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# *Arsenic Chemistry in Soils and Sediments*

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# INTRODUCTION

Arsenic is a naturally occurring trace element that poses a threat to human and ecosystem health, particularly when incorporated into food or water supplies. The greatest risk imposed by arsenic to human health results from contamination of drinking water, for which the World Health Organization recommends a maximum limit of 10 μg $L^{-1}$. Continued ingestion of drinking water having hazardous levels of arsenic can lead to arsenicosis and cancers of the bladder, skin, lungs and kidneys . Unfortunately, arsenic tainted drinking waters are a global threat and presently having a devastating impact on human health within Asia. Nearly 100 million people, for example, are presently consuming drinking water having arsenic concentrations exceeding the World Health Organization's recommended limit (Ahmed et al., 2006).

Arsenic contamination of the environment often results from human activities such as mining or pesticide application, but recently natural sources of arsenic have demonstrated a devastating impact on water quality. Arsenic becomes problematic from a health perspective principally when it partitions into the aqueous rather than the solid phase. Dissolved concentrations, and the resulting mobility, of arsenic within soils and sediments are the combined result of biogeochemical processes linked to hydrologic factors. Processes favoring the partitioning of As into the aqueous phase, potentially leading to hazardous concentrations, vary extensively but can broadly be grouped into four categories: (1) ion displacement, (2) desorption (or limited sorption) at pH values > 8.5, (3) reduction of arsenate to arsenite, and (4) mineral dissolution, particularly reductive dissolution of Fe and Mn (hydr)oxides . Although various processes may liberate arsenic from solids, a transition from aerobic to anaerobic conditions, and commensurate arsenic and iron/manganese reduction, appears to be a dominant, but not exclusive, means by which high concentrations of dissolved arsenic are generated. Within the subsequent sections of this chapter, we explore and describe the biological and chemical processes that control the partitioning of arsenic between the solid and aqueous phase.

# CHEMISTRY OF ARSENIC

## *Solution Phase*

Two oxidation states of arsenic, As(V) and As(III), predominate in surface and near-surface environments. In solution, arsenic exists primarily as oxyanionic acids; arsenate [As(V) as $H_3AsO_4$] has $pK_a$'s of 2.2, 6.9 and 11.5 while arsenite [As(III) as $H_3AsO_3$] has $pK_a$'s of 9.2, 12.1 and 13.4 (Goldberg and Johnston, 2001; Smith et al., 1998). Thus, at circumneutral pH, $H_2AsO_4^-$, $HAsO_4^{2-}$ and $H_3AsO_3^o$ species dominate. Plant and microbial activity may methylate As(V) or As(III), forming, for example, dimethylarsenic acid (DMAA) and monomethylarsonous acid (MMAA) (Cullen and Reimer, 1989). However, methylated species are usually not abundant in aqueous solutions compared to inorganic forms of arsenic (Smedley and Kinniburgh, 2002; Smith et al., 1998). Thio- and carbonato- complexes of arsenic also exist within anaerobic systems; thiolated forms of arsenic may, in fact, represent an important reactive component within sulfidic environments (Wilkin et al., 2003).

## *Adsorption Reactions*

Partitioning of arsenic onto soil solids is foremost dependent on its oxidation state. In general, As(V) binds extensively and strongly to most mineral constituents of soils and sediments, while As(III) retention is more convoluted and dependent on specific soil chemical conditions (Table 1). As a consequence of arsenate's strong retention, arsenic tends to impose a limited impact on environmental quality in aerobic soils except at very high pH ($pH > 8.5$). Surface complexes (the variations of which are shown in Figure 1) of arsenate on iron and aluminum oxides, examined using both infrared (Lumsdon et al., 1984; Sun and Doner, 1996) and extended x-ray absorption fine structure (EXAFS) spectroscopy (Waychunas et al., 1993; Manceau, 1995; Fendorf et al., 1997; Arai et al., 2001; Sherman and Randall, 2003), are dominated by bidentate, binuclear (double-corner sharing) moieties. The dominant surface complex of arsenate is consistent with infrared studies of phosphate on iron (hydr)oxides —a factor supporting the analogous strong retention of phosphate. Recent evidence revealed from X-ray scattering, however, also illustrates that an appreciable portion of arsenate may reside as outer-sphere complexes on iron and aluminum oxides (Catalano et al. 2008).

Aluminum hydroxides and aluminosilicate clay minerals may also retain appreciable concentrations of arsenate, and they exhibit a strong preference for arsenate relative to arsenite (Tables 1 and 2) (Manning and Goldberg, 1997a; Manning and Goldberg, 1997b; Smith et al., 1998; Xu et al., 1988). Similarly, Mn oxides may impart a strong influence on arsenic binding. Reaction of arsenite solutions with Mn oxides such as birnessite results in extensive and rapid uptake, but arsenic is retained as arsenate surface complexes owing to arsenic oxidation by Mn(III/IV) (Manning et al., 2002; Oscarson et al., 1981).

Arsenic may also bind to organic matter in soils and sediments, with arsenate and arsenite having maximum adsorption on humic acids at pH 5.5 and 8.0, respectively (Grafe et al., 2001; Grafe et al., 2002; Ko et al., 2004). Arsenate adsorbs onto solid phase humic acids more extensively than arsenite, with amine ($NH_2$) groups suspected as the primary functional group responsible for arsenic retention (Thanabalsingam and Pickering, 1986a). Arsenic adsorption by humic substances is also enhanced by cation addition, particularly Fe, Al and Mn, whereby the cations act as bridging complexes for arsenate on humic acids (Lin et al., 2004). Nevertheless, organic matter tends to be poorly correlated with total As in comparison to Fe, Al, or P (Chen et al., 2002), suggesting that its contribution to arsenic retention in soils and sediments is limited.

In contrast to arsenate, arsenite exhibits a limited binding to most soil minerals with the exception of iron (hydr)oxides, for which it has a high adsorption maximum (Dixit and Hering 2003; see Table 1). In fact, arsenite has a greater adsorption maximum on ferric (hydr)oxides and magnetite than arsenate at all but acidic conditions (Figure 2). Similar to arsenate, arsenite, in part, also forms a bidentate, binuclear complex, albeit with a slightly longer As-Fe distance, on goethite ($\alpha$-FeOOH) (Manning et al., 1998; Ona-Nguema et al., 2005) and lepidocrocite ($\gamma$-FeOOH) (Ona-Nguema et al., 2005); on ferrihydrite and hematite, arsenite again forms bidentate, binuclear complexes but also is present in bidentate, mononuclear and, to a small degree, monodentate coordination on the mineral surface (Ona-Nguema et al., 2005). Despite the multitude of potential surface complexes on ferric (hydr)oxides, the observation of inner-sphere arsenite moieties appears to account for its extensive retention on such phases (Dixit and Hering, 2003). However, surface complexes of arsenite, although extensive, are far more labile than for its oxidized counterpart, arsenate (Kocar et al., 2006; Tufano et al., 2008).

## *Precipitation of Arsenic Phases*

Both As(V) and As(III) may precipitate within soils and sediments, but the constituents inducing precipitation vary dramatically. Arsenate, similar to phosphate, tends to precipitate with hard, multivalent cations such as aluminum and ferric-iron under acidic conditions and calcium and magnesium under alkaline conditions; arsenate may also replace $SO_4^{2-}$ or, in particular, $PO_4^{3-}$ in minerals due to similar size and charge characteristics (Smedley and Kinniburgh, 2002). Various heavy metals (e.g., Mn, Cd, Pb) and alkali earth metals (Ca, Mg, Ba) also have the capacity to precipitate with arsenate, albeit that these phases tend to be relatively soluble and thus have a limited impact on dissolved concentrations of arsenic—particularly in anaerobic environments (Rochette et al., 1998).

Arsenite, in contrast to arsenate, undergoes ligand displacement and incorporation into sulfidic solids (Bostick and Fendorf, 2003). In fact, the solubility of As(III) is often controlled by sulfide precipitates, particularly in regions where sulfidogenesis occurs, limiting As(III) concentrations in extremely reducing environments (Moore et al., 1988). Under hydrothermal conditions with high $Fe^{2+}$, sulfides may coprecipitate with Fe and As as arsenopyrite (FeAsS) or arsenic-rich (arsenian) pyrite $[Fe(S,As)_2]$; at lower levels of ferrous-iron, orpiment ($As_2S_3$) or realgar (AsS) may form. Dissimilatory $SO_4^{2-}$ and As(V) reduction may similarly induce precipitation of orpiment and realgar under ambient surface conditions (Ahmann et al., 1994; Newman et al., 1997a). Furthermore, adsorption of As(III) onto metal sulfides is often followed by incorporation of As into mineral structures (Bostick and Fendorf, 2003).

## Arsenic Biogeochemistry

### *Arsenate Reduction: Detoxification*

Because of arsenic's inherent toxicity, many organisms have evolved mechanisms to convert As to forms that are readily removed from the cell (Oremland and Stolz, 2003). Certain higher eukaryotic organisms (e.g., fungi) along with specific archaea and aerobic eubacteria can convert As(V) to As(III), which is then methylated to form less toxic species, such as MMA, DMA or trimethylarsine (TMA) (Cullen and Reimer, 1989). The most common means of arsenic detoxification involves the ArsC enzyme system; As(V) is brought into the cytoplasm, reduction transpires, and then As(III) is pumped across the cell membrane into the external milieu with a specific transporter. Unlike respiratory reduction of As(V), the detoxification pathway requires energy. Even dissimilatory As(V) reducing microorganisms may have the ArsC enzyme system, as recently shown for *Shewanella* strain ANA-3 (Saltikov et al., 2003). Microbial As(V) detoxification mechanisms may affect the overall As speciation in contaminated environments; however, dissimilatory Fe(III) and As(V) reduction processes are more likely to mobilize arsenic within reducing environments (Jones et al., 2000; Langner and Inskeep, 2000).

