorption data is approximately 65% and 30% at similar initial As concentration (100 mg L^{-1}), which is close to reported data in the literature. Although other work has been performed on the sequestration of As via microbial oxidation of Fe(II) or by the products of microbial of Fe(III) reduction (Hohmann et al., 2009; Muehe et al., 2013), no suitable comparison to our biogenic data exists in the literature.

For both As(III) and As(V), external 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 oxide minerals can vary with time, as formation process may vary with environmental factors, such as groundwater flow rates,

temperature, iron concentrations, and microbial communities (Duckworth et al., 2009; Jambor & Dutrizac, 1998). In our data, this variability manifests itself in the variation in composition (including iron and carbon) and surface area 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 oxides, as it typically is for abiotic minerals of the same phase (Dixit & Hering, 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 0.30 to 0.35 mg As m⁻²), such that all environmental Fe(III) biomineral data was 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) biomineral was found to sorb As(V) to approximately three times the extent that was observed synthetic 2-line ferrihydrite. Additionally, both As(V) and As(III) were found to sorb to at least the extent of synthetic 2-line ferrihydrite when normalized to external surface area; however, differences in As(V) and As(III) sorption between environmental and synthetic samples lead to the use of As EXAFS shell fitting analysis to probe mechanisms of As sorption.

2.4.3 Surface Binding of As to Fe Mineral Surfaces

As EXAFS data provides information on As bond distances between surrounding atoms, which relates to As sorption mechanism. Overlaid EXAFS spectra for both As(V) and As(III)

(figure 12a and 12b, respectively) show qualitatively that spectra are similar for all samples, suggesting a uniform binding mechanism for all As(III) and As(V) samples (i.e., binding structure is the same for synthetic and environmental samples, and is invariant with concentration for environmental samples).

For all As samples, first shell coordination numbers were systematically lower than expected for sorbed arsenate and arsenite. This low N was accompanied by concomitant decrease in σ^2 , which results in a similar amplitude in FT space. This systematic misfit is likely due to an issue with the scattering path generated from scorodite, and is unlikely to significantly impact the rest of the EXAFS fit.

Previous studies employing As K-edge EXAFS for As-bearing synthetic 2-line ferrihydrite have shown that both As(V) and As(III) sorb to 2-line ferrihydrite via inner sphere complexation as the primary sorption mechanism (Gao et al., 2013). As(V) sorbs predominately through bidentate binuclear complexes (3.28 Å, As-Fe corner sharing) whereas As(III) may sorb through bidentate mononuclear (2.92 Å, As-Fe edge sharing) and bidentate binuclear (3.42 Å, As-Fe corner sharing) complexation reactions (Gao et al., 2013). After shell fitting all As samples, it was found that synthetic and environmental As(V) and As(III) samples corresponded well to the previously measured As-O and As-Fe distances. As(III)-bearing environmental Fe(III) biomineral shared a similar fit (parameters listed in table 6) to As(III)-bearing synthetic 2-line ferrihydrite, with approximately 60% of the complexes estimated to be bidentate mononuclear edge sharing complexes. Bond lengths for all environmental and synthetic samples were similar (within uncertainty) and corresponded well to past literature (Gao et al., 2013). Sorption mechanism directly relates to cycling as it may dictate resilience to competitive factors.

2.4.4 Why Does As(V) bind differently to synthetic and environmental Fe(III) oxides?

Although all As(III) sorption data converged when normalized to surface area for all minerals tested, a large disparity in sorbed As(V) concentration was observed between the synthetic and environmental Fe(III) oxides. We speculate that this may be explained by several interrelated factors. We expect that the environmental Fe(III) biomineral has smaller domain sizes compared to synthetic 2-line ferrihydrite. Although less surface area was measured for the environmental Fe(III) biomineral, there may be a higher proportion of smaller domains present on the environmental Fe(III) biomineral surfaces compared to synthetic 2-line ferrihydrite (Cismasu et al., 2011). Based on the small domain size, we speculate that the environmental Fe(III) biomineral contains more sites for corner sharing complexes. 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), favoring sorption of As(V) to environmental minerals. Although this explanation is plausible, more work, including careful determination of domain size (e.g., paired distribution function analysis or high resolution TEM) (F. M. Michel et al., 2007) and surface complexation modeling of sorption (Dzombak & Morel, 1990), is needed to better elucidate the drivers of the differences in sorption reactivity of As species on environmental oxides.

2.5 Conclusions

Iron (oxyhydr)oxides are a major mediator of As cycling in the environment (Rochelle M Cornell & Schwertmann, 2003; Mandal & Suzuki, 2002). As is a major environmental contaminant and it is currently poorly understood how environmental Fe(III) biominerals

interact with As cycling. Therefore, we conducted research to address this knowledge gap by determining the relative reactivities and elucidating the mechanisms of As(V) and As(III) sorption for biogenic Fe(III) (oxyhydr)oxides compared to synthetic 2-line ferrihydrite. This contributes to the larger goals of furthering our understanding of As cycling in the environment and developing improved As remediation strategies/technologies.

All Fe(III) minerals were characterized to elucidate differences in mineralogical properties. Microscopy suggested that environmental samples were biogenic. XRD was used in conjunction with EXAFS LCF analysis to confirm that all environmental samples consisted of predominantly 2-line ferrihydrite; however DGC-produced biomineral is suspected to consist of predominantly lepidocrocite, indicating that it may be a poor surrogate for environmental biominerals. In addition to 2-line ferrihydrite, EXAFS LCF analysis suggested environmental Fe(III) biominerals also contain an Fe-organic complex fraction. External surface area, Fe content, and C content were also characterized for all samples; however, external surface area was found to be the most effective normalization parameter across all environmental samples.

Environmental Fe(III) biominerals were found to have a high reactivity for As that either met or exceeded what was measured for synthetic 2-line ferrihydrite. Also, environmental Fe(III) biominerals collected on different dates were observed to sorb variable quantities of As, which could be effectively explained by differences in surface area. Compared to synthetic 2-line ferrihydrite, environmental Fe(III) biomineral was found to sorb three times the concentration of As(V) per surface area. This result suggests that environmental Fe(III) biominerals have greater reactivity per external surface area for As(V) than synthetic 2-line ferrihydrite. However, external surface area-normalized As sorption data was accurately

modeled with a single fit for As(III) sorption to synthetic 2-line ferrihydrite and environmental Fe(III) biomineral, indicating similar As(III) reactivity per m^2 for all Fe(III) minerals. DGC-produced biomineral sorbed the lowest concentration of As(V). This result was expected as the mineral is predominately of higher crystallinity and subsequently, has less affinity and fewer surface complexation sites for As. Differences in Fe(III) mineral reactivity between As oxidation states were also observed. As(III) has a 60% higher sorbed As concentration per external surface area to environmental Fe(III) biominerals compared to As(V). As(III) has been shown to sorb to a higher extent to Fe(III) (oxyhydr)oxide minerals than As(V) in batch experiments at pH 7 (Goldberg & Johnston, 2001), potentially explaining the observed difference in reactivity.

As K-edge EXAFS revealed that both As species were determined to sorb through inner sphere complexation to environmental Fe(III) biomineral. The binding environment of environmental and synthetic minerals was not quantitatively different for our samples. However, it is speculated that more corner sharing sites are available (due likely to smaller mineral domain size) on the environmental Fe(III) biomineral compared to synthetic 2-line ferrihydrite, resulting in sorption data differences between environmental and synthetic samples. Both species were found to sorb As through complexation reactions similar to synthetic 2-line ferrihydrite.

Overall, our research suggests that environmental Fe(III) biomineral effectively sequesters As and may be treated to, at least, have the same reactivity for As as synthetic 2-line ferrihydrite in aqueous environments at circumneutral pH. As sorption mechanisms to environmental Fe(III) biomineral were also found to be analogous to the complexation mechanisms observed for synthetic 2-line ferrihydrite; therefore, environmental Fe(III)

biomineral is expected to be of equal or greater effectiveness when immobilizing As. From this conclusion, the presence of environmental Fe(III) biomineral is not expected to interfere with current As filtration systems and management practices utilizing synthetic 2-line ferrihydrite. Rather, environmental Fe(III) may potentially be utilized to improve As filtration technologies and remediation practices; however, further research needs to be conducted to test the As reactivity of environmental Fe(III) biominerals in specific systems. Also, variability in external surface area of environmental Fe(III) biomineral is expected to have substantial impacts on the potential for As sequestration in environmental systems. Observed variability in external surface area is suspected to be affected by the variety of environmental conditions from which environmental Fe(III) biominerals form (Jambor & Dutrizac, 1998; Toner et al., 2012). Based on results observed for As(V) and As(III), it is recommended that future work involving the reactivity of environmental Fe(III) biominerals be modeled using external surface area as a normalization parameter. As noted earlier, we speculate that As(V) sorption to environmental biominerals was higher due to environmental samples potentially having more corner sharing sites and smaller domain size compared to synthetic 2-line ferrihydrite. However, future work needs to be performed to fully explore this phenomena.

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Fe(III) Standards Tested
2-line Ferrihydrite
Lepidocrocite
Hematite
Goethite
Magnetite
Fe(III)PO ₄
FeS ₂
Scorodite
Fe(III)-rhizoferrin (carboxylate complex)
Fe(III)-protochelin (catecholate complex)

Table 1. All Fe standards that were considered when performing XANES and EXAFS LCF. Those standards in bold were used in final fits.

Sorbate	Sample	Surface Area (m ² g ⁻¹)	Fe Content (%)	C Content (%)
As(V)	Synthetic	210	50.0	---
	Env_6/19/15	132	36.1	8.2
	Env_8/22/15	83	19.7	10.4
	Env_1/8/16	156	35.3	9.7
As(III)	Synthetic	210	50.0	---
	Env_9/11/15	86	28.7	11.1
	Env_1/8/16	159	35.3	8.7
	Env_2/12/16	163	33.9	9.5

Table 2. Characterization factors for synthetic 2-line ferrihydrite and environmental Fe(III) biomineral. All reported values have an error estimated at approximately 10%.

XANES LCFs			
Sample	Standard	%	R-factor
DGC	Fe(III) Phosphate	10 ± 1	0.00023
	Synthetic Ferrihydrite	28 ± 1	
	Lepidocrocite	39 ± 2	
	Hematite	22 ± 2	
EnvFe_As(V)	Fe(III)-rhizoferrin	26 ± 1	0.00025
	Synthetic Ferrihydrite	22 ± 1	
	Lepidocrocite	52 ± 1	
EnvFe_As(III)	Synthetic Ferrihydrite	100 ± 2	0.00042

Table 3. Percent mineral compositions for biomineral samples using X-ray absorption near edge structure (XANES) spectroscopy data collected at the Stanford Synchrotron Radiation Lightsource. Linear combination fitting was performed in SIXPACK.

EXAFS LCFs			
Sample	Standard	%	R-factor
DGC	Fe(III) Phosphate	18 ± 1	0.01547
	Synthetic Ferrihydrite	27 ± 3	
	Lepidocrocite	55 ± 1	
EnvFe_As(V)	Fe_Rhiz	12 ± 3	0.027771
	Synthetic Ferrihydrite	74 ± 7	
	Lepidocrocite	14 ± 3	
EnvFe_As(III)	Synthetic Ferrihydrite	100 ± 3	0.054730

Table 4. Percent mineral compositions for biomineral samples using extended X-ray absorption fine structure (EXAFS) spectroscopy data taken at the Stanford Synchrotron Radiation Lightsource. Linear combination fitting was performed in SIXPACK.

Data Type	Data Set	K_f	n	E
Raw As(V)	Synthetic	12970 +/- 1308	0.17 +/- 0.028	0.919
	Env_6/19/15	19370 +/- 1013	0.21 +/- 0.020	0.984
	Env_8/22/15	14450 +/- 700.3	0.17 +/- 0.011	0.992
	Env_1/8/16	24430 +/- 1367	0.18 +/- 0.023	0.974
	DGC	3090 +/- 527	0.51 +/- 0.087	0.805
SA Norm. As(V)	Synthetic	0.06 +/- 0.014	0.18 +/- 0.023	0.915
	Env_6/19/15	0.15 +/- 0.021	0.21 +/- 0.024	0.984
	Env_8/22/15	0.18 +/- 0.010	0.16 +/- 0.010	0.992
	Env_1/8/16	0.18 +/- 0.024	0.15 +/- 0.013	0.983
	Combined Env.	0.16 +/- 0.021	0.19 +/- 0.028	0.979
Raw As(III)	Synthetic	30390 +/- 1629	0.33 +/- 0.017	0.944
	Env_9/11/15	14600 +/- 886	0.31 +/- 0.032	0.933
	Env_1/8/16	27360 +/- 1412	0.36 +/- 0.023	0.976
	Env_2/1/16	27960 +/- 1487	0.32 +/- 0.024	0.962
SA Norm. As(III)	Synthetic	0.14 +/- 0.018	0.33 +/- 0.040	0.954
	Env_9/11/15	0.18 +/- 0.016	0.31 +/- 0.034	0.933
	Env_1/8/16	0.18 +/- 0.010	0.36 +/- 0.027	0.976
	Env_2/1/16	0.14 +/- 0.028	0.40 +/- 0.037	0.976
	All Combined	0.17 +/- 0.023	0.31 +/- 0.041	0.972

Table 5. Freundlich parameters used to model As(V) and As(III) sorption to synthetic 2-line ferrihydrite and environmental Fe(III) biomineral samples. Raw data sets are representative of As mass sorbed per mass of sorbent and SA data sets are those normalized to external surface area. K_f = sorption constant; n = exponential constant; E = model efficiency.

Sample	Atom	N	R (Å)	σ^2	E_0	f	R Factor
As(V)_Syn. Ferrihydrite	O	2.0 +/- 0.4	1.68 +/- 0.01	0.0003 +/- 0.002	7 +/- 3	---	0.0545
	Fe	2*	3.23 +/- 0.06	0.018 +/- 0.007			
As(V)_DGC Mineral	O	1.8 +/- 0.2	1.67 +/- 0.01	0.000 +/- .001	2 +/- 2	---	0.0253
	Fe	2*	3.32 +/- 0.04	0.020 +/- 0.005			
Low As(V)_Env. Fe(III)	O	1.7 +/- 0.3	1.68 +/- 0.01	0.0007 +/- 0.001	8 +/- 3	---	0.0408
	Fe	2*	3.32 +/- 0.06	0.023 +/- 0.008			
High As(V)_Env. Fe(III)	O	1.7 +/- 0.3	1.68 +/- 0.01	0.0008 +/- 0.001	7 +/- 2	---	0.0390
	Fe	2*	3.31 +/- 0.05	0.020 +/- 0.006			
As(III)_Syn. Ferrihydrite	O	1.7 +/- 0.2	1.76 +/- 0.01	0.004 +/- 0.001	8 +/- 2	0.7 +/- 0.2	0.0361
	Fe	1*	2.89 +/- 0.04	0.015 +/- 0.003			
	Fe	2*	3.33 +/- 0.05	0.015 +/- 0.003			
Low As(III)_Env. Fe(III)	O	1.6 +/- 0.3	1.79 +/- 0.01	0.002 +/- 0.002	9 +/- 3	0.6 +/- 0.3	0.0878
	Fe	1*	2.97 +/- 0.06	0.012 +/- 0.004			
	Fe	2*	3.35 +/- 0.06	0.012 +/- 0.004			
High As(III)_Env. Fe(III)	O	1.5 +/- 0.2	1.79 +/- 0.01	0.002 +/- 0.001	10 +/- 2	0.7 +/- 0.3	0.0579
	Fe	1*	2.95 +/- 0.05	0.015 +/- 0.002			
	Fe	2*	3.35 +/- 0.07	0.015 +/- 0.002			

Table 6. Parameters of the EXAFS equation used to model As EXAFS data. *Fixed parameter. N = number of backscattering atoms; R = bond length; σ^2 = disorder factor; E_0 = binding energy; f = complexation fraction factor.

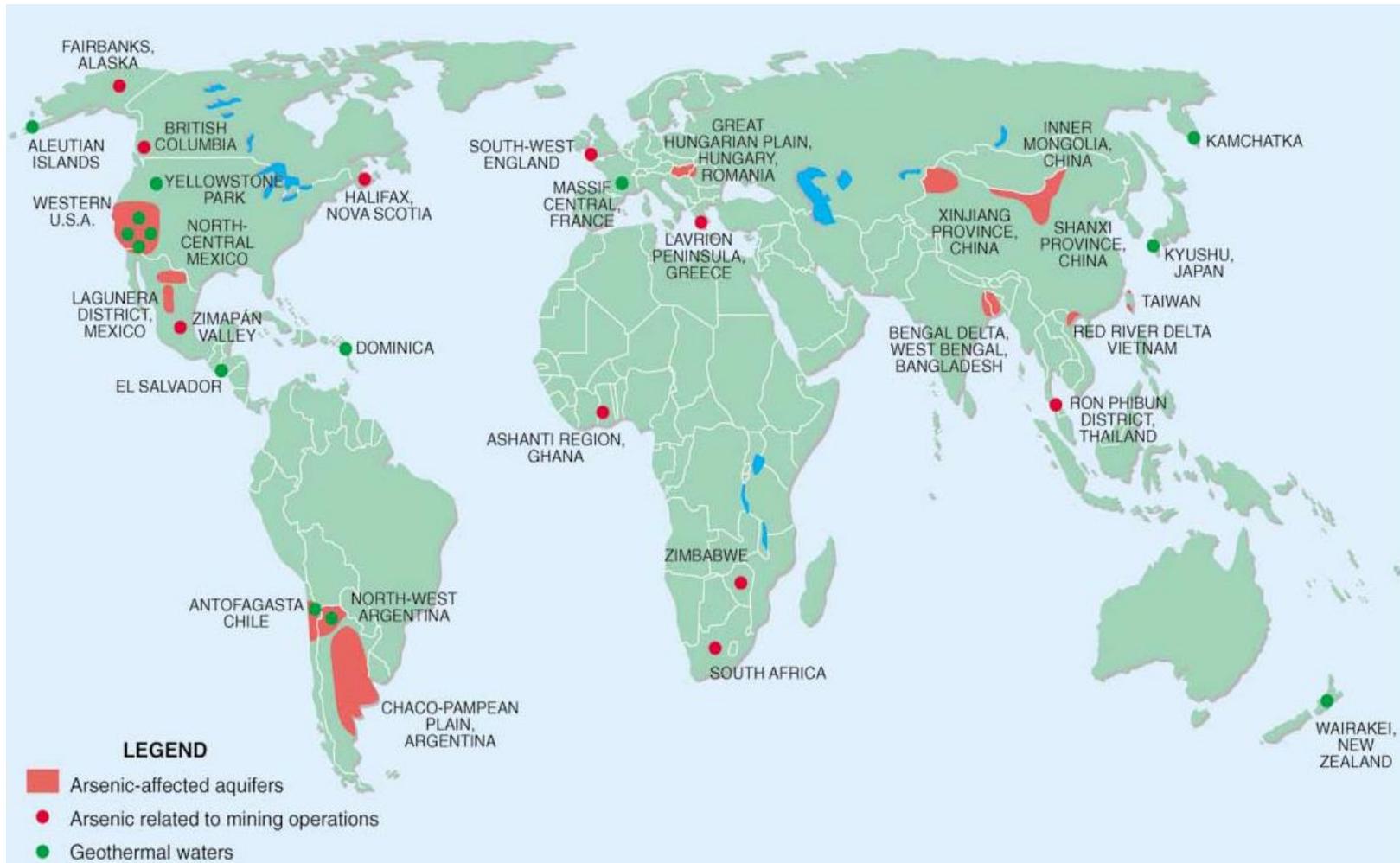


Figure 1. Map showing sites of anthropogenic and natural arsenic contamination on a global scale. Figure is taken from Smedley & Kinniburgh, 2013.

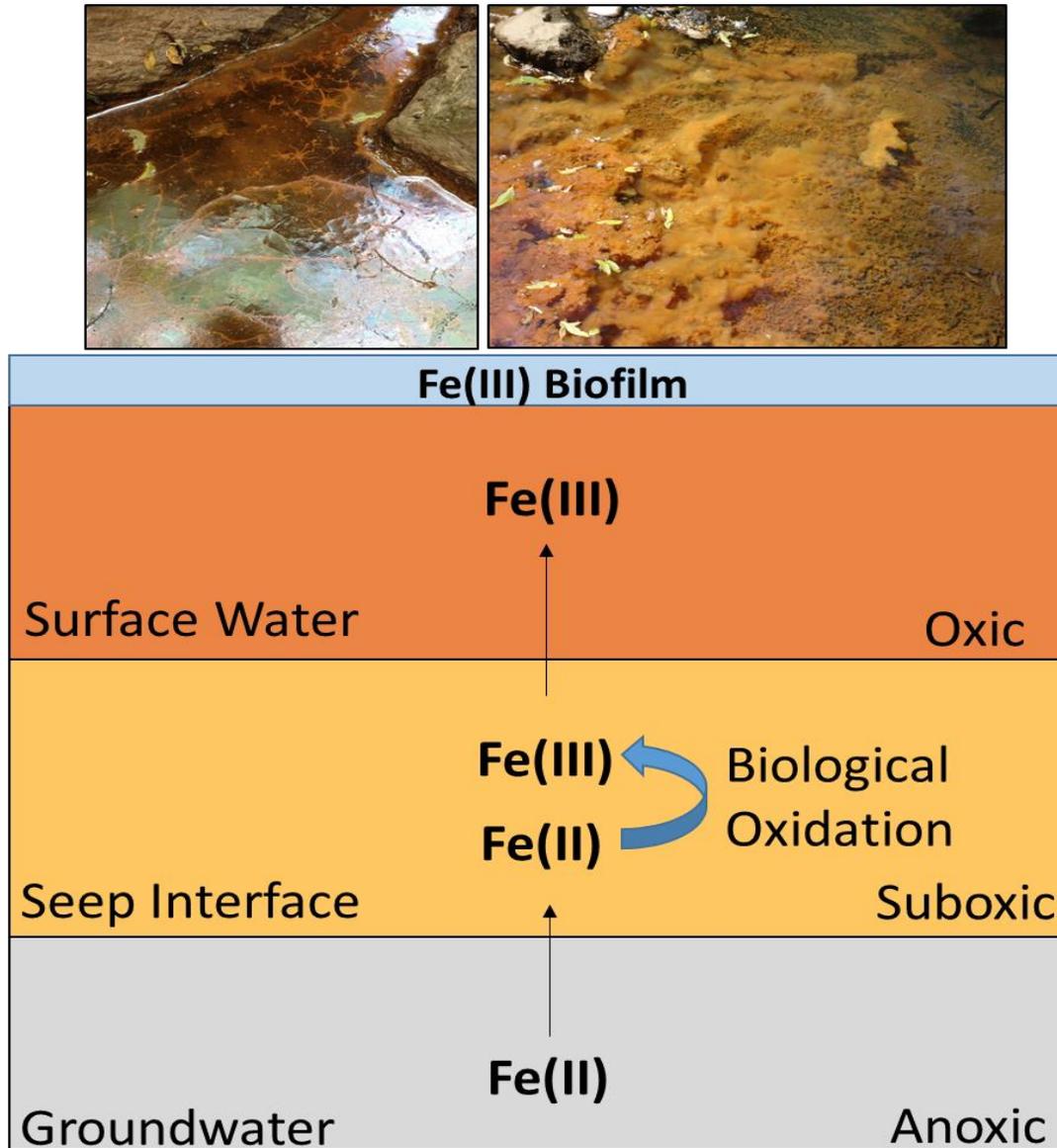


Figure 2. Schematic depicting environmental redox gradients that promote Fe(III) biomineral production.



Figure 3. Pictures showing the location of sampling sites of environmental Fe(III) biominerals.

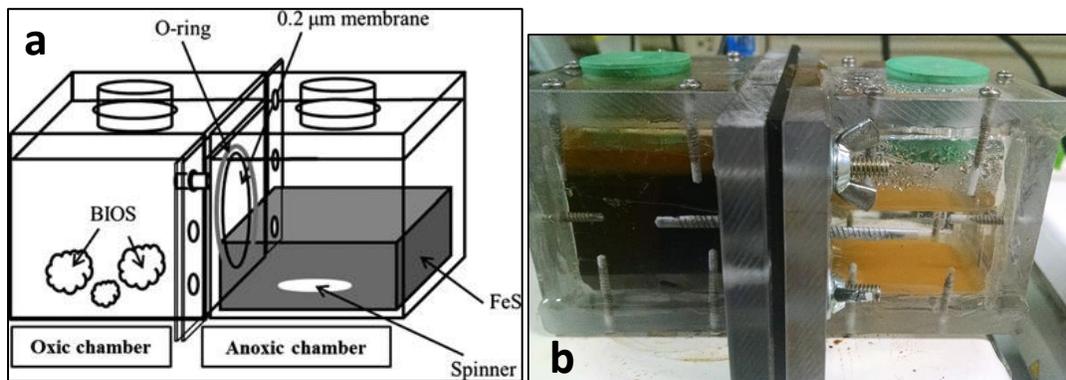


Figure 4. (a) A schematic of a diffusion gradient chamber used to generate biogenic Fe(III) oxide minerals in the laboratory (Kikuchi et al., 2014). **(b)** Diffusion gradient chambers after 7 to 9 days after inoculation.

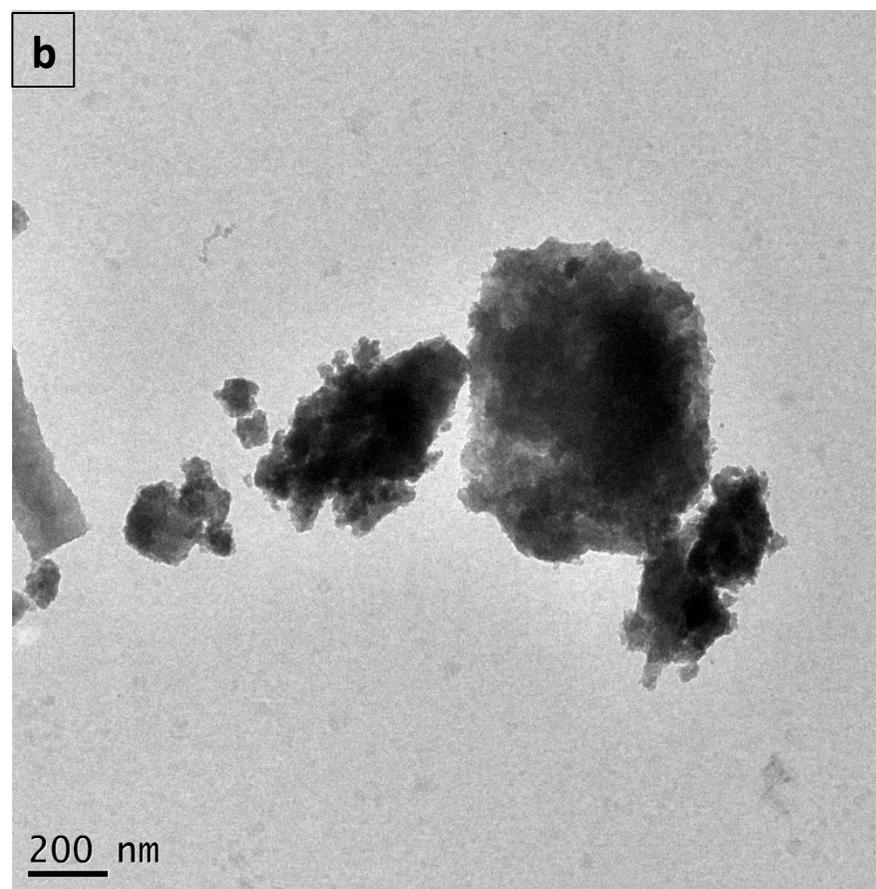
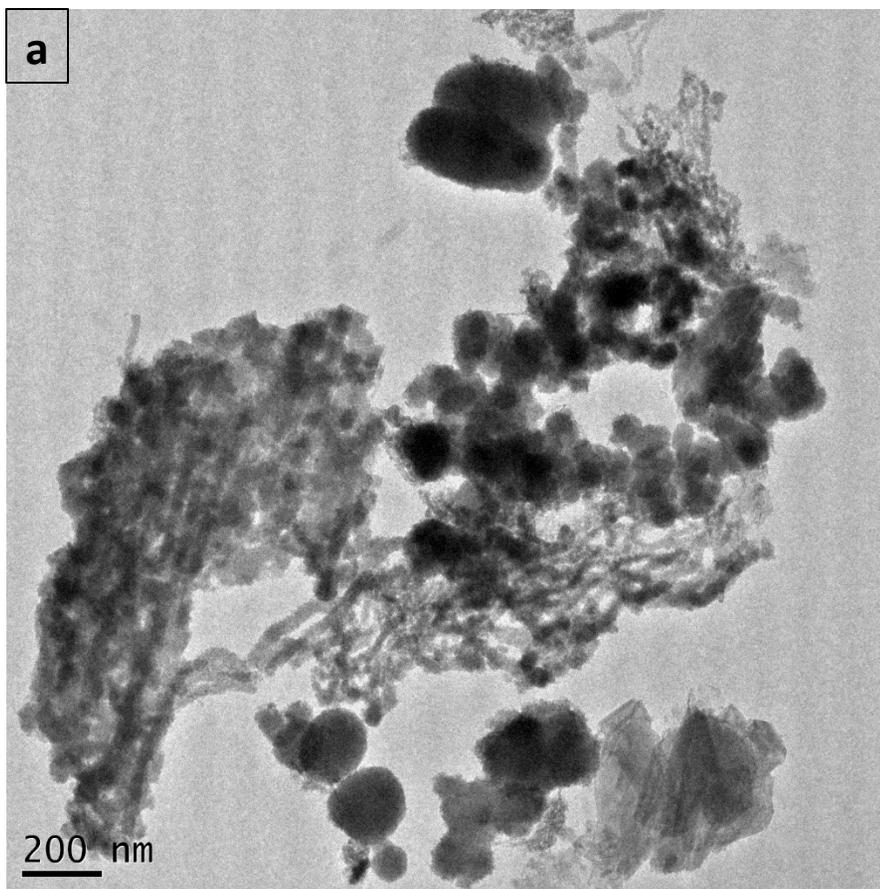


Figure. 5 TEM images of environmental Fe(III) biomineral (a) and synthetic 2-line ferrihydrite (b) samples. The environmental Fe(III) biomineral has a different morphology than synthetic 2-line ferrihydrite that is diagnostic of iron-oxidizing bacteria.

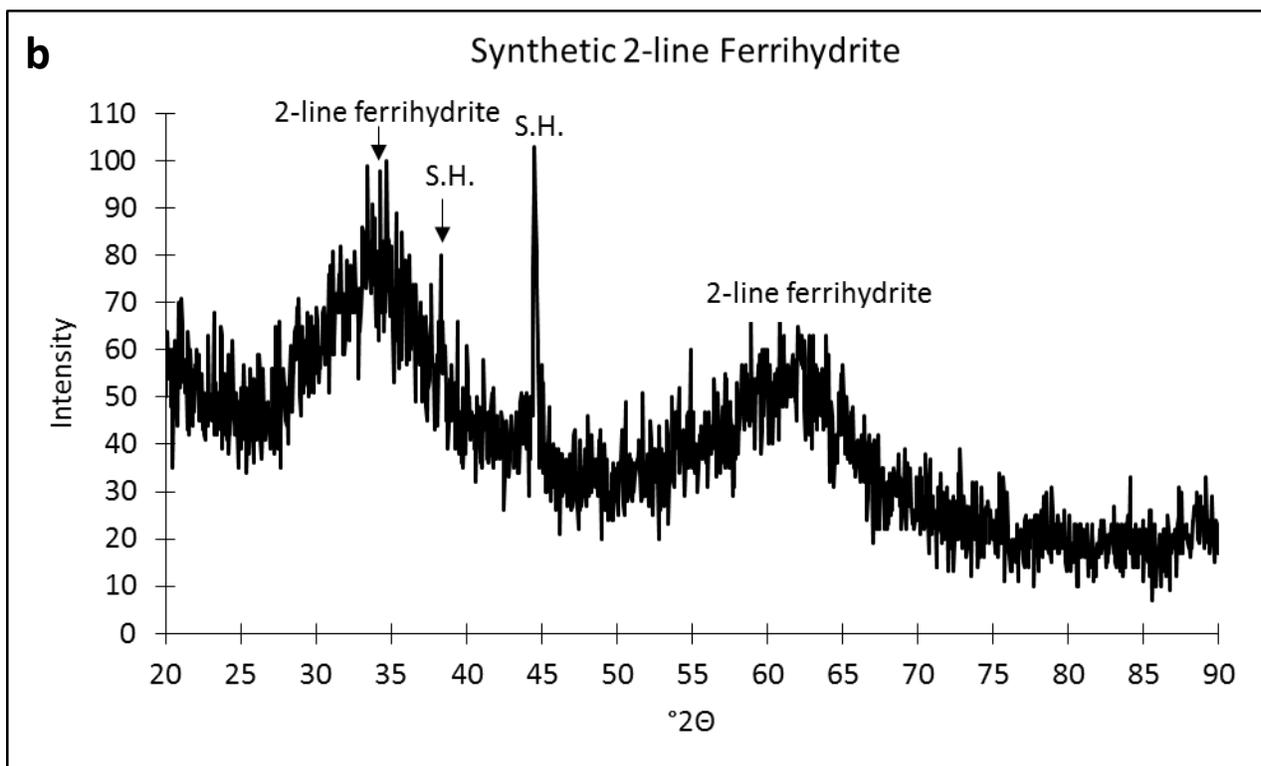
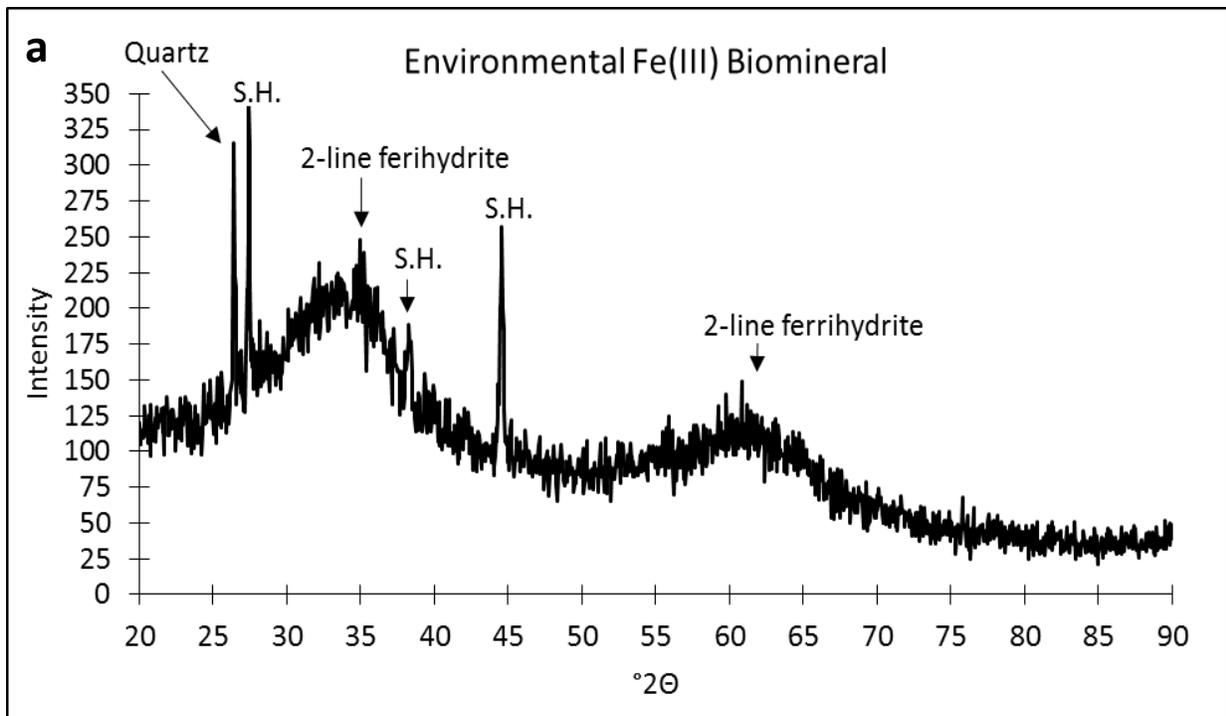


Figure 6a, b. XRD data for environmental Fe(III) biomineral (a) and synthetic 2-line ferrihydrite samples (b). Both were found to consist of predominately 2-line ferrihydrite. S.H. indicated peak arising from the the sample holder.

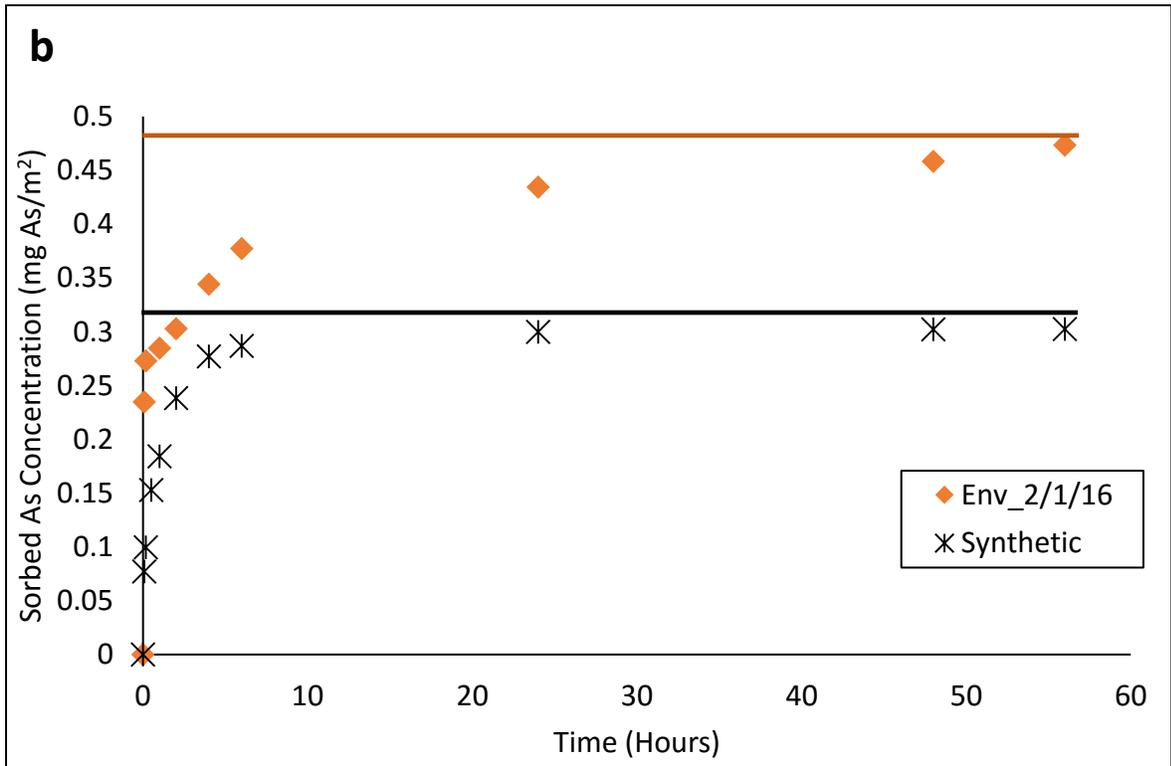
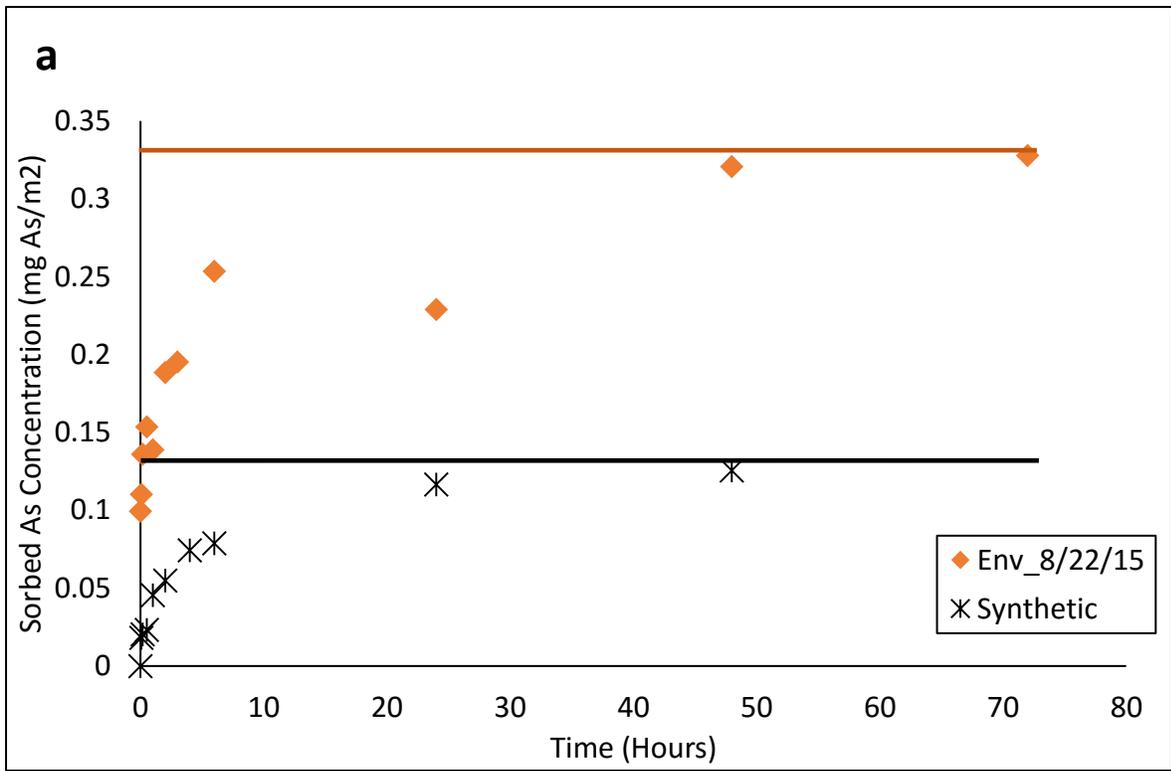


Figure 7a,b. Rate of (a) As(V) sorption and (b) As(III) sorption to synthetic 2-line ferrihydrite and environmental Fe(III) biomineral. Solid lines are added to aid the eye and do not represent a model fit.

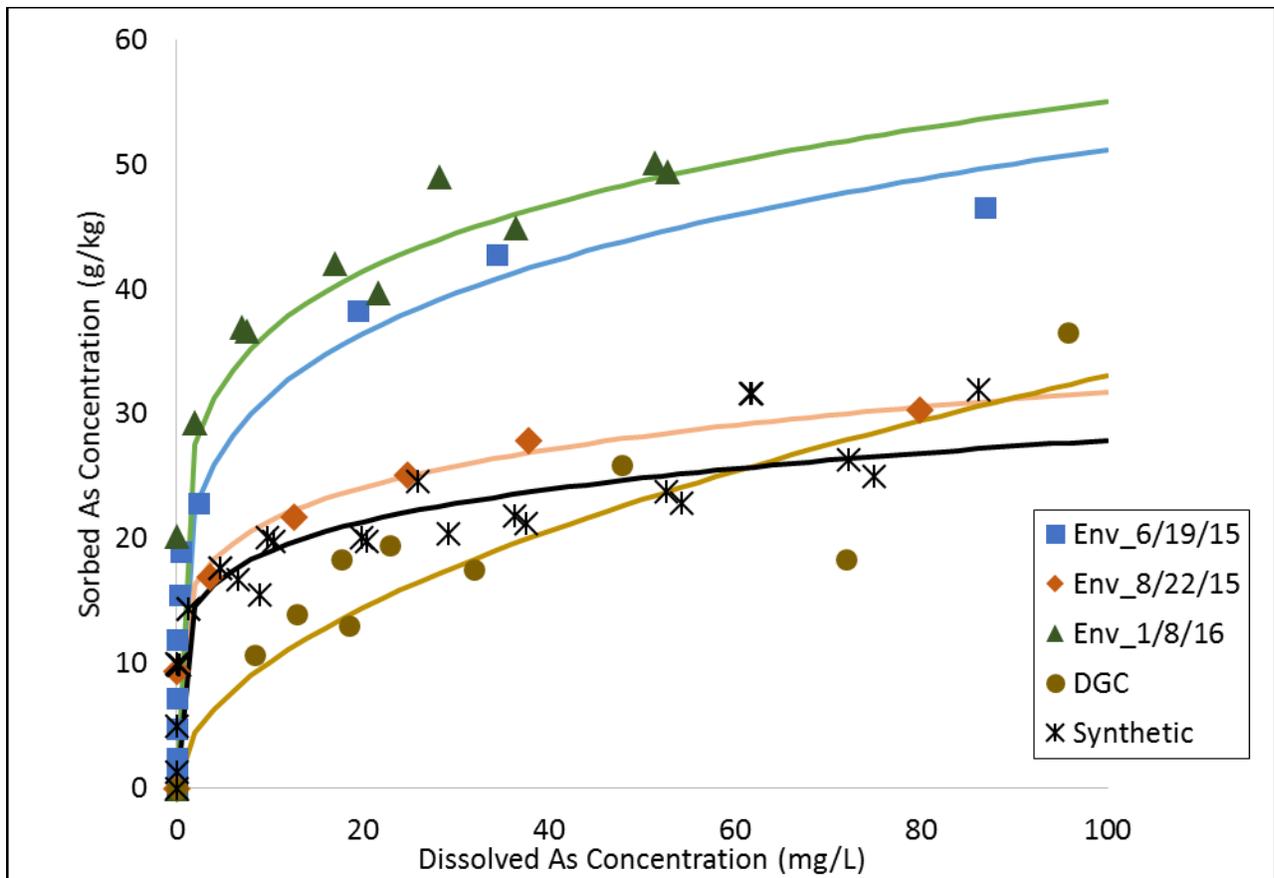


Figure 8a. As(V) sorption to environmental Fe(III) biominerals, diffusion gradient chamber (DGC) synthesized minerals, and synthetic 2-line ferrihydrite. All data was modeled using a Freundlich sorption isotherm model, with fit parameters shown in Table 5.

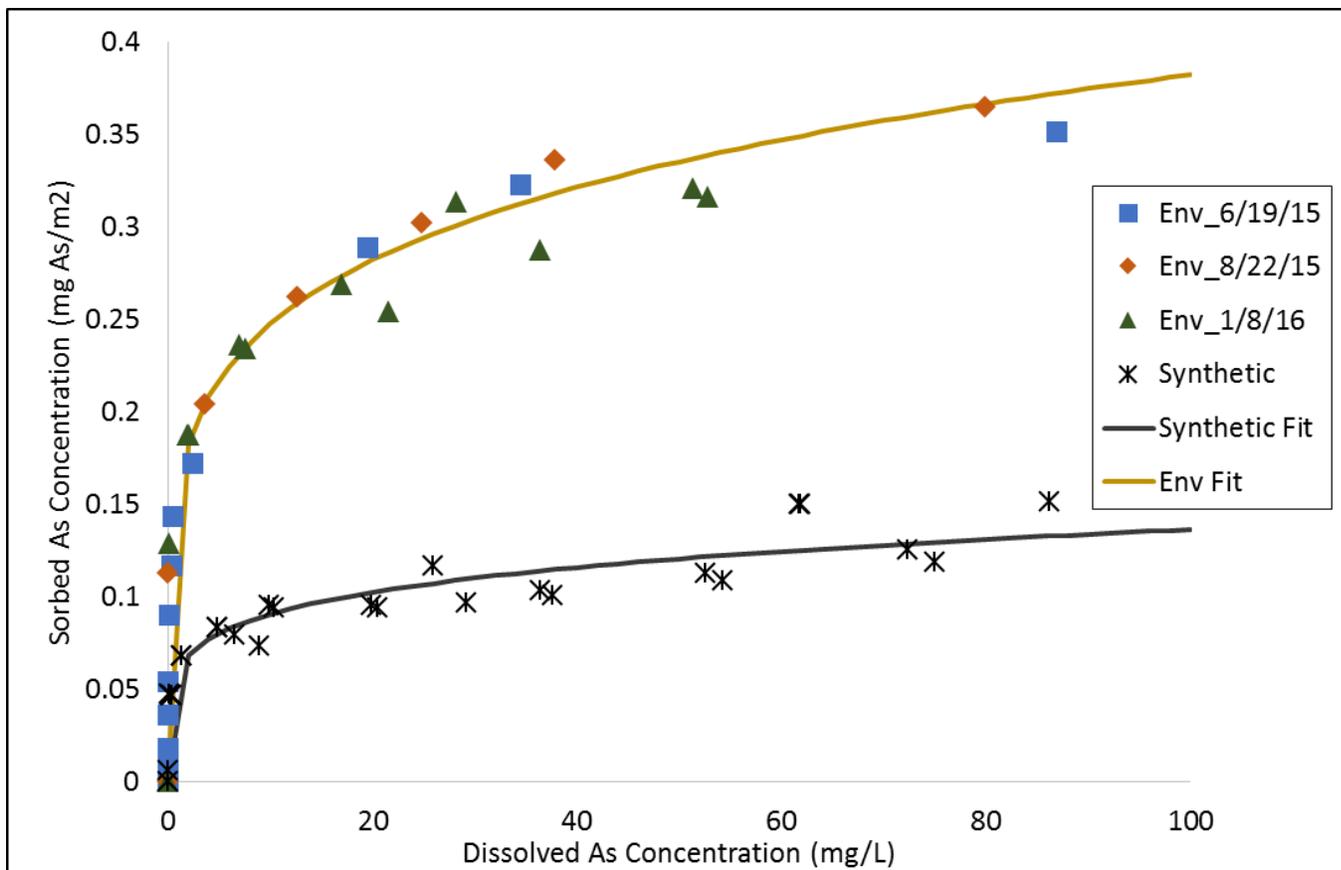


Figure 8b. As(V) sorption to environmental Fe(III) biominerals and synthetic 2-line ferrihydrite normalized to surface area. Data was modeled using a Freundlich sorption isotherm model, with fit parameters shown in Table 5.

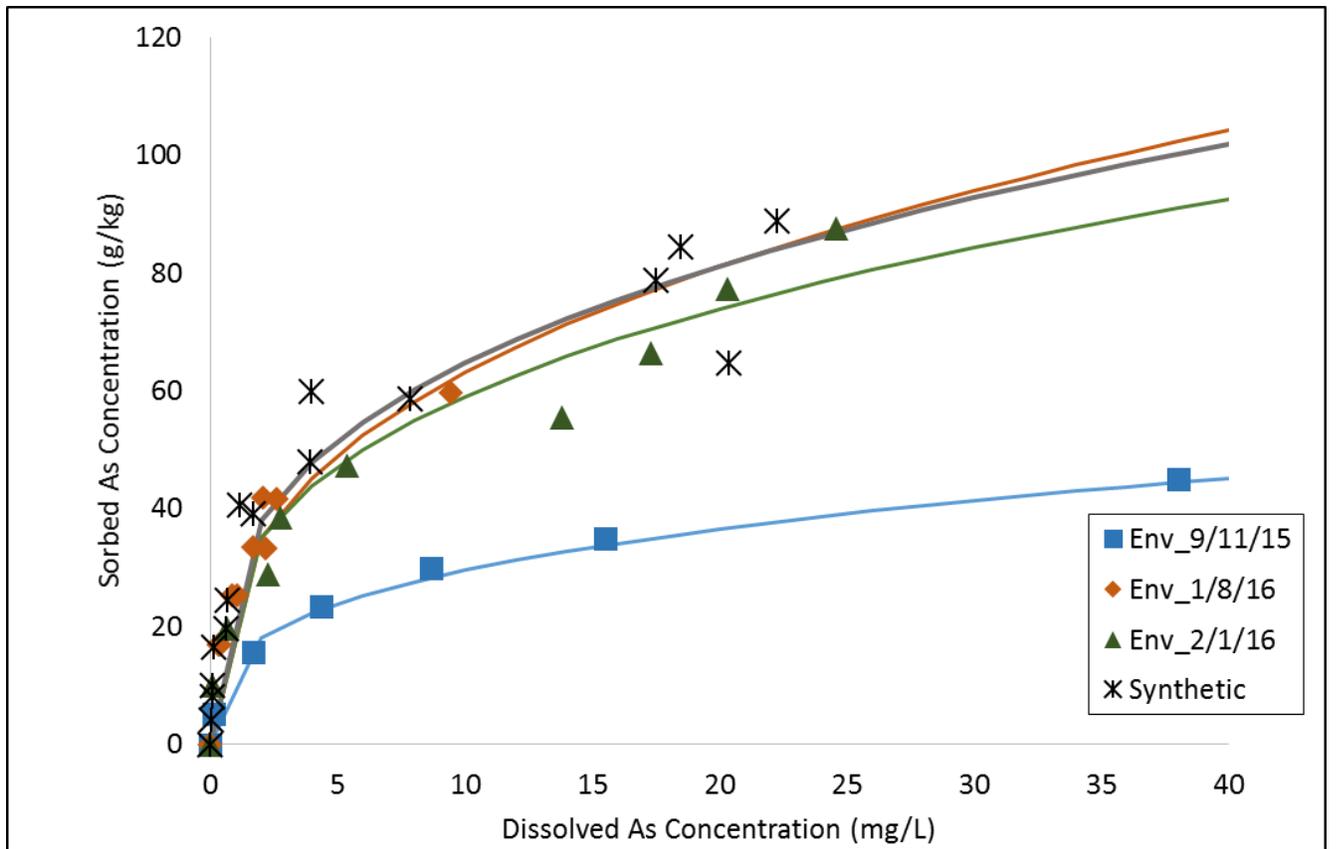


Figure 9a. As(III) sorption to environmental Fe(III) biominerals and synthetic 2-line ferrihydrite. All data was modeled using a Freundlich sorption isotherm model, with fit parameters shown in Table 5.

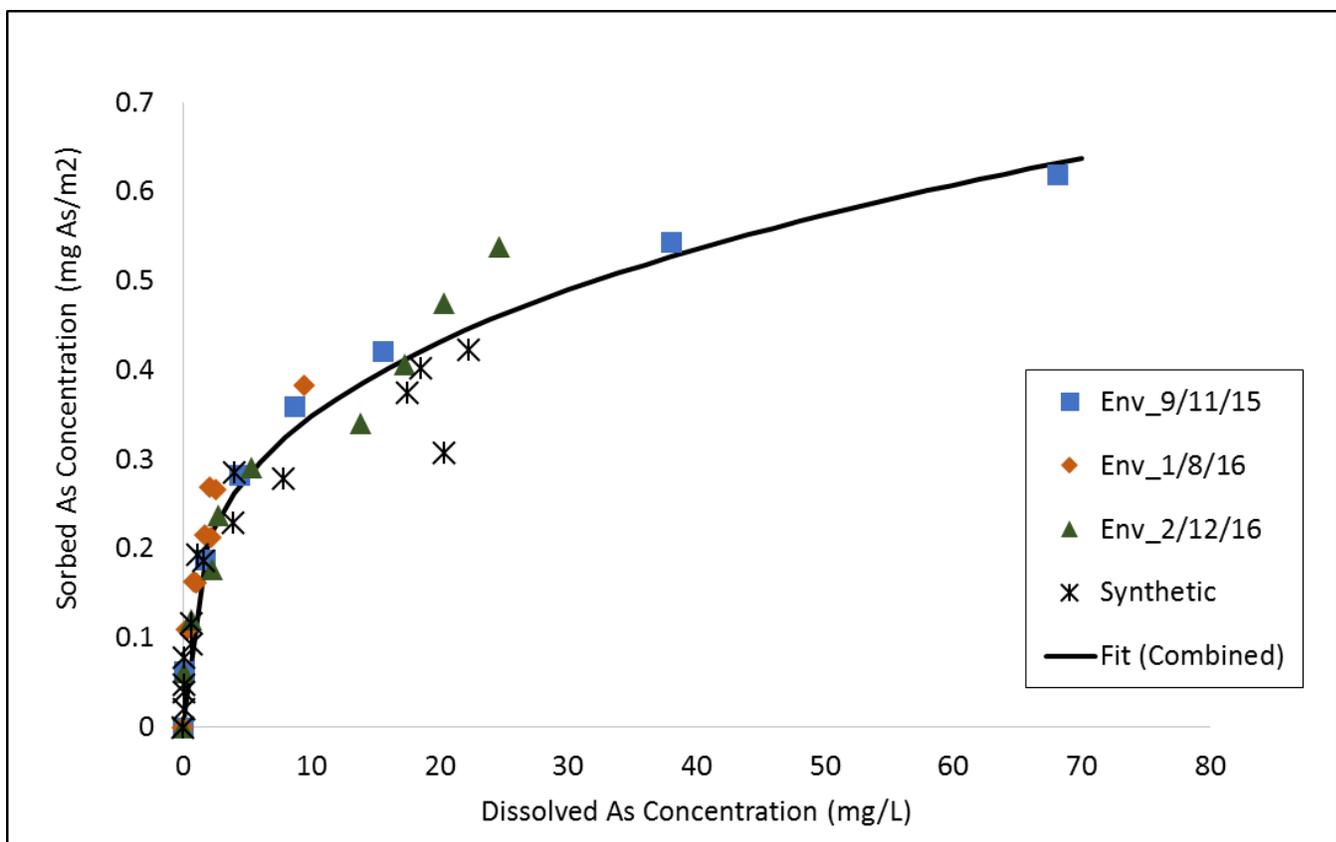


Figure 9b. As(III) sorption to environmental Fe(III) biominerals and synthetic 2-line ferrihydrite normalized to surface area. Data was modeled using a Freundlich sorption isotherm model, with fit parameters shown in Table 5. One fit was used to model the data for all minerals.

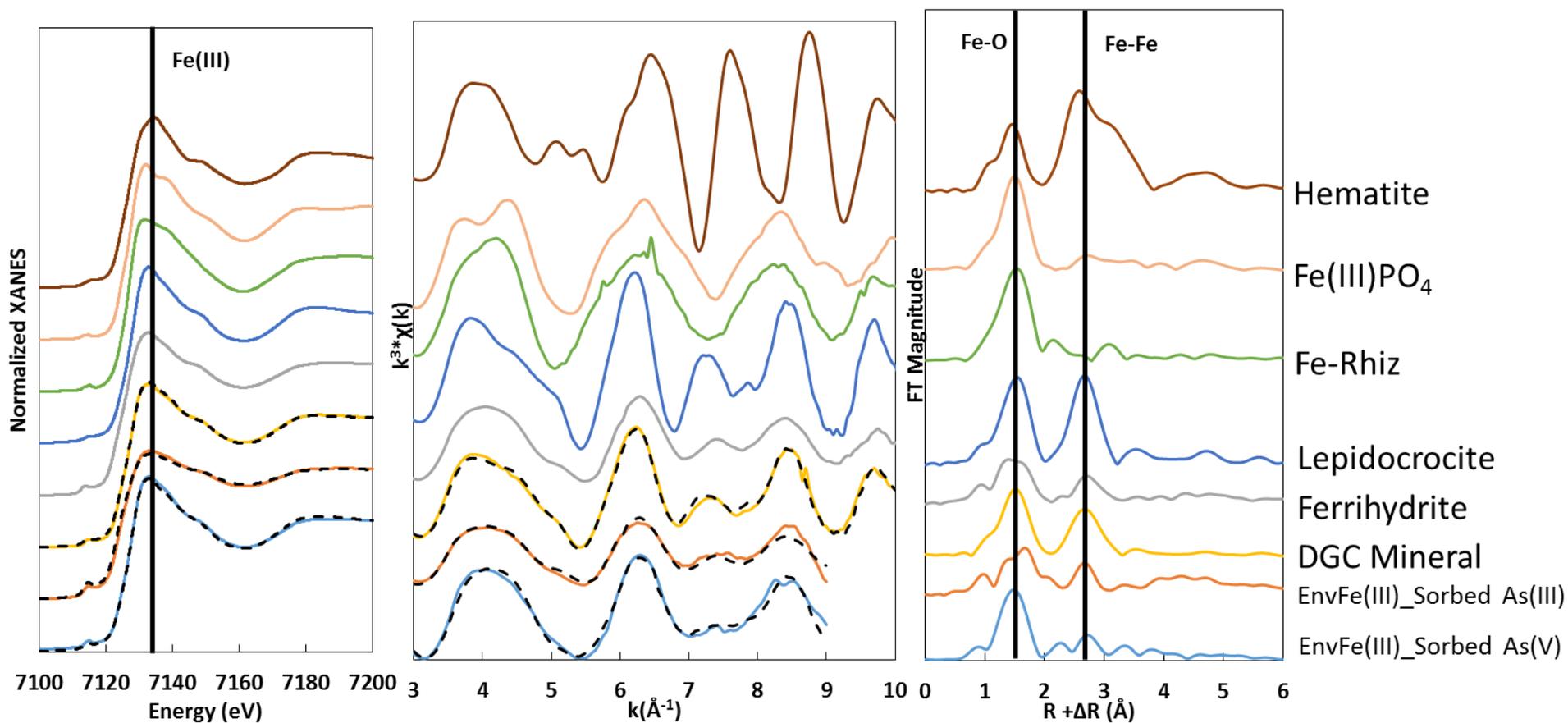


Figure 10. Fe XANES spectra, EXAFS spectra, and FT magnitude plots for Fe(III) mineral standards and samples. Linear combination fitting was performed for each sample of the three differing formation settings and is represented with an overlaid, dashed line, with fit parameters shown in table 6.

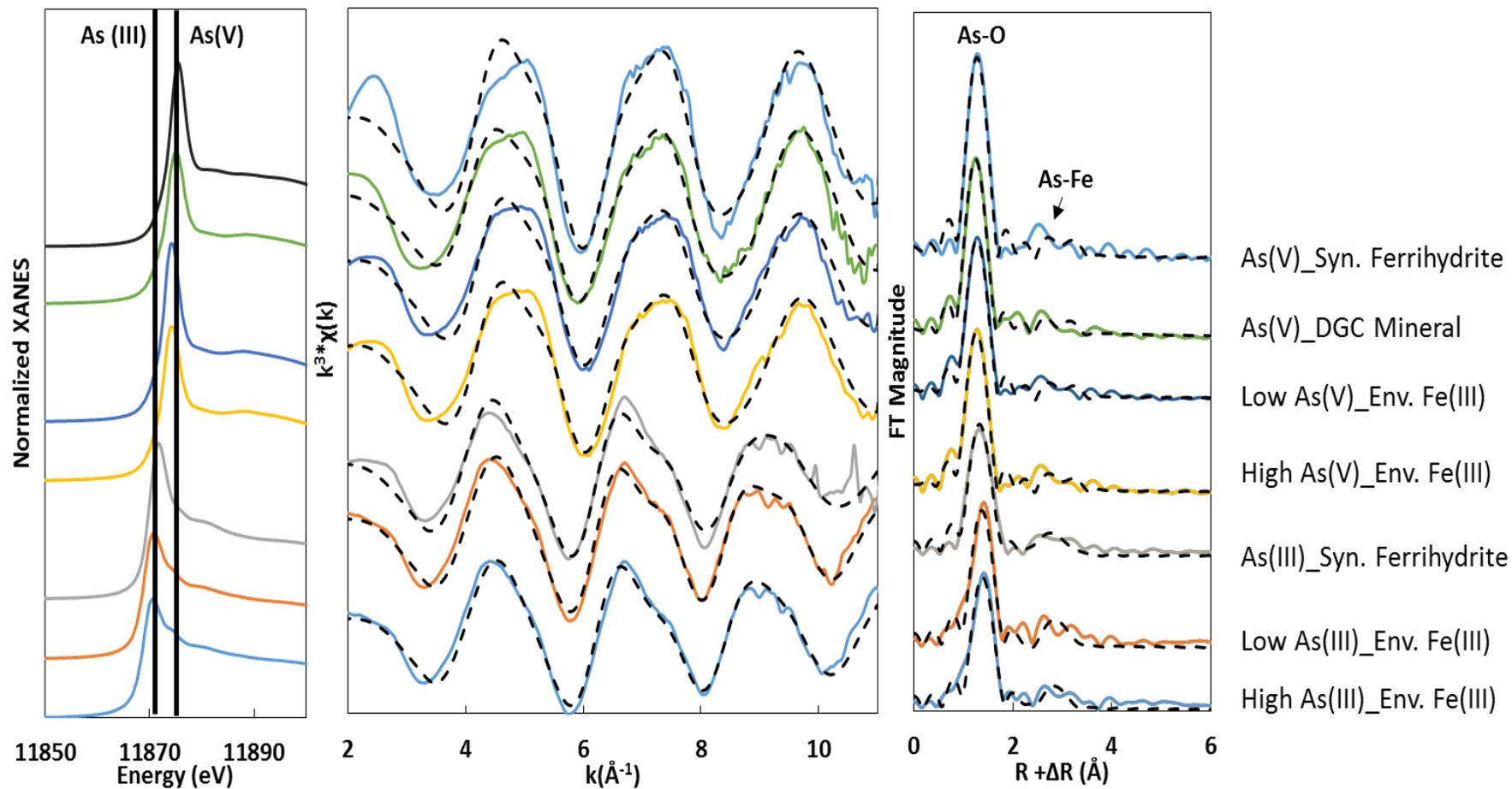


Figure 11. Arsenic XANES, K-spacing, and R-spacing for Fe(III) (oxyhydr)oxide mineral standards and those used in sorption isotherm experiments, with fit parameters shown in table 6.

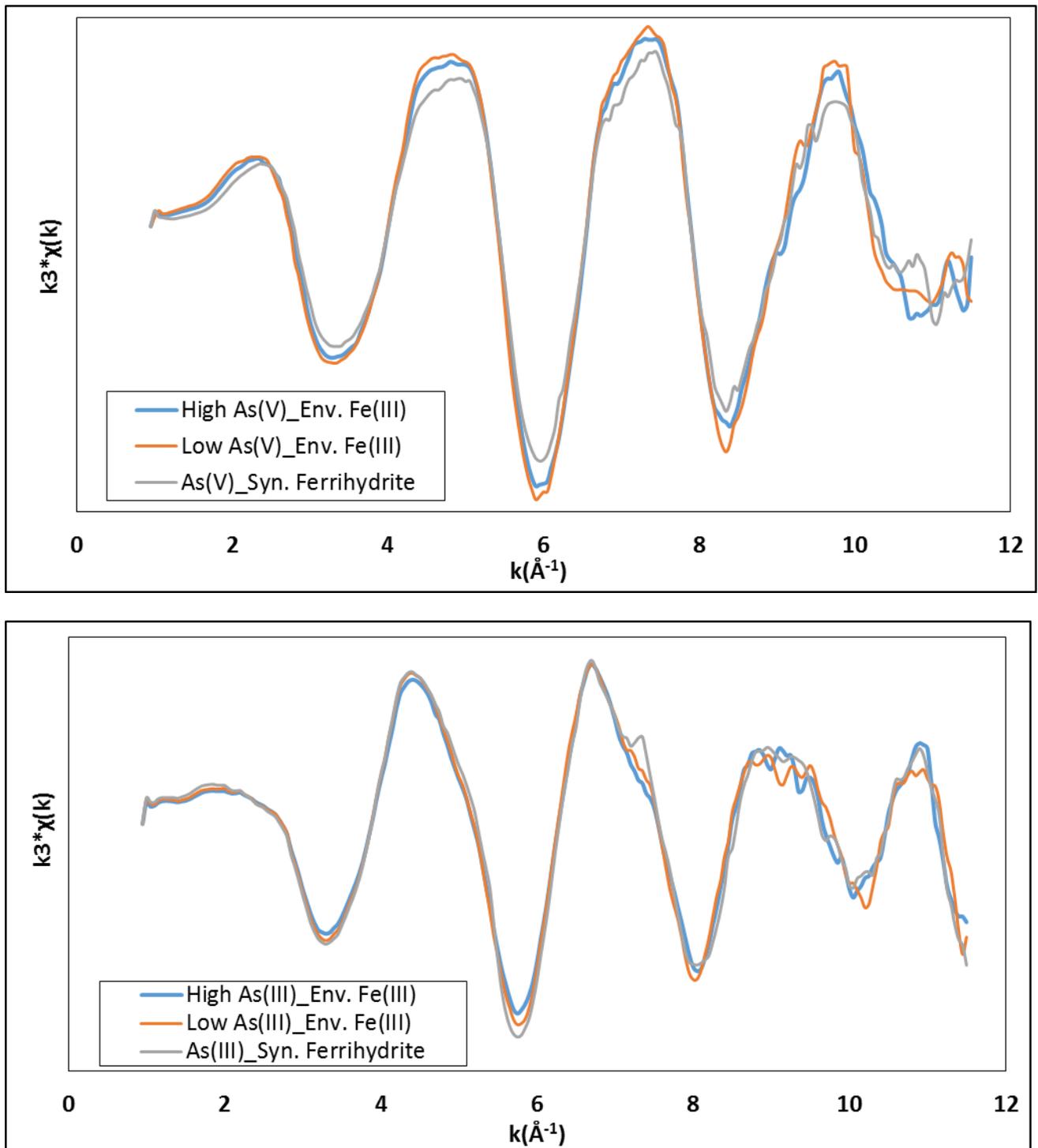


Figure 12. Overlaid As K-edge EXAFS data for (a) As(V) and (b) As(III) emphasizing the spectral similarity for each dataset.

Chapter 3: Research Outcomes and Areas of Improvement and Future Investigation

3.1 Major findings

The extent and mechanism of arsenic (As) sorption to environmental Fe(III) biominerals at circumneutral pH was determined and then compared to synthetic and biogenic laboratory analogues. The rate of As sorption to all Fe(III) (oxyhydr)oxide minerals was found to be similar; however, the extent of As sorption varied with As species and sorbent. The major finding of the presented research is as follows: **As(V) was found to sorb to an equal or greater extent (on a per sorbent surface area basis) onto environmental Fe(III) biominerals compared to synthetic 2-line ferrihydrite, whereas As(III) sorbed to a mostly equal extent.** From this, it can be concluded that environmental Fe(III) biomineral has a high As sorption potential for both environmentally common As species that can exceed the reactivity of synthetic 2-line ferrihydrite. When comparing As oxidation states, As(III) was observed to have approximately a 60% higher sorbed As concentration to environmental Fe(III) biominerals compared to As(V). As(III) has been shown to sorb to a greater extent to Fe(III) (oxyhydr)oxide minerals than As(V) in batch experiments at pH 7 (Goldberg & Johnston, 2001), potentially explaining the observed difference in reactivity.

Laboratory synthesized Fe(III) biominerals (DGC-produced) were found to sorb less As(V) than all environmental Fe(III) biominerals tested; therefore, our data suggests that laboratory-produced biominerals may not accurately represent As(V) sorption to Fe(III) biominerals formed in the environment. Further research needs to be conducted to prove this conclusion because of limited As sorption data for laboratory synthesized Fe(III) biominerals. Differences in As

loading to environmental Fe(III) biomineral on sorbent mass basis corresponded to differences in sampling date. It was suspected that these differences are attributable to heterogeneous biomineral characteristics as a result of flux environmental conditions, resulting in an investigation of suitable normalization parameters that may accurately account for observed differences in As sorption to environmental Fe(III) biomineral.

Interestingly, these differences in sorbent reactivity for environmental samples were effectively described by differences in surface area. External surface area most effectively normalized As(III) sorption isotherm data, where it was observed that both environmental Fe(III) biomineral and synthetic 2-line ferrihydrite sorbed As(III) to a similar extent. However, this trend was not observed for external surface area normalized As(V) sorption isotherm data. External surface area normalized As(V) sorption isotherm data revealed that As(V) sorbs to a concentration per surface area for environmental Fe(III) biominerals that is approximately three times greater than what is sorbed to synthetic 2-line ferrihydrite. Overall, our data suggest that As(III) sorption extent to environmental Fe(III) biominerals per surface area can be accurately modeled by synthetic 2-line ferrihydrite whereas the reactivity of environmental Fe(III) biominerals to As(V) is significantly higher per surface area compared to synthetic 2-line ferrihydrite.

Fe EXAFS supported observed differences in surface area. EXAFS LCF suggests that environmental Fe(III) biomineral is predominately 2-line ferrihydrite with varying degrees of crystalline phases. Sample EnvFe(III)_Sorbed As(V) consisting of more crystalline phases and sample EnvFe(III)_Sorbed As(III) consisting of poorer crystallinity/amorphous phases. These results explain why differences in measured external surface area among environmental Fe(III)

biomineral were observed, as EnvFe(III)_Sorbed As(V) was found to have lower external surface area and consists of more crystalline Fe(III) mineral phases. In addition to 2-line ferrihydrite and minor crystalline phases (such as lepidocrocite), EXAFS LCF analysis suggests environmental Fe(III) biominerals also contain an Fe-organic complex fraction, potentially signifying a reason for observed differences in reactivity compared to synthetic 2-line ferrihydrite.

As EXAFS shell-by-shell fitting analysis was performed for As(V) and As(III) loaded environmental Fe(III) biomineral and synthetic 2-line ferrihydrite to determine As sorption mechanism. Current analysis of As EXAFS for As-loaded environmental Fe(III) biomineral reveals that inner sphere complexation is suggested to be the predominate mechanism of sorption for both As(V) and As(III). We speculate that more corner sharing sites are present on environmental Fe(III) biominerals, which would explain the increased reactivity of the environmental samples for As(V) compared to synthetic. However, the complexation processes of As sorption to environmental Fe(III) biomineral is congruent with reported As sorption mechanisms to synthetic 2-line ferrihydrite (Gao, Root, Farrell, Ela, & Chorover, 2013). Overall, the determination of inner sphere complexation as the predominate As(V) and As(III) sorption complexation mechanism indicates that both As species should be effectively sequestered by environmental Fe(III) biominerals.

3.2 Research Implications

The presented research provides insight into how As interacts with biogenic Fe(III) (oxyhydr)oxide minerals found commonly in aqueous environmental systems. Research elucidating the sequestration of As by Fe(III) (oxyhydr)oxides has been performed extensively

(Cornell & Schwertmann, 2003; Dixit & Hering, 2003; Fendorf, Eick, Grossl, & Sparks, 1997; Mandal & Suzuki, 2002; Manning, Fendorf, & Goldberg, 1998); however, little research exists on the reactivity of environmental Fe(III) biominerals found in circumneutral, aqueous environments. Our results show that environmental Fe(III) biominerals have diverse reactivities for As that were observed to change for those sampled at different dates. However, a majority of the tested environmental biominerals were found to sorb As(V) and As(III) at concentrations that are at least equivalent to the As concentration sorbed by synthetic 2-line ferrihydrite. **From these results, it is expected that environmental Fe(III) biomineral may be treated to, at least, have the same reactivity for As as synthetic 2-line ferrihydrite in aqueous environments at circumneutral pH.** The primary implication of this conclusion is that environmental Fe(III) biominerals may potentially be an effective component in As remediation strategies and will help researchers to model the cycling of As in aqueous systems, ultimately leading to improved water quality. The normalization to external surface area largely accounted for the variation in sorption reactivity of environmental Fe(III) biominerals and may further facilitate future modeling of As loading to environmental Fe(III) biominerals.

Although As(III) sorption to environmental Fe(III) biominerals per surface area was similar to 2-line ferrihydrite, environmental Fe(III) biomineral was observed to have a much higher affinity for As(V) per surface area compared to synthetic 2-line ferrihydrite. This difference has potential implications on future research regarding why As(V) sorbs to a higher extent to environmental Fe(III) biominerals compared to synthetic 2-line ferrihydrite, although we speculate that this trend is due to environmental samples having smaller domain size. Also important to note, As(III) sorbed to a much higher extent to environmental Fe(III) biomineral

than As(V). As(III) is more toxic to biotic life; therefore, environmental Fe(III) biomineral may play a critical role in the safeguarding biotic health in water systems. Sorption mechanism of As to Fe(III) minerals is a major factor affecting the potential benefit to biotic life. It was found that both environmental Fe(III) biominerals and synthetic 2-line ferrihydrite surface complex As through similar mechanisms; therefore, synthetic 2-line ferrihydrite may be an effective analogue when studying the longevity of As immobilization by environmental Fe(III) biominerals. Overall, the presented research provides relevant findings that will improve current understanding of how As is cycled in environmental water systems, which has the potential to catalyze the advancement of As remediation strategies and technologies.

3.3 Thoughts on Improvement and Future Investigation

The research presented in this report makes strides towards addressing knowledge gaps key to understanding environmental As cycling, but there are ways in which the experimental plan I conducted may be improved and areas in need of future investigation. The primary limitation in my research concerns the laboratory-produced biomineral that was synthesized in diffusion gradient chambers (DGC). The DGC system succeeded in producing Fe(III) biominerals; however, the rate and quantity produced were key limiting factors that prevented extensive characterization and sorption experiments from being conducted. The results obtained using the DGC-produced biomineral indicate that the As sorption behavior of laboratory-produced biomineral may not be an accurate representation of environmental Fe(III) biominerals, but replicates are needed to prove this. Also, only one FeOB (Fe(II) oxidizing bacteria) was tested due to the slow biomineral production rate. Variations in morphology are expected among

Fe(III) biominerals produced from different FeOB; therefore, further research determining the effect of FeOB on As reactivity by Fe(III) biominerals is recommended.

Another potential aspect that may have improved my research is the use of stream water as the matrix solution of all my batch experiments. NaCl (0.01M) solution was used as a matrix since it is commonly used for As sorption isotherms presented in the literature (Dixit & Hering, 2003; Raven, Jain, & Loeppert, 1998). The use of NaCl allowed for a more consistent measure of the reactivity of the environmental Fe(III) biominerals at controlled conditions; however, using stream water would provide a more environmentally realistic As sorption concentration for the tested environmental Fe(III) biominerals. Conversely, stream water taken over different times may consist of variable components, resulting in variable ionic strengths and the potential presence of competitive sorptives. Future kinetic and isotherm experiments with environmental Fe(III) biomineral using stream water as a matrix solution would provide useful insights into how As is cycled in an environmental matrix and could be compared to the results obtained in this study.

Based on the results of this report, environmental Fe(III) biomineral may have the potential to be used effectively in As filtration systems. Both As species were found to sorb at aqueous As concentrations that can exceed that of synthetic 2-line ferrihydrite, a commonly used sorbent in As filtration technologies (Katsoyiannis & Zouboulis, 2002; Mohan & Pittman Jr, 2007). This observation indicates that environmental Fe(III) biomineral may be used to improve existing As removal technologies; however, there are many factors that must be accounted for to prove this is true. These factors include testing As immobilization in the presence of varying concentrations and types of competitive sorbates, differing ionic strengths, and other

biogeochemical conditions. Also important to consider are changes to the environmental Fe(III) biomineral that may occur when it is used as an As sorbent. For example, quantifying rate of mineral aging is crucial due to the potential transformation of the environmental Fe(III) biomineral to more crystalline phases, reducing As immobilization. Finally, research elucidating mechanisms for mass production of environmental Fe(III) biomineral may facilitate its use as the core of future As filtration technology. However, producing similar biominerals in an industrial setting may prove difficult. This issue is well represented by DGC produced biomineral. Although the DGC system closely models Fe(III) biomineral production, higher crystallinity phases were produced and was a poor analogue to environmental Fe(III) biomineral. Much work lies ahead if environmental Fe(III) biominerals are to be effectively utilized in As filtration systems; however, the reward for such work may significantly impact human well-being.

Research conducted with environmental Fe(III) (oxyhydr)oxide biominerals is of critical importance to developing a realistic model of how oxyanions are cycled in the environment. My work begins to address this need but would most benefit from future research characterizing the heterogeneity of environmental Fe(III) biominerals over spatial and temporal scales and determining the affinity of oxyanions other than As(V) and As(III). Such research has the potential to expand my results to variable environmental settings and lead to advancements in the remediation of other contaminants. I chose to pursue this research topic because of the potential implications to the advancement of both fundamental and applied biogeochemistry, stimulating the development of As remediation strategies and filtration technologies that positively impact human health. Further exploring the remaining knowledge gaps related to the

reactivity of Fe(III) biominerals will not only result in increased understanding of As environmental fate, but may provide necessary information for engineering high-efficiency As removal systems.

Arsenic is a prevalent world-wide contaminant of drinking water that is significantly affecting the well-being of diverse populations from developed and developing countries. Research presented in this report was performed in the hope that results provided meaningful answers helping to address this issue; however, future research testing the diverse reactivity of environmental and laboratory-produced Fe(III) biominerals is needed to have a broad impact on global and environmental health.

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