Chapter 2

Biogeochemical arsenic and iron cycling in freshwater sediments

2.1 Arsenic in the environment

2.1.1 Sources of Arsenic

With the relatively recent discovery that millions of people worldwide are affected by arsenic (As) contaminated drinking water, there has been a renewed interest in arsenic sources and biogeochemical processes that lead to As mobilization. Although there are both natural and anthropogenic inputs of As to the environment, elevated As concentrations in groundwater are often due to naturally-occurring As deposits. While the average abundance of As in the earth's crust is between 2 and 5 mg/kg, enrichment in igneous and sedimentary rocks, such as shale and coal deposits, is not uncommon (Cullen and Reimer 1989; Smedley and Kinniburgh 2002). Arsenic can co-occur with nickel (Ni), cobalt (Co), copper (Cu), and iron (Fe), as well as precious metals such as silver (Ag) and gold (Au), especially in sulfidic ores (Tamaki and Frankenberger 1992). Arsenic-containing pyrite (FeS) is probably the most common mineral source of As, although As is often found associated with more weathered phases (Nordstrom 2002). Mine tailings can contain substantial amounts of As, and the weathering of these deposits can liberate As into the surface- or groundwater, where numerous chemical and biological transformations can take place (Harrington et al. 1998; Cummings et al. 2000).

Arsenic can also be directly released into the aquatic environment through geothermal water, such as the hot springs in Hot Creek (Willets et al. 1967; Wilkie and Hering 1998). Anthropogenic sources of As include pesticide application, coal fly ash, smelting slag, feed additives, semiconductor chips, and As-treated wood, which can cause local water contamination.

High As concentrations in groundwater are not necessarily directly linked to geologic materials with high As content. Hering and Kneebone calculated that, in sediment with an As concentration of 1.8 mg/kg (crustal abundance), only a small fraction of the total As in the solid phase would be needed to account for a dissolved As concentration of ≥10 µg/L (Hering and Kneebone 2001). Therefore, As mobility is related not only to the amount of As in the geological source material, but also to the environmental conditions that control chemical and biological transformation of the material.

Iron-, aluminum (Al)-, and manganese (Mn)-rich minerals are an important sink for As in sediments, particularly through adsorption to mineral surfaces. Arsenic associated with Fe(III) oxide coatings on weathered alluvial sediments has been hypothesized to be the primary source of As in the Bengal delta aquifer, and release to groundwater occurs upon reductive dissolution of the Fe(III) oxide coating (Nickson et al. 1998; Nickson et al. 2000; Acharyya 2002; McArthur et al. 2004). Sedimentary biogeochemical processes are the focus of this work, with particular emphasis on Fe and As transformations.

2.1.2. Arsenic speciation

Arsenic is stable in several oxidation states (-III, 0, +III, +V), but the +III and +V states are the most common in natural systems. Arsine (-III), a compound with extremely high toxicity, can be formed under very reducing conditions, but its occurrence in nature is relatively rare. Both inorganic and organic species of As are present in the environment, although inorganic forms are typically more abundant in freshwater systems. Mobility and toxicity strongly depend on the oxidation state and structure. The inorganic species are more acutely toxic than organic species, and inorganic As(III) has a higher acute mammalian toxicity than As(V) (Ng et al. 2003). The effects of oxidation state on chronic toxicity are confounded by the redox conversion of As(III) and As(V) within human cells and tissues.

2.1.2.1 Inorganic As

Arsenite [As(III); $H_xAsO_3^{x-3}$, x=0-3] and arsenate [As(V); $H_xAsO_4^{x-3}$, x=0-3] are the two most environmentally-relevant inorganic forms of arsenic in freshwater systems. Arsenate is an anion at the pH of most natural waters ($H_2AsO_4^-$ and $HAsO_4^{2-}$), while arsenite is a neutral species (Table 2.1). The structure and chemistry of arsenate is similar to phosphate ($H_xPO_4^{x-3}$, x=0-3); this similarity has significant implications for sorption behavior and microbial metabolism. The toxicity of As(V) is due to its interference with oxidative phosphorylation in cells, by substituting for P in adenosine triphosphate (ATP) synthesis, essentially deactivating intracellular energy storage. As(III) toxicity is caused by a strong affinity for sulfhydryl groups, such as thiol groups in enzymes (NRC 1999).