Great strides in resolving the physiological and enzymatic mechanisms of As(V) uptake and reduction by As(V)-reducing organisms are presently being made. In arsenic-resistant bacteria, As(V) enters the cell via nonspecific outer membrane porins or through phosphate specific transporters (Oremland and Stolz, 2003; Oremland et al., 2002; Rosen, 2002). It can then undergo respiratory reduction in the periplasm or be transported into the cytoplasm for detoxification. The As(V)-detoxifying ArsC enzymes typically reside in the cytoplasm, and As(III) formed in the process is exported across the cell membrane using the ArsA and ArsB enzymes (Mukhopadhyay et al., 2002; Oremland and Stolz, 2003). In contrast, As(V)-reductases (ArrA, ArrB, etc.) reside interior to the outer membrane—within the periplasm for Gram(-) bacteria (Afkar et al., 2003; Oremland and Stolz, 2003; Saltikov and Newman, 2003).

Transformation of As(V) to As(III) via the microbial detoxification mechanism can have important implications on arsenic transport—as well as its toxicity. There are two important aspects of the detoxification pathway that should be recognized when considering the biogeochemical fate of arsenic. First, the detoxification pathway is operative under aerobic conditions, thus creating conditions where arsenite can be produced in environments where arsenate is the stable form. Second, a higher dissolved concentration of arsenic (typically about

100 μM) needs to be reached before the genes responsible for the detoxification pathway are up-regulated (i.e., before the pathway is operational).

### *Arsenate Reduction: Respiration*

Over the last decade, at least 16 species of As(V)-respiring bacteria and two species of archaea have been isolated from a diversity of natural environments, including freshwater sediments, alkaline and saline lakes, and hot springs (Huber et al., 2000; Oremland and Stolz, 2003; Oremland et al., 2002; Stolz and Oremland, 1999). Dissimilatory As(V) reduction transpires in environments ranging from estuarine sediments to gastrointestinal tracts of animals with the addition of arsenate and electron donor (Dowdle et al., 1996; Herbel et al., 2002), suggesting that As(V)-respiring microorganisms are widespread. Additionally, As respiring bacteria are capable of reducing As(V) within solids such as scorodite (Newman et al., 1997b), with recent evidence suggesting that dissolution and subsequent uptake of As precedes reduction on the basis of the reductases residing within, rather than outside, the outer-membrane (Saltikov and Newman, 2003). These prokaryotic organisms can link the reduction of soluble, adsorbed, or mineralized As(V) with the oxidation of a wide variety of electron donors, including lactate, acetate, pyruvate, glucose, and $H_2$, in order to gain energy for cell growth. To date, no obligate As(V)-respiring microbes have been identified; all of the As(V)-reducing organisms can respire on other electron acceptors inclusive of $NO_3^-$, Fe(III), and $SO_4^{2-}$. The ability to utilize a variety of electron acceptors and donors implies that the As(V)-respiring prokaryotes are opportunists, and that they can thrive on other available electron acceptors in environments when As(V) concentrations become depleted.

## Desorption of Arsenic in Soils and Sediments

In surface and subsurface environments, changes in water chemistry often result in release of As from solid phases through various desorption pathways. As noted above, processes leading to arsenic desorption can broadly be grouped into four categories: (1) ion displacement, (2) alkalinity (pH values > 8.5), (3) reduction of arsenate to arsenite, and (4) mineral dissolution, particularly reductive dissolution of Fe and Mn (hydr)oxides.

### *Ion Displacement*

Competitive ion displacement can represent an important means by which arsenic is released to the aqueous phase and subject to transport. Displacement and mobilization of As by phosphates is of particular concern (Manning and Goldberg, 1996; Reynolds et al., 1999; Violante and Pigna, 2002; Dixit and Hering, 2003), and regions where fertilizer or pesticide runoff and leaching occurs are specifically at risk for this mobilization pathway (Jain and Loeppert, 2000; Peryea and Kammerack, 1997). Both dissolved silicate (Luxton et al., 2008) and organic matter (Grafe et al., 2001, 2002) can also competitively limit arsenic adsorption or promote desorption, with concentrations common to soils and sediments having an appreciable impact on dissolved arsenic concentrations. Carbonate can also compete with arsenic for adsorption sites on mineral surfaces ( Van Geen et al., 1994; Kim et al, 2000; Villalobos and Leckie, 2001; Appelo et al., 2002; Lee and Nriagu, 2003 ), and natural organic matter may also compete with As and inhibit arsenic adsorption onto iron (hydr)oxides due to competitive adsorption (Xu et al., 1991; Redman et al., 2002). Other anions, such as $Cl^-$, $SO_4^{2-}$, and $NO_3^-$, have minimal impact on As desorption, yet these ions can contribute to ionic strength and salinization effects on As retention in soils and sediments (Gupta and Chen, 1978; Smith et al., 1998) that are potentially important in the desorption of arsenite.

## Arsenic Desorption Upon Anaerobiosis

The greatest likelihood for As release in soils and sediments typically occurs upon a transition from oxidizing to reducing conditions. Under saturated conditions, the rapid consumption of $O_2$ by aerobic microbes combined with the low solubility of $O_2$ induces anaerobic bacteria to utilize alternative electron acceptors. Arsenic may be displaced either through reduction of arsenate to arsenite or through mineralogical transformations (inclusive of dissolution) of the soil matrix.

### *Impact of Arsenate Reduction*

The conception that arsenite is a more mobile species than arsenate has been challenged during the past decade on the basis of arsenic retention to various ferric (hydr)oxides (see Figure 2, for example). Despite a higher adsorption maximum of arsenite on ferric (hydr)oxides relative to arsenate, greater quantities and resulting aqueous concentrations occur for arsenite desorption (Tufano et al., 2008; Figure 3). In particular, higher surface coverage (expressed as proportion of the adsorption maximum) enhances the difference between desorption from arsenite-loaded as compared to arsenate-loaded columns—with much higher proportion of arsenic being desorbed as arsenite. At surface coverages near 50%, arsenite desorption results in initial aqueous concentrations exceeding 500 μM while for arsenate concentrations are below 200 μM (Figure 3). For both arsenite and arsenate, desorption decreases exponentially with time (represented by pore-volumes eluted through the column at a flow-rate of ca. 3 pore-volumes per day); by 20 pore-volumes, both species of arsenic are below 50 μM aqueous concentration and continuing to diminish. The rapid decline in desorption is indicative of a fixed surface population residing in a highly labile state, which rapidly responds to disequilibrium. The difference in arsenite/arsenate desorption from ferrihydrite is also striking (Herbel and Fendorf, 2006; Kocar et al., 2006; Tufano et al., 2008). Rather than exhibiting a rapid decay in the concentration desorbing from ferrihydrite, aqueous concentrations remain greater than 70 μM even after 20 pore-volumes (under similar condition to those used for the goethite experiments described above). Furthermore, the cumulative loss of As(III) from ferrihydrite-sand columns (27.4% of the initial loading) was more than twice that of As(V) (10.8%) (Herbel and Fendorf, 2006).

Arsenate desorption from iron (hydr)oxides is measurable but limited, while arsenite, in comparison, undergoes extensive release under hydrodynamic conditions. The extensive yet apparently weaker adsorption of arsenite can again be rectified simply by considering the multitude of potential surface complexes resulting on mineral surfaces. Arsenite, in particular, is thought to bind on iron (hydr)oxides through multiple inner-sphere complexes (Ona-Nguema et al., 2005), having a range of binding strengths, in combination with outer-sphere and H-bonded moieties, giving rise to extensive but weak complexes. As a consequence, an appreciable fraction of arsenite appears to reside in weakly adsorbed complexes that rapidly desorb in response to decreases in aqueous concentrations. The observation that arsenite forms more labile complexes on ferric (hydr)oxides challenges the presumption that iron reduction is the primary factor liberating arsenic to the aqueous phase. Arsenic reduction, in fact, may have a more pronounced role in destabilizing arsenic and allowing its transport within soils. Although iron reduction has been suggested as a means for arsenic desorption, and in fact would lead to the depletion of a prominent sorbent, arsenic reduction may be more influential. The expression of the *arrA* gene, responsible for respiratory arsenate reduction (Saltikov and Newman, 2003), may be useful as a proxy for arsenic migration (Malasarn et al., 2004), although the actual transport of arsenic will depend on a host of reactions far more extensive than just Fe(III) or As(V) reduction.

It has also been noted that in iron oxide columns inoculated with arsenic and iron reducing bacteria, higher concentrations of dissolved As are sustained in columns initially loaded with As(V) (Herbel et al., 2006). The increased tailing (longer-term desorption) of As in columns initially having As(V), relative to those having As(III), appears related to the pathway (desorption and transport across bacterial membranes) by which As(V) is enzymatically reduced.

Dissimilatory reduction of As(V) could, hypothetically, transpire either through the terminal reductase being located on the exterior of the bacterial membrane (the outer membrane in the case of Gram-negative bacteria) or through arsenic desorption and transport within (or through) the bacterial membrane. Current findings on the location and behavior of As(V)-reducing enzymes in dissimilatory As(V) reducing bacteria does not support the premise of an arsenate reductase located on the cell exterior (Krafft and Macy, 1998; Stolz and Oremland, 1999; Oremland and Stolz, 2003; Saltikov and Newman, 2003). An alternative, and more likely, mechanism thus requires As(V) to desorb from ferrihydrite, pass through (or into) a bacterial membrane, and undergo respiratory reduction. Although arsenate is (relatively) strongly retained on ferrihydrite, it is likely that bacteria maintain a gradient in As concentrations promoting desorption and diffusion of As(V) to the cell. Expulsion of As(III) into the external media then occurs via As(III)-specific transporter proteins. This scenario would facilitate As(III) transport away from the ferrihydrite surface and would enhance movement of As through the column. Furthermore, it would result in down-field migration and elution of arsenic, both of which are observed (Herbel and Fendorf, 2006), and therefore explain the greater concentration of arsenic tailing in columns where both As(V) and Fe(III) reduction transpires relative to those having only Fe(III) reduction.

### *Desorption upon Metal Reduction*

Many bacteria and archaea can respire on Mn(III/IV)- and Fe(III)-oxides leading to their dissolution with the potential for concomitant displacement of arsenic into the aqueous phase (Cummings et al., 1999). In fact, within most soils and sediments, total As levels correlate with Fe content rather than Al or clay content (Smedley and Kinniburgh, 2002), and thus reductive dissolution/transformation of Fe(III) phases should have a major impact on arsenic. Respiratory reduction of Fe in sediments generally occurs in zones where $O_2$, $NO_3^-$, and Mn(IV) (all being oxidants of Fe(II) and alternative electron acceptors) are diminished (Lovley, 2000).

The most readily bioreducible Fe(III) (hydr)oxides are the high surface area, least thermodynamically stable phases such as ferrihydrite (Lovley, 1991; Roden and Zachara, 1996; Schwertmann and Taylor, 1989). Reduction of Fe(III) within such phases, however, does not lead to simple congruent dissolution but rather initiates production of a convoluted assortment of secondary phases (Figure 4). Ferrous iron produced during Fe(III) reduction induces a transformation of ferrihydrite (or lepidocrocite) to more stable minerals such as goethite (α-FeOOH) and magnetite ($Fe_3O_4$) (Zachara et al., 2002; Hansel et al., 2003). Hansel et al. (2003), for example, illustrate that dissimilatory respiration on Fe(III) within ferrihydrite results in a cascade of geochemical reactions that lead to a series of secondary solids induced by back-reaction with Fe(II) (Figure 4). Ferrihydrite (when supported by a quartz sand substrate) undergoes a mineralogical shift to goethite at Fe(II) loadings less than 1 mmol/g (resulting from 0.3 mM aqueous Fe(II) in their experiments) or to magnetite at higher Fe(II) loadings. Despite having a nearly equal affinity for As (Dixit and Hering, 2003), transformation of ferrihydrite to more crystalline phases (goethite, hematite, or magnetite) decreases the available surface area (Appelo et al., 2002) and thus diminishes their capacity to retain arsenic.

Congruent dissolution of Fe(III) (hydr)oxides would be expected to release arsenic until the surface site concentration is depleted below the level of adsorbed arsenic (in combination with other high-affinity anions such as phosphate). Secondary mineralization of iron, however, convolutes this view, leading to the potential for arsenic to be incorporated on or in the newly forming solids. Recently observed elution trends of arsenic from ferrihydrite under iron reducing conditions are inconsistent with arsenic desorption upon reductively induced mineralogical transition (Herbel and Fendorf, 2006; Kocar et al., 2006). In fact, it was illustrated that arsenic release from As(III) loaded ferrihydrite-coated sand under hydrodynamic conditions occurs more extensively for abiotic than biotic systems (Figure 5). A rapid mineralogical transition occurs within the inoculated column as (principally) magnetite is generated at the expense of ferrihydrite. The mineralogical transformation results in limiting the extent of desorption, as noted by the suppression in desorption upon the production (or introduction) of Fe(II) within columns and concomitant ferrihydrite transformation (Herbel and Fendorf, 2006; Kocar et al., 2006; Tufano et al., 2008). It therefore appears that while reductive dissolution of ferric (hydr)oxides can lead to arsenic release, under conditions conducive to re-mineralization arsenic desorption is suppressed rather than promoted. The recent observation of a ferrous-arsenite precipitate (Thoral et al., 2005) may in part account for arsenic retention under conditions of intense Fe(II) production. We have not observed such a solid within the bioreduced columns described here, however, and rather find arsenic incorporated in or adsorbed on the secondary solids, consistent with structural incorporation of As on the magnetite surface (Coker et al., 2006).

### *Contributions of Iron and Arsenic Reduction*

For iron oxides such as goethite or hematite that do not undergo reductive transformation (dissolution and reprecipitation), and rather just dissolution, iron reduction will lead to arsenic desorption once the surface site density is sufficiently decreased to challenge site occupancy of arsenic. However, for iron oxides such as ferrihydrite that undergo rapid transformation upon reaction with Fe(II) produced under iron reducing conditions, arsenic adsorption/desorption becomes more complex. The processes controlling As(III) release to pore-water from ferrihydrite, in fact, change with reaction time (Tufano et al., 2008). A period of As(III) retention results during iron reduction concomitant with ferrihydrite transformation to magnetite (Figure 6a); however, prolonged periods of iron reduction and associated dissolution eventually lead to As(III) release and elution (Figure 6b). In essence, there are three competing processes that occur during the course of reaction which in concert dictate the dissolved concentrations of As(III): (1) Desorption promoted by chemical disequilibrium during pore water replacement (flow); (2) Retention on transforming iron phases; (3) Release from dissolving ferric-bearing phases.

Over 90 days of reaction (270 pv), we recently noted three distinct periods of arsenic elution from ferrihydrite columns inoculated with an As-Fe reducing bacteria. Initially (*ca.* 13 d), there was simultaneous As(III) desorption (abiotic) from ferrihydrite along with As(III) sequestration by biologically mediated transformation products of ferrihydrite (magnetite most appreciably) (Figure 6). With continued reductive transformation of ferrihydrite (*ca.* 13-33 d), arsenic release is limited, resulting in a plateau of effluent As(III) concentration. A final period dominated by reductive dissolution of Fe(III) (hydr)oxides and concomitant As(III) release (Figure 6).

The initial period of elution (0–13 d or 0-40 pv) is marked by a rapid decrease in As(III) accompanying iron reduction; arsenic(III) desorption is far less extensive in biotic than abiotic systems (Figure 3). During subsequent cessation of desorption (middle reaction period), As(III) concentrations reach a minimum due to a depletion of labile As(III) and concomitant retention by transforming iron (hydr)oxides. Continued Fe(II) induced ferrihydrite transformation exerts a dominant control on As(III) partitioning here, retaining As(III) through incorporation on magnetite (Coker et al., 2006). Interestingly, despite variations in the extent and rate of iron elution (measured by effluent Fe(II) concentrations), nearly identical As(III) elution profiles result during this reaction period (Figure 6), indicating that the extent of ferrihydrite reductive transformation was similar, consistent with ferrihydrite transformation models. By *ca.* 100 pore volumes, however, iron phase transformations are nearly complete; a depletion of sorption sites resulting from iron reductive dissolution thus stimulates As(III) desorption. This final period of As(III) release is marked by a prolonged period of iron reduction; dissolution of iron (hydr)oxides is results in substantial loss of As(III) to effluent solution as a result of diminishing surface area and thus binding sites. During this reaction period we observe variation in As(III) release with initial lactate concentrations; higher lactate concentrations promote As(III) release. Increasing extents of iron reduction, which result in dissolution rather than secondary transformation, lead to substantially greater amounts of aqueous As(III) concentrations in effluent water (Figures 6b). Thus, iron reduction can have a paradoxical impact on arsenic; ferrihydrite reductive transformation initially enhances As(III) retention (relative to abiotic systems) while prolonged reduction enhances arsenic desorption.

## Advancements Through Synchrotron Science

Arsenic retention on soil solids is critical for regulating the dissolved concentrations of this hazardous element, thus helping to limit its exposure to living organisms and migration within the environment. Elucidating the mechanisms that control As retention requires the ability to determine the oxidation state and bonding environment of As, and other important elements like Fe, in both the aqueous and solid phase. Synchrotron based spectroscopic techniques are instrumental in supplying this crucial information. This is particularly true when it comes to understanding changes in local coordination of As and Fe within the solid state, as there are few, if any, alternative analytical techniques capable of providing the necessary information. Of the large array of synchrotron based analytical techniques, X-ray absorption spectroscopy (XAS) is most frequently used for understanding the chemical environment of As within solids of soils and sediments. In general, the X-ray absorption near-edge structure (XANES) region of the spectrum is used to distinguish oxidation states and thus As(III) from As(V) (Rochette et al., 2000; Manning et al., 2002); the higher oxidation state of As(V) causes the core electrons in the As to be more tightly bound thereby shifting the As(V) XANES spectrum to higher energy than the As(III) spectrum. In addition, linear combination reconstructions of XANES spectra from standard compounds provides quantitative speciation of solid state As (see, for example, Rochette et al., 2000). Linear combination fitting using standards is also useful for interpreting the Extended x-ray absorption fine structure (EXAFS) spectral region, and it has been used extensively for quantifying changes in Fe mineralogy (Benner et al., 2002; Hansel et al., 2003; Tufano et al., 2008). When an appropriate set of standards is not available, theoretical fitting of the EXAFS spectrum using *ab initio* calculations can be used to determine the local bonding environment of As (or Fe or other elements of interest). This approach is particularly well suited for understanding the detailed bonding geometries of surface adsorption complexes (Waychunas et al,. 1993, 1995; Manceau, 1995; Fendorf et al., 1997; Manning et al., 1998; Arai et al., 2001; Bostick et al., 2003; Sherman et al., 2003; Ona-Nguema et al., 2005; Grafe et al., 2008a); From these multiple analyses, it is evident that double corner-sharing (bidendate, binuclear) complexes dominate on a multitude of surface (ranging from Fe, Al, to Mn minerals) but that various proportions of bidentate mononuclear and monodentate complexes are also present (Waychunas 1993, 1995; Fendorf et al., 1997; Ona-Nguema et al., 2005; Grafe et al., 2008a)..

Complimentary to the solid state work, which has been the predominant utility of XAS in environmental science, XANES and EXAFS have also proven invaluable for deciphering aqueous speciation of arsenic. Using XAS to determine As speciation in sulfidic solution, Helz et al. (2005) demonstrated the presence of As-S oligomers in solutions of As(III) and $S^{2-}$ (Helz et al., 1995).

Over the past decade (or so), microfocused synchrotron techniques have become increasing available and useful for determine the partitioning, associations, and varying structural environments of arsenic within soils and sediments. Micro-focused techniques provide spatially resolved XANES and EXAFS spectra as well as two dimensional maps of element distribution through X-ray fluorescence mapping. Using spatially resolved X-ray fluorescence and XAS, the distribution and speciation of arsenic has been ascertained on aquatic plant roots (Hansel et al., 2002; Blute et al., 2004; Voeglin et al., 2007) and within copper-chromium-arsenic treated wood and within CCA soils (Nico et al., 2004; Grafe et al., 2008b).

New advancements in synchrotron based techniques continue to become available and are providing new information on the chemical fate of arsenic. Waychunas et al. (2005) use a combination of crystal truncation rod (CTR) surface diffraction and gracing incident EXAFS

(GIXAFS) to demonstrate that arsenate adsorbed to a single crystal hematite surface adopts predominately bidentate binuclear and bidentate mononuclear complexes. CTR surface diffraction is a method by which the diffraction patterns associated with the differences between the surface structure of a crystal and the bulk structure are measured in order to give a detailed model of the crystal surface structure. Because these CTR features are small as compared to the major Bragg peaks, the high intensity X-ray beam provide by a synchrotron is required for the measurement. The GIXAFS measurement is similar to a regular EXAFS measurement except that the X-ray beam impinges on the sample at a shallow angle close to critical angle for total reflection. While this technique requires a smooth single crystal surface, it makes up for this limitation by providing surface sensitive information with a larger (~500x) signal to noise ratio and the ability to use the polarized nature of the synchrotron X-ray beam to provide a more detailed understanding of the orientation of surface complexes relative to the mineral surface.

Additional surface sensitive X-ray techniques such as X-ray standing wave (XSW) are also useful for studying arsenic on single crystal surfaces such as hematite {Catalano et al., 2007). The XSW investigation of Catalano et al. (2007) provides evidence for not only the standard model of arsenate absorption, bidentate binuclear complex, but also for the possibility of additional As complexes. These unknown complexes were recently identified with a further advancement, resonant anomalous X-ray reflectivity (RAXR), a combined X-ray scattering and spectroscopic technique, that demonstrated the presence ofouter-sphere arsenate complexes coexisting with inner-sphere complexes on the corundum and hematite surfaces (Catalano et al., 2008).

## Summary and Conclusions

Strong partitioning of arsenic on soil solids is most prevalently disrupted by the onset of anaerobic conditions (anaerobiosis), leading to increased aqueous concentrations of arsenic. Variations in arsenic chemistry, compounded by biogeochemical transformations of the soil matrix, upon the onset of anaerobic conditions transpire to produce a convolution of reactions that have varying impacts on arsenic retention—a summary of which are illustrated in Figure 7.

Arsenic desorption upon anaerobiosis has been ascribed to both the reduction of arsenic, from arsenate to arsenite, and iron(III)—the latter leading to the reductive dissolution of ferric (hydr)oxides that act as principal sinks of arsenic (Delemos et al., 2006; Islam et al., 2004; Jones et al., 2000; McCreadie et al., 2000; McGeehan and Naylor, 1992; Zobrist et al., 2000). Recent advances in our knowledge of arsenic reduction mechanisms, binding affinities, and (bio)reductive transformation of Fe(III) (hydr)oxides, lead to a more complex view of arsenic dynamics under reducing conditions. We first consider the implications of As(V) reduction (left side of Figure 7). Reduction of As(V) to As(III) leads to Fe(III) (hydr)oxides becoming the dominate controlling solid phase as a consequence of arsenite having great specificity for this solid(Manning and Goldberg, 1997a) and the adsorption capacity of arsenite being relatively small on Al (hydr)oxides and aluminosilicates (see Table 1). However, release of Asfrom solids subjected to advective flow is substantially greater for arsenite than arsenate (Figure 3). X-ray absorption spectroscopy provides information for resolving the varying affinity of arsenic species for Fe (hydr)oxides and the apparent discrepancy between adsorption maximum and lability . On the basis of different structures of arsenite elucidated using EXAFS spectroscopy, the propensity to form labile surface complexes was illustrated using molecular modeling (Sverjensky et al., 2006)

Given recent advances in modes of bacterial arsenate reduction (Saltikov and Newman, 2003), the primary means by which arsenic is reduced in nonsulfidic systems, and likely in all systems that have pH values in the circumneutral range or higher (Rochette et al., 2000), we can further extend our view of arsenic retention upon reduction of arsenate to arsenite. The two modes of arsenic reduction, respiratory or detoxification, both require arsenic to be released from the solid phase. The primary reductases for respiratory reduction, ArrA and ArrB, both reside interior to the outer membrane of bacteria (Saltikov and Newman, 2003), and thus it is likely that As(V) must desorb from the surface, cross the outer membrane, and then undergo reduction. Arsenate reduction through detoxification is also restricted by membrane translocation, since this process takes place in the cytoplasm. In either case, it appears that for arsenate reduction to occur, it must desorb from mineral surfaces before reduction; only if the reductase(s) reside on the external portion of the outer membrane could reduction transpire in the absence of desorption, and this is not apparent for known reduction pathways. After As(V) is reduced, arsenite would be expelled from the cell and would undergo more extensive transport than its oxidized precursor.

Iron reduction will also take place under anaerobic conditions, and thus we need to consider its implications on arsenic partitioning and transport (right portion of Figure 7). Iron reduction will lead, in part, to the dissolution of the mineral phase and thus diminish the number of adsorption sites. We therefore need to consider the ratio of arsenic to potential reactive surface sites on the Fe(III) (hydr)oxide surface. For a soil having 50 mg $Kg^{-1}$ As, 120 $m^2$ $Kg^{-1}$ Fe(III) (hydr)oxide is conservatively needed to adsorb all the As (and considering that all surface sites could be occupied by As); this translates to 5 g Fe $Kg^{-1}$ soil of goethite with a conservative specific surface area of 20 $m^2$ $g^{-1}$. For soils having a total of 10 g $Kg^{-1}$ Fe as goethite and 2 g $Kg^{-}$

$^{1}$ Fe as ferrihydrite, 50 mg Kg$^{-1}$ As would occupy less than 10% of the surface sites. Hence, depending on the specific solid-phase arsenic concentration and iron (hydr)oxide content/surface area, Fe(III) mineral transformations may directly impact dissolved concentrations of arsenic (conditions of high As:Fe) or have a minimal impact (low As:Fe conditions) until extensive (90% removal) dissolution/transformation has transpired.

We next need to consider the Fe transformation pathway and whether dissolution is the sole fate of the mineral or whether secondary minerals are generated that may sequester arsenic. In this effort, EXAFS again plays a crucial role. The Fe phases that have the highest surface area, are the most easily reduced, and are the most likely to form secondary minerals are amorphous and/or nano-crystalline phases such as ferrihydrite. Using synchrotron X-ray techniques, the transformation of ferrihydrite to secondary minerals, even nano-phase or poorly crystalline, secondary minerals, such as magnetite and goethite can be quantified; linear combination EXAFS fitting, for example, has proven particularly useful (e.g., Hansel et al., 2003) Using this capability, recent work illustrates that the intensity of iron reduction (indicated by the resulting dissolved Fe(II) concentration) is a key factor controlling iron mineralogical transformations (see, for example, Hansel et al., 2003) and thus the fate of arsenic. For soils with labile iron oxides (typically ferrihydrite, but also possibly lepidocrocite or proported nano-goethite), stimulation of iron reduction would lead to a sequence of iron transformations (as illustrated in Figure 4) and lead to arsenic incorporation and adsorption—as demonstrated here by the noted increased sequestration of arsenic under Fe(III) reducing conditions of ferrihydrite (Figure 5). The site specific substitution of arsenic into secondary Fe minerals can be included in this conceptual model largely on the strength of the direct evidence of As substituted into magnetite provided by two synchrotron techniques, EXAFS and X-ray magnetite circular dichroism (XMCD) (Coker et al., 2006). XMCD is a soft X-ray XAS technique in which the absorption edge of a sample is measured under different magnetite fields in order to provide further information about the local electronic and magnetic structure of the sample. Additionally, generation of high concentrations of Fe(II) and As(III) can lead to the formation of secondary Fe(II)-As(III) precipitates, the existence and potential structure of which were estimated using As and Fe EXAFS analysis (Thoral et al., 2005)

While we have considered Fe(III) or As(V) reduction independently, each of which could have important implications on the fate and transport of arsenic, As(V) and Fe(III) reduction will typically transpire in concert (as projected in Figure 7, bottom right panel). Obligate As(V) reducing bacteria have not been identified to date; rather they have a capacity to respire on a diverse set of electron acceptors and, in particular, many are noted iron reducers (Oremland and Stolz, 2003). Furthermore, on the basis of As(III) nearly always being the dominant species of arsenic under iron reducing conditions, we may speculate that As(V) reduction coincides with Fe(III) reduction. We therefore postulate that Fe-As reducing bacteria promote simultaneous reduction of As(V) and Fe(III), resulting in parallel rather than sequential reduction.

Summarizing the fate of arsenic under anaerobic conditions we should note two important points: (1) dissolved concentrations and migration of arsenic are typically promoted under reducing conditions, but (2) the intensity of iron reduction (measured by dissolved Fe(II) concentrations) and concomitant extent of iron bioreductive mineralization will be the primary variable influencing the extent of release. Arsenate reduction is the largest single factor promoting arsenic release but will be invariant under reducing conditions. The second point (the intensity of iron reduction controlling arsenic release) results from the potential for arsenic to be sequestered in secondary mineralization products or precipitates and that less intense reduction will promote arsenic transport while more intense reduction will lead to As incorporation in or adsorption on secondary bioreduction products such as magnetite.

So what does this synopsis tell us about the expected fate of arsenic under anaerobic conditions? First, owing to the weaker surface complexes of As(V) versus As(III), arsenic migration will be greater under anaerobic than aerobic conditions (with the exception of environments having high dissolved concentrations of sulfide, which can lead to sequestration of As). Sedimentary basins of Southeast Asia experiencing high concentrations of As in groundwater, for example, have prolonged periods (months) of anaerobic conditions; arsenic within these environments would therefore be expected to be relatively mobile. However, the extent of arsenic release will be appreciably modified by the fate or Fe. Under conditions conducive to rapid and extensive Fe(III) reduction (anaerobic conditions, high concentrations of labile DOC, bioavailable Fe(III), and warm temperatures), secondary mineralization will help to sequester arsenic. Returning to the situation in Southeast Asia, surface soils (upper ca. 0.5 m) undergo rapid fluctuating redox conditions, leading to high-surface area, short-range order Fe(III) (hydr)oxides such as ferrihydrite during the aerobic periods. Conditions conducive to intense iron reduction during monsoonal flooding would stimulate secondary Fe phases, such as biogenic magnetite, providing a suitable host for arsenic even under anaerobic conditions. In this projection, arsenic would be cycled from one type of solid to another during aerobic-anaerobic transitions.

Two remaining factors need to be considered in addressing the ultimate fate of arsenic within the sedimentary basins of Southeast Asia. First, arsenic, while cycled in the surface soils, is partially leached into deeper portions of the profile (i.e., As is not conserved during the anaerobic cycle). Secondly, these basins are active and continue to receive sediment loads, leading to continual burial of arsenic deeper in the soil profile. Once deeper in the soil, the cycling of iron, and hence fate of arsenic, is altered. Dampened fluctuation in anaerobic-aerobic transitions results in more crystalline Fe(III) phases during aerobic periods and, in combination with diminishing concentrations of labile DOC with depth, less intense Fe(III) reduction and secondary mineralization during anaerobic periods. In combination, subsurface processes will lead to enhanced As mobility and thus transport to aquifers residing deeper in the sediment profile.

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**Table 1**. Retention maxima for arsenic on various solids common to soils and sediments derived from adsorption isotherms at fixed pH.

| Adsorbent | As(V) (mmole Kg$^{-1}$) | pH | As(III) (mmole Kg$^{-1}$) | pH | Reference |
|---|---|---|---|---|---|
| **Al Oxides** | | | | | |
| Gibbsite | 35 | 4.0 | | | Approximate (Hingston et al., 1971) |
| | 15 | 9.0 | | | |
| Amorphous Al hydroxide | 1500 | 4.0 | | | (Hingston et al., 1971) |
| | 600 | 9.0 | | | |
| | 1600 | 5.0 | | | (Anderson et al., 1976) |
| | 1200 | 7.0 | | | |
| | 500 | 9.0 | | | |
| Activated alumina | 2-fold higher for As(V) than As(III) | | | | (Gosh and Yuan, 1987) |
| | 67 | 6-7 | 14 | 6.5-8.5 | “ “ |
| Bauxite | 52 | 6-7 | 16 | 6.5-8.5 | “ “ |
| **Aluminosilicates** | | | | | |
| Montmorillonite | 8 | 5.0 | 3 | 5.0 | Using landfill leachate, (Frost and Griffin, 1977) |
| Kaolinite | 7 | 5.0 | 1 | 5.0 | “ “ |
| **Fe (hydr)oxides** | | | | | |
| Hydrous ferric oxide | 3514 | 4.0 | 2675 | 8.0 | (Dixit and Hering, 2003) |
| Goethite | 173 | 4.0 | 173 | 8.0 | “ “ |
| Magnetite | | | 332 | 8.0 | “ “ |
| 2-line ferrihydrite | 2000 | 4.6 | $\geq$ 6000 | 4.6 | (Raven et al., 1998) |
| | 1500 | 9.2 | $\geq$ 6000 | 9.2 | |
| 2-line ferrihydrite on quartz sand | 483 | 7.1 | 1206 | 7.1 | (Herbel and Fendorf, 2006) |
| **Others** | | | | | |
| Birnessite (δ-MnO$_2$) | 100 | | | | (Lenoble et al., 2004) |
| Pyrolusite | 10 | 6.5 | | | (Thanabalsingam and Pickering, 1986b) |
| Cryptomelane | 25 | 6.5 | | | |
| Calcite (CaCO$_3$) | ND[†] | | ND | | (Oscarson et al., 1983)<br>(Goldberg and Glaubig, 1988) |
| Activated Carbon | 10 | 3-4 | | | (Gupta and Chen, 1978) |
| Humic Acids | 90-110 | 5.5 | | 5.5 | (Thanabalsingam and Pickering, 1986a) |

[†] - Not detected

**Table 2.** Adsorption envelopes for As(V) and As(III) on various soil and sedimentary solids.

| Adsorbent | As(V)$_{aq}$ $^{a}$; As(V)$_{ads}$ $^{b}$ | pH$^{c}$ maximum | As(III)$_{aq}$ $^{a}$; As(III)$_{ads}$ $^{b}$ | pH$^{c}$ maximum | Reference |
|---|---|---|---|---|---|
| **Al Oxides** | | | | | |
| Amorphous Al hydroxide | 1600; 1700 (4.5) | 4-7 | | | (Anderson et al., 1976) |
| | 133; 900 (4.5) | 4-7 | | | |
| | 20; 20 (2-10) | 2-10 | 20; 16 (8.5) | 7-9.5 | (Goldberg, 2002) |
| Activated alumina | 53.4; 26.5 (3-7) | 3-7 | 26; 11 (8.2) | 3-10 | (Gupta and Chen, 1978) |
| Bauxite | 53.4; 26.5 (3-7) | 3-7 | 16; 9 (8.5) | 3-10 | (Gupta and Chen, 1978) |
| **Aluminosilicates** | | | | | |
| Montmorillonite | 20; 0.41 (5, 12.5) | 5-7, >11 | | | (Goldberg and Glaubig, 1988) |
| | 20; 0.35 (5) | 5-7 | 20; 0.4 (3) | 3-4 | (Goldberg, 2002) |
| Kaolinite | 20; 0.5 (5) | 3-9 | 20; 0.25 (8-10) | 7-11 | (Goldberg, 2002) |
| Illite | 20; 0.5 (4-6) | 3-7 | 20; 0.22 (8-9) | 7-10 | (Goldberg, 2002) |
| **Fe (hydr)oxides** | | | | | |
| Hydrous ferric oxide | 20; 40 (2-9) | 2-10 | 20; 40 (2-11) | 2-11 | (Goldberg, 2002) |
| | 100; 2100 (4.0) | <7 | | | (Dixit and Hering, 2003) |
| Hydrous ferric oxide | | | 100; 1500 (8-9) | 5-9.5 | (Dixit and Hering, 2003) |
| Goethite | 100; 140 (4.0) | <8 | 100; 120 (8-9) | 4-10 | (Dixit and Hering, 2003) |
| Magnetite | | | 100; 140 (9.0) | 8-9.5 | (Dixit and Hering, 2003) |
| 2-line ferrihydrite | | | | | |
| **Others** | | | | | |
| Hydrous manganese oxide | 10; 16 (3.0) | 2.5-5 | | | (Thanabalsingam and Pickering, 1986b) |
| Calcite (CaCO$_3$) | 20; 2.0 (11) | 9-13 | | | (Goldberg and Glaubig, 1988) |
| Activated Carbon | 19.4; 5.3 (4) | 3-5 | | | (Gupta and Chen, 1978) |
| Humic Acids | 5-100; 80-140 (6) | 5-7 | 20; 110 (8) | 7-9 | (Thanabalsingam and Pickering, 1986a) |

a: Initial aqueous concentration (μM)
b: maximum adsorption (mmole Kg$^{-1}$) at indicated pH
c: pH range over which which maximum adsorption occurred.

# Figure Captions

**Figure 1**. Possible inner-sphere surface structures of arsenate on ferric (hydr)oxides (illustrated here using goethite) showing single corner-sharing (monodentate), double corner-sharing (bidentate, binuclear), and edge-sharing (bidentate, mononuclear) complexes.

**Figure 2**. Magnitude and pH-dependency of As(V) (arsenate) and As(III) (arsenite) adsorption on hydrous ferric oxide; reaction conditions were 50 mM arsenic reacted with 0.03 g/L hydrous ferric oxide (data from Dixit and Hering, 2003)

**Figure 3**. Desorption of As(III) and As(V) from goethite upon the onset of dynamic flow conditions. Goethite-coated quartz sand was loaded with As at various fractions of the adsorption maxima, as determined by batch incubations and Langmuir isotherm fits, and then subjected to continuous injection of a minimal groundwater media.

**Figure 4**. Schematic illustration of ferrihydrite transformations upon reaction with biologically produced Fe(II).

**Figure 5**. Arsenic elution from abiotic and biotic (*S. putrefaciens*, an Fe(III) reducing bacterium) columns initially containing As(III)-ferrihydrite-quartz sand. The initial surface coverage (ca. 800 mg $Kg^{-1}$ ferrihydrite-sand) is approximately 50% of the adsorption maximum. A flow rate of 1 pore volume $d^{-1}$ was maintained with an artificial ground-water medium (see Herbel and Fendorf (2006) for a detailed description of the medium).

**Figure 6.** As(III) desorption for three influent lactate concentrations supplied to ferrihydrite-sand columns inoculated with *S. putrefaciens* CN-32.; initial loading of arsenic (4.48 mmol $Kg^{-1}$) was 28% of the adsorption maximum at pH 7.1. (A) Initial period during which ferrihydrite transforms to magnetite and (B) extended reduction period showing eventual reductive dissolution stimulating arsenic release. (Data from Tufano and Fendorf, 2008).

**Figure 7.** Postulated pathways and changes in arsenic partitioning (and transport) under As(V) (left side), Fe(III) (top right), or Fe(III) and As(V) reducing conditions. Width of arrows denote magnitude of reaction.

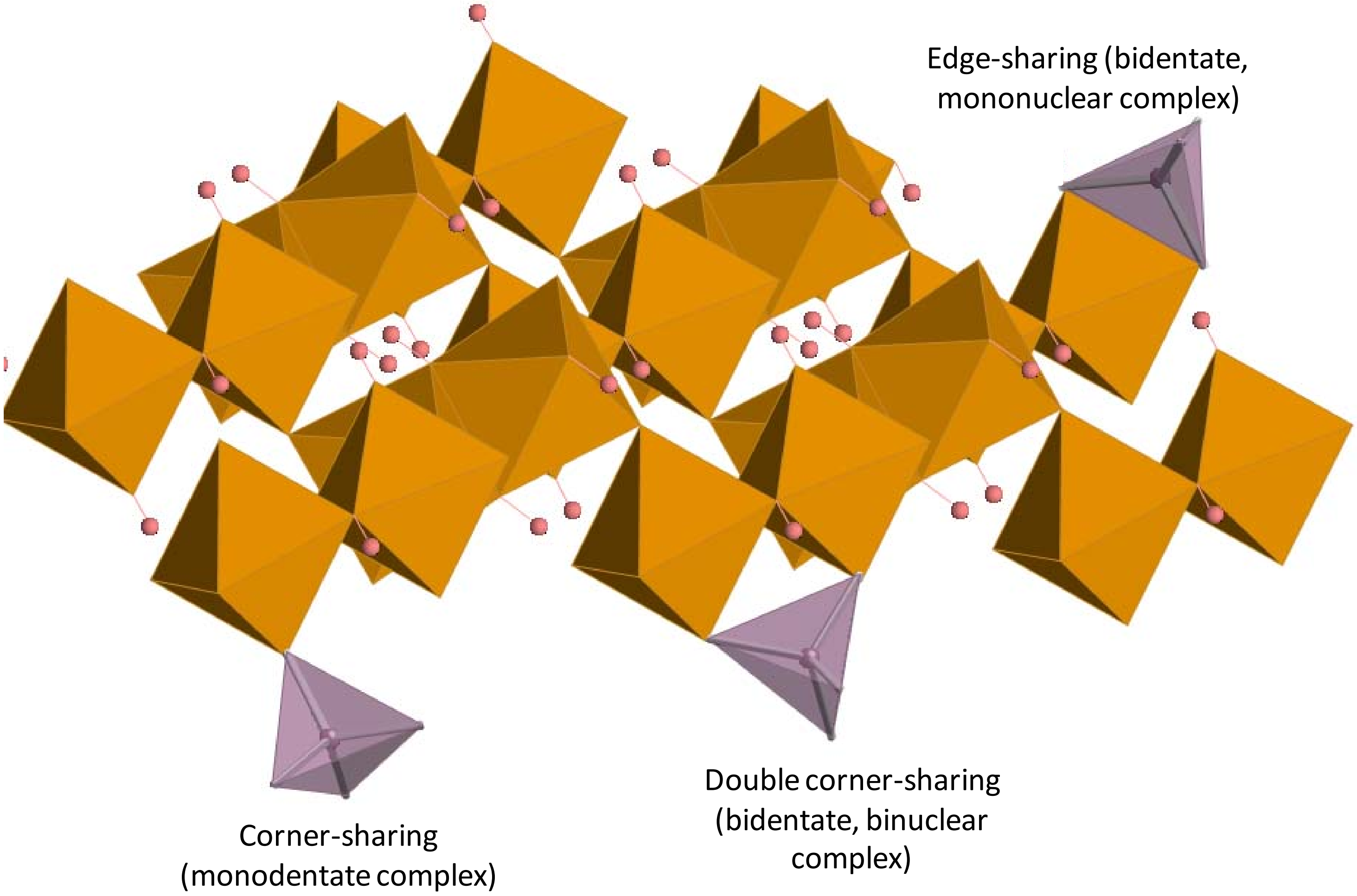

Edge-sharing (bidentate, mononuclear complex)
Double corner-sharing (bidentate, binuclear complex)
Corner-sharing (monodentate complex)

Figure 1.

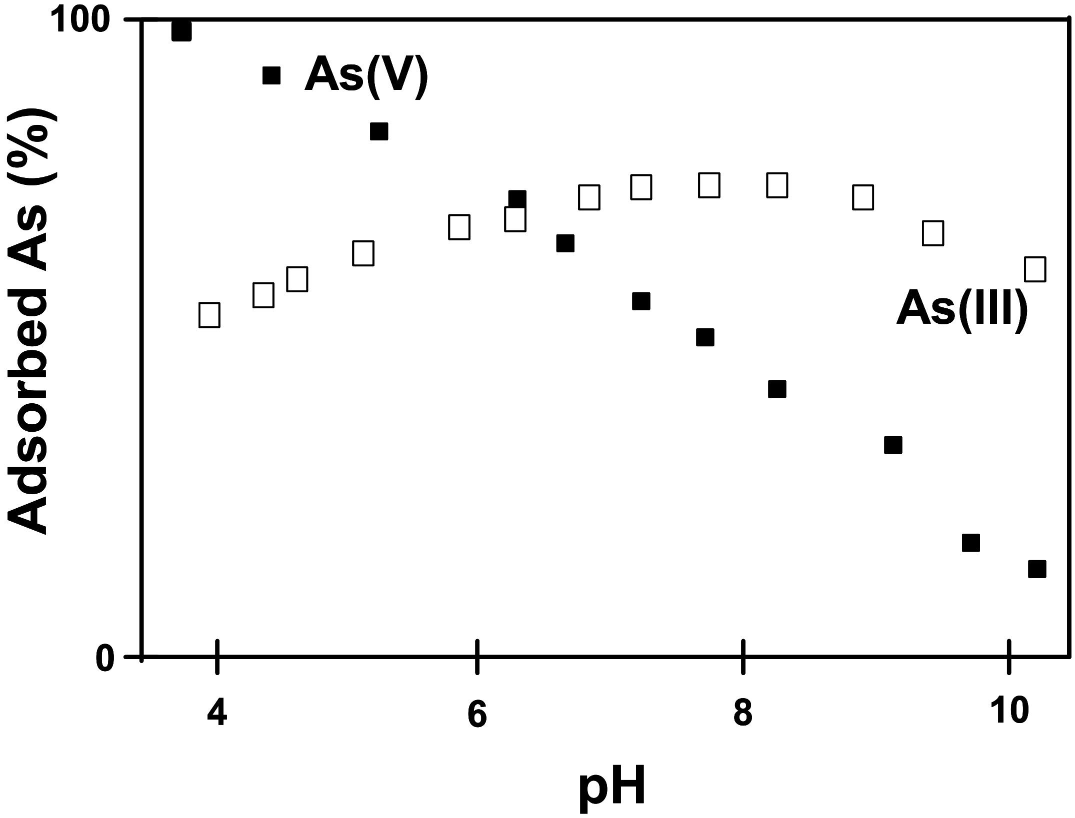


Figure 2.

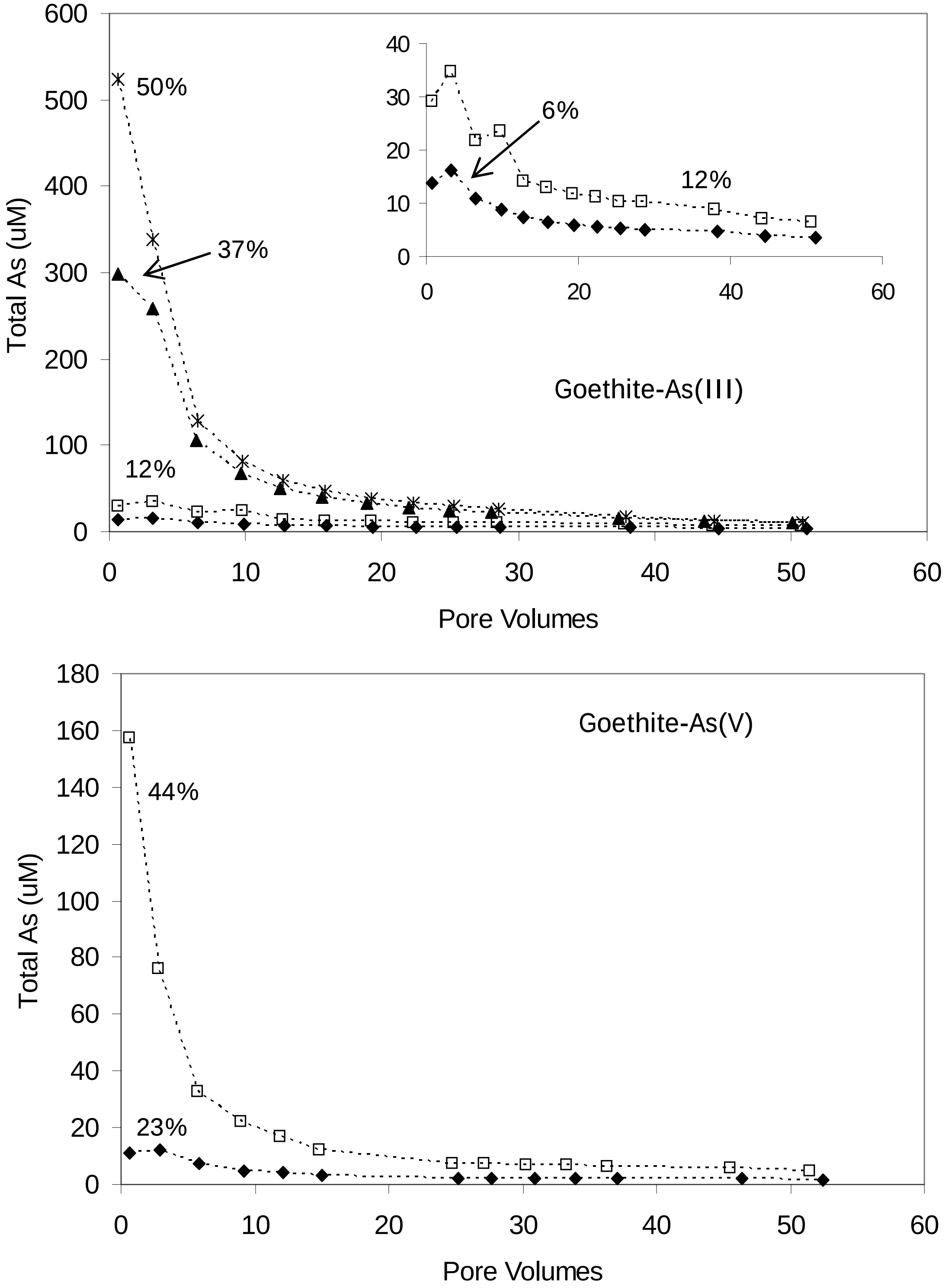

Total As (uM)
Pore Volumes
600
500
400
300
200
100
0
0
10
20
30
40
50
60
50%
37%
12%
40
30
20
10
0
0
20
40
60
6%
12%
Goethite-As(III)
Total As (uM)
Pore Volumes
180
160
140
120
100
80
60
40
20
0
0
10
20
30
40
50
60
Goethite-As(V)
44%
23%

Figure 3.

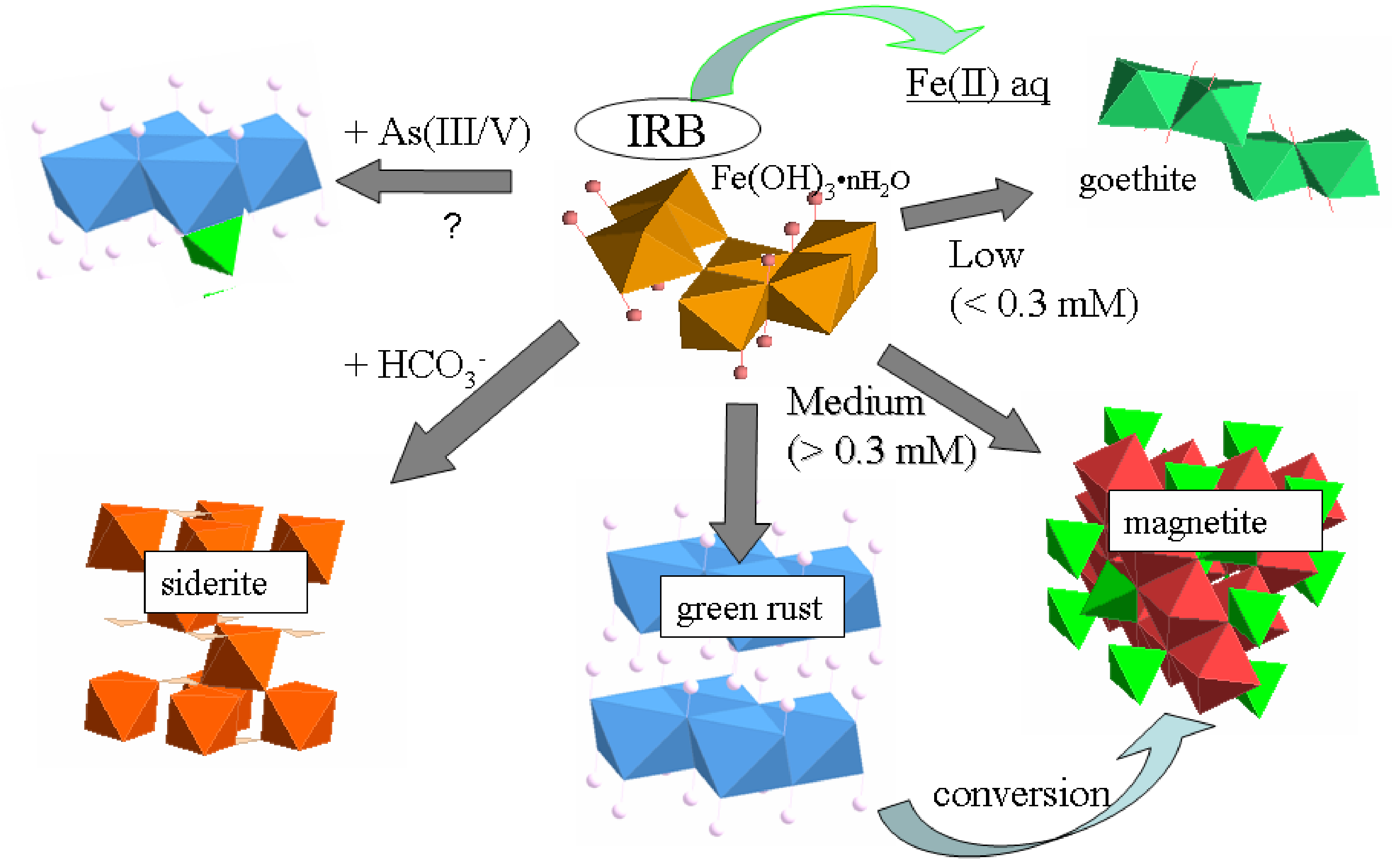
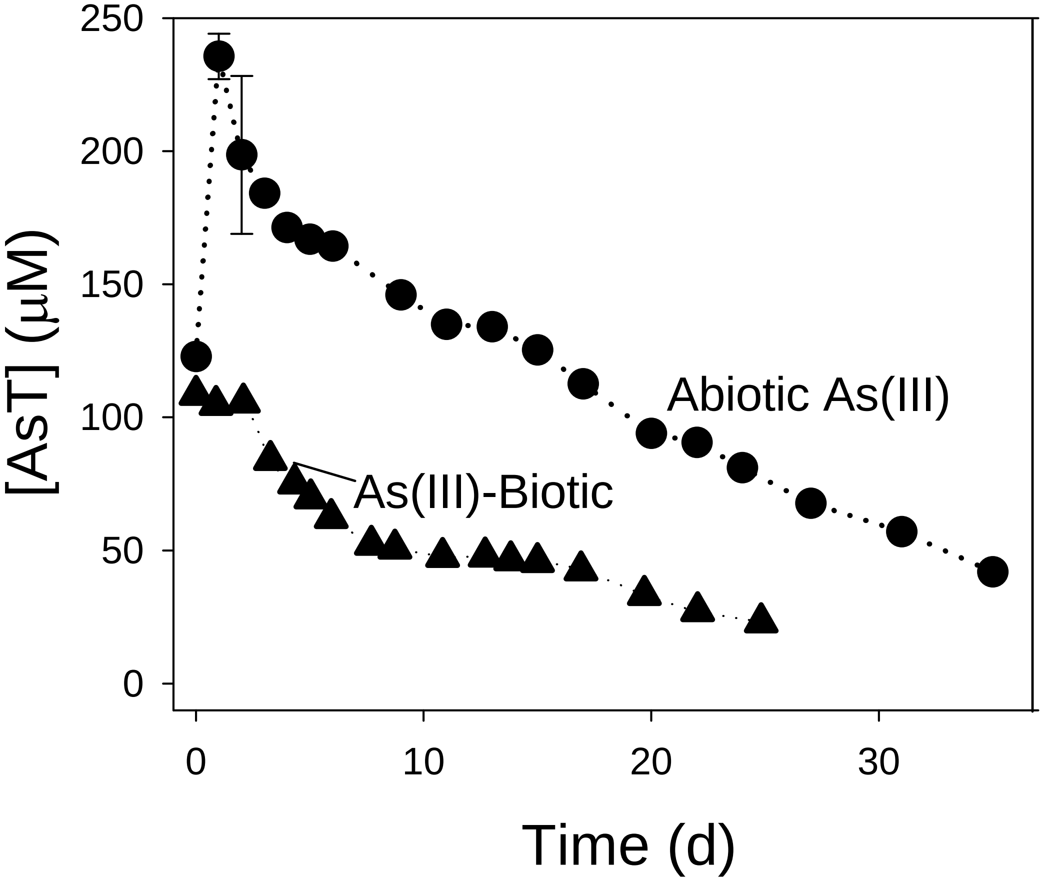
Fe(II) aq
IRB
+ As(III/V)
?
$Fe(OH)_3 \cdot nH_2O$
goethite
Low
(< 0.3 mM)
$+ HCO_3^-$
Medium
(> 0.3 mM)
siderite
green rust
magnetite
conversion

Figure 4.



250
200
150
100
50
0
[AsT] (μM)
0
10
20
30
Time (d)
Abiotic As(III)
As(III)-Biotic

Figure 5.

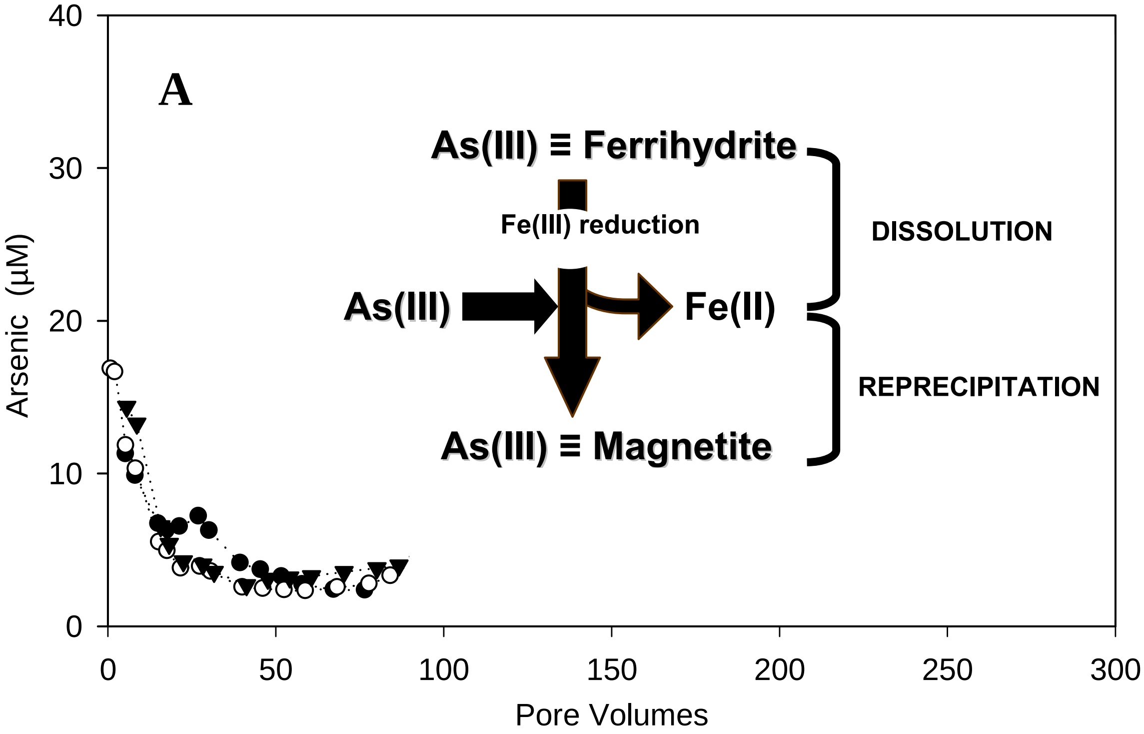

A
As(III) ≡ Ferrihydrite
Fe(III) reduction
As(III)
Fe(II)
As(III) ≡ Magnetite
DISSOLUTION
REPRECIPITATION
Arsenic (µM)
0
10
20
30
40
Pore Volumes
0
50
100
150
200
250
300

Figure 6A.

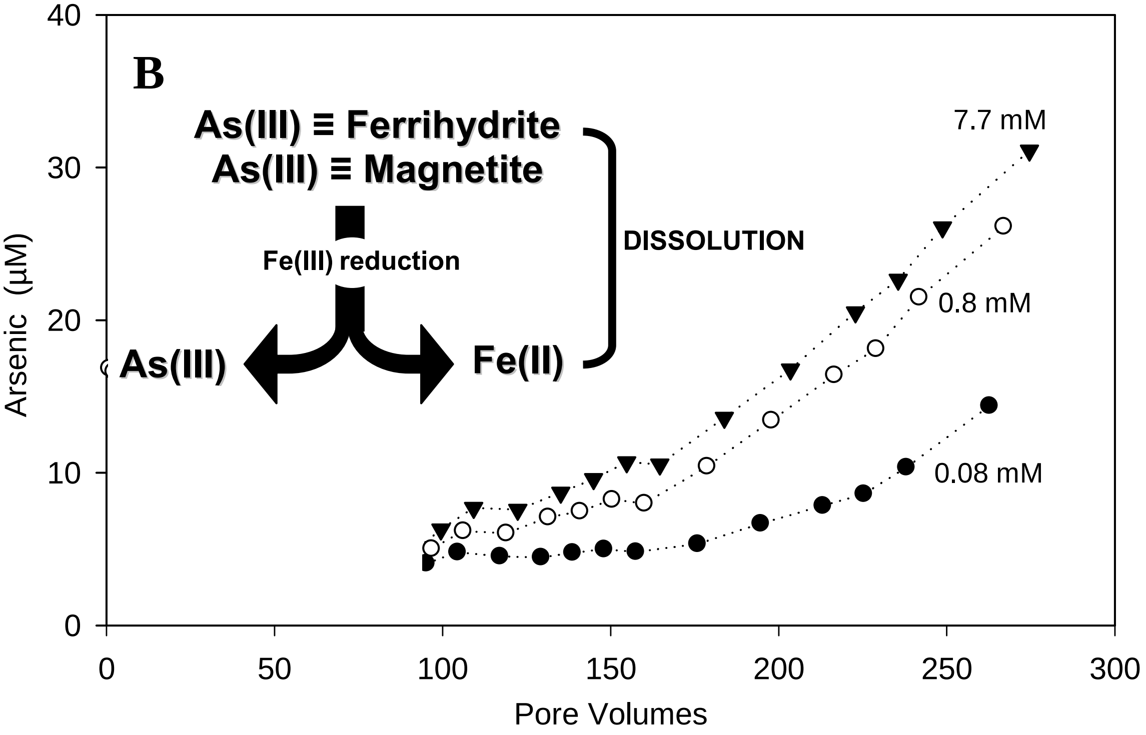
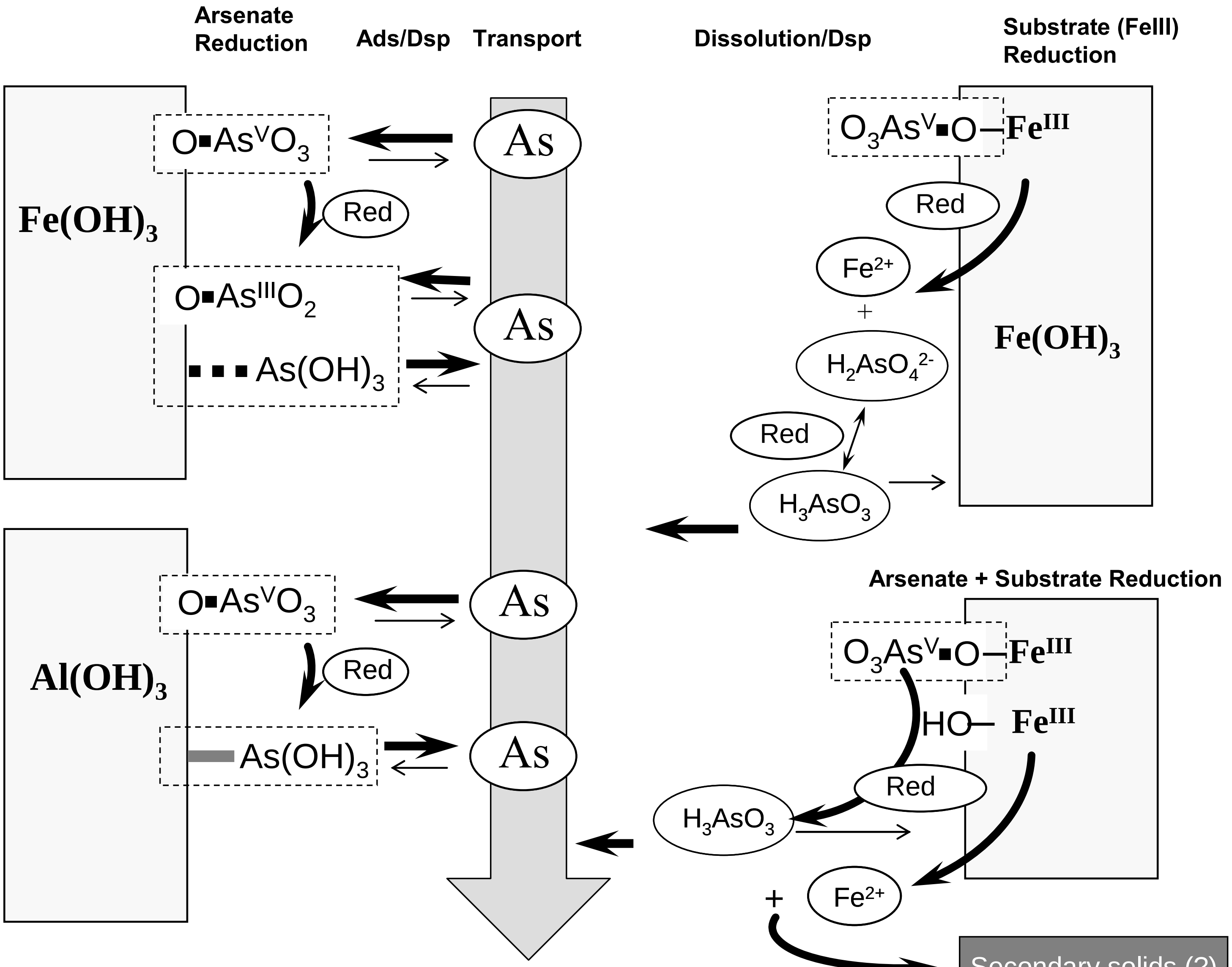

B
As(III) ≡ Ferrihydrite
As(III) ≡ Magnetite
Fe(III) reduction
DISSOLUTION
As(III)
Fe(II)
7.7 mM
0.8 mM
0.08 mM
Arsenic (μM)
Pore Volumes
0
10
20
30
40
0
50
100
150
200
250
300

Figure 6B.



Arsenate Reduction
Ads/Dsp
Transport
Dissolution/Dsp
Substrate (FeIII) Reduction
Fe(OH)$_3$
$O \blacksquare As^{V}O_3$
Red
$O \blacksquare As^{III}O_2$
$\blacksquare\blacksquare\blacksquare As(OH)_3$
As
As
As
As
$O_3As^{V} \blacksquare O - Fe^{III}$
Red
$Fe^{2+}$
+
Fe(OH)$_3$
$H_2AsO_4^{2-}$
Red
$H_3AsO_3$
Al(OH)$_3$
$O \blacksquare As^{V}O_3$
Red
$As(OH)_3$
Arsenate + Substrate Reduction
$O_3As^{V} \blacksquare O - Fe^{III}$
$HO - Fe^{III}$
Red
$H_3AsO_3$
+
$Fe^{2+}$
Secondary solids (?)

Figure 7.