As(V) is thermodynamically stable under oxic conditions, while As(III) is stable under more reducing conditions. However, As(V) and As(III) are often found to co-occur in both oxic and anoxic waters and sediments (Anderson and Bruland 1991) due to redox kinetics. For example, the oxidation of As(III) by O_2 is slow (on the order of several weeks), while bacterially-mediated redox reactions can be much faster (Cullen and Reimer 1989; Dowdle et al. 1996). The observed speciation of As in natural water depends on the local environmental conditions such as bacterial activity, sediment mineralogy, pH, and redox potential.

Table 2.1. Acidity constants for As(V) and As(III) at zero ionic strength from Nordstrom and Archer (Nordstrom and Archer 2003). The symbol "=" denotes chemical equilibrium.

Reactions	pK_a
Arsenate:	
$H_3AsO_4 = H_2AsO_4^- + H^+$	2.30
$H_2AsO_4^- = HAsO_4^{2-} + H^+$	6.99
$HAsO_4^{2-} = AsO_4^{3-} + H^+$	11.80
Arsenite:	
$H_3AsO_3 = H_2AsO_3^- + H^+$	9.17

2.1.2.2 Organic arsenic

Although there are many forms of organic As, the most common organic species are monomethylated and dimethylated As(III) and As(V). Organic As is less acutely toxic than the inorganic species, and methylation of inorganic As is one type of detoxification mechanism for some bacteria, fungi, phytoplankton, and higher level organisms such as humans. Methylation can also occur when organisms are stressed from nutrient limitation

(Cullen and Reimer 1989; Anderson and Bruland 1991; Ng et al. 2003). Organoarsenicals are typically direct metabolic products and should not be confused with inorganic As complexed with natural organic matter (NOM) (see section 2.4.2).

Both inorganic and organic As can be adsorbed onto mineral surfaces, a reaction which is strongly dependent on pH. Inorganic As adsorption will be discussed in greater depth in section 2.2.1. In adsorption studies with monomethylarsonic acid (MMAA) and dimethlyarsinic acid (DMAA), the affinity of the organoarsenic species for Fe oxides was observed to be less than that of As(V) and greater than that of As(III) below pH 7, but less than that of both inorganic forms of As above pH 7 (Xu et al. 1991; Bowell 1994). In sediment environments at circumneutral pH, organoarsenicals may be more mobile than inorganic forms.

Significant levels of organoarsenicals can be found seasonally in surface waters, but organoarsenicals generally contribute less than 10% of the total As in interstitial water except in isolated instances (Cullen and Reimer 1989; Anderson and Bruland 1991; Azcue and Nriagu 1994; NRC 1999; Newman 2000). Thus, inorganic As will be the focus of further discussion in this work.

2.2 Interactions of arsenic with iron

2.2.1 Adsorption of As onto Fe surfaces

Dissolved As concentrations can be controlled by precipitation or by sorption onto mineral phases such as Fe(III) oxyhydroxides, Fe(III) hydroxides, and Fe(III) oxides (hereafter collectively referred to as Fe(III) oxides) (Hering and Kneebone 2001).

Adsorption of As onto Fe oxides has been observed to be an important environmental process and is prevalent in many different sediment environments, including Haiwee Reservoir (Root et al. 2006).

2.2.1.1 Structure of HFO

Fe(III) oxides are ubiquitous in nature, and are often the result of aerobic weathering of magmatic rocks. Fe(III) is very insoluble at circumneutral pH and can precipitate as a number of different Fe(III) oxide minerals. Fe(III) oxides can form coatings on other mineral grains, making them chemically important substrates in the environment, even if they are not the dominant mineral by weight (Dzombak and Morel 1990). Amorphous Fe oxyhydroxide, also known as hydrous ferric oxide (HFO) or ferrihydrite, has the highest solubility of the Fe(III) oxides, and is often the first mineral type to precipitate upon hydrolysis of Fe(III) (Zachara et al. 2002). HFO has a very poorly ordered crystal structure with high surface area and is an excellent sorbent for a wide range of chemical species. Because of its amorphous structure and large water content, a molecular formula has not been established, and is often approximated by $Fe(OH)_3$, FeOOH, Fe_2O_3, or empirical formulae such as $Fe_5O_{12}H_9$ (Eggleton and Fitzpatrick 1988; Dzombak and Morel 1990; Cornell and Schwertmann 1996; Janney et al. 2000; Zachara et al. 2002). Depending on precipitation conditions, the degree of order can vary in both synthetic and natural HFO. Surface area measurements can be made by nitrogen gas adsorption (BET analysis), but it is often hard to reproduce the results due to the porous nature of HFO. A value of 600 m^2/g is accepted as an appropriate estimate of HFO surface area (Dzombak and Morel 1990). During precipitation, HFO initially forms spherical precipitates ranging from 30 to 100 Å in diameter, but will form larger aggregates on the order of several microns within minutes to hours of precipitation (Eggleton and Fitzpatrick 1988; Cornell and Schwertmann 1996). Because of the disordered structure and large water content, HFO resembles a gel rather than a homogeneous solid phase (Dzombak and Morel 1990).

In general, HFO will tend to recrystallize into more thermodynamically stable Fe(III) oxides, such as hematite (Fe_2O_3), goethite (α-FeOOH), and lepidocrocite (γ-FeOOH) (Cornell and Schwertmann 1996; Zachara et al. 2002). HFO will primarily transform into goethite, although mixtures of several minerals can also form. Goethite formation requires local dissolution of the HFO followed by nucleation and re-crystallization. This process occurs over a period of weeks to months in the laboratory in the absence of adsorbing ions (Raven et al. 1998). Transformation to hematite is also possible through dehydration and rearrangement of the crystal structure and does not require the local dissolution of the HFO. The rates of transformation to goethite and/or hematite increase with increasing pH and temperature (Cornell and Schwertmann 1996; Makris et al. 2005), although hematite is preferentially formed at pH 7-8 and higher temperatures, while goethite is formed at higher pH values and lower temperatures (Baltpurvins et al. 1996). The presence of sorbed ions on the HFO surface also affects the rate of transformation. Numerous studies have found that nitrate, chloride, sulfate, silicate, phosphate, Al, titanium (Ti), Mn, organic matter, and various trace elements such as Cu, Ni, cadmium (Cd), vanadium (V), Co, zinc (Zn) and As retard the conversion of HFO (Waychunas et al. 1993; Baltpurvins et al. 1996; Cornell and Schwertmann 1996; Ford et al. 1997; Ford 2002; Makris et al. 2005). Adsorbed ions can stabilize natural ferrihydrite in soil environments by inhibiting internal reordering or dissolution.

Waychunas et al. observed that as the concentration of As(V) on the surface increased, the disorder of the HFO also increased (Waychunas et al. 1993). Adsorbed compounds such as organic carbon may also change the relative amounts of the transformation products (Cornell and Schwertmann 1996). The presence of Fe(II) can affect the transformation products substantially, and will be discussed in section 2.2.3.3.

As HFO transforms into more thermodynamically stable phases, it can either incorporate trace elements into the crystal structure or release them into the porewater as the surface area decreases during recrystallization (Ford et al. 1997). When Ford co-precipitated As(V) with HFO, As(V) was eventually incorporated into the hematite structure but not into goethite (Ford 2002). In natural sediments, As may be more permanently sequestered if it is incorporated into a mineral structure. However, if As is not incorporated, a decrease in available surface sites might release As into the porewaters. The fate of As also depends on the relative surface binding strengths of As onto the transformation products. Dixit and Hering found that the intrinsic surface complexation constant for As(V) on goethite was stronger than the corresponding constant for As(V) on HFO, implying that transformation to goethite will not necessarily release As(V), unless the total number of surface sites is substantially decreased (Dixit and Hering 2003).

2.2.1.2 As(V) and As(III) adsorption onto HFO

Sorption reactions at equilibrium satisfy a mass law equation, similar to aqueous equilibrium reactions. For surface reactions, the equilibrium constant is a product of an intrinsic term, corresponding to the chemical free energy of binding, and a coulombic term, which describes the effect of electrostatic charge at the surface.

Surface sites exhibit acid-base chemistry. Positive, negative, and neutral surface groups can be present depending on extent of protonation, and can be described by equations (2.1) and (2.2), where the symbol "≡" denotes a surface site and "=" signifies chemical equilibrium (Dzombak and Morel 1990).

$$\equiv FeOH = \equiv FeO^{-} + H^{+} \qquad (2.1)$$

$$\equiv FeOH_2^{+} = \equiv FeOH + H^{+} \qquad (2.2)$$

Adsorption of As(V) and As(III) occurs via ligand exchange reactions with hydroxyl surface groups, also known as inner sphere complexation (Dzombak and Morel 1990). Neither the adsorption of As(III) nor As(V) is strongly affected by changes in ionic strength, which is indicative of inner sphere complexation (Pierce and Moore 1982; Hsia et al. 1994; Jain et al. 1999; Goldberg and Johnston 2001). Further evidence of specific adsorption has been obtained by spectroscopic data and is discussed in section 2.2.1.3.

Adsorbed As species are weak acids and can affect the surface charge due to proton exchange reactions. Whether As adsorbs as a mononuclear or binuclear complex has implications for the level of protonation of the surface species, illustrated in equations (2.3) and (2.4) with adsorbed As(III) species as an example. Binuclear complexes have fewer acidic protons due to the binding with the Fe oxide surface.

$$\equiv FeOH + H_3AsO_3 = \equiv FeH_xAsO_3^{x-2} + H_2O + (2-x)H^{+} \qquad \text{where } x=0\text{-}2 \qquad (2.3)$$

$$(\equiv FeOH)_2 + H_3AsO_3 = (\equiv Fe)_2H_yAsO_3^{y-1} + 2H_2O + (1-y)H^{+} \qquad \text{where } y=0,1 \qquad (2.4)$$

Adsorption isotherms (adsorbed As vs. dissolved As) and envelopes (adsorbed As vs. pH) have shown that As(V) and As(III) adsorption onto HFO depends strongly on pH and As concentration. Arsenate adsorption decreases with increasing pH, particularly above pH 7-8, and maximum sorption occurs at low pH values (pH 3-7) (Pierce and Moore 1982; Raven et al. 1998; Goldberg 2002; Dixit and Hering 2003). Arsenite has a broad maximum adsorption at circumneutral pH, and decreasing sorption at high and low pH values (Pierce and Moore 1982; Dixit and Hering 2003). Arsenite is often considered to be more mobile than As(V), but this generalization is not always true; the relative affinity for HFO depends strongly on pH as well as the presence of other adsorbed ions (Dixit and Hering 2003).

The initial rate of As adsorption is fast (~90% within 2 hours) onto pre-formed HFO, followed by a period of slower uptake (>100 hours) (Pierce and Moore 1982; Fuller et al. 1993; Raven et al. 1998). Fuller et al. accurately modeled this observation with As(V) diffusion into a sphere, with a subset of adsorption sites located in the interior requiring longer diffusion times than exterior surface sites (Fuller et al. 1993). Physically, this spherical model could correspond to an aggregate of HFO particles with surface sites in the interior requiring molecular diffusion of As into the aggregate. After aging the HFO for 6 days before As adsorption, the total amount of adsorbed As decreased by 20%, but the rates were unchanged (Fuller et al. 1993). Co-precipitated As(V) and HFO had significantly higher As adsorption initially but the As slowly desorbed as aggregation and aging occurred. The co-precipitated As(V) and HFO approached a steady-state concentration similar to As(V) adsorbed onto pre-synthesized HFO after >400 hours, indicating that the rate of As adorption/desorption onto HFO may be diffusion controlled (Fuller et al. 1993). As(III) may have slightly faster adsorption kinetics, although this appears to be highly dependent on experimental conditions (Raven et al. 1998).

2.2.1.3 Molecular structure of adsorbed As onto Fe(III) oxide surfaces

X-ray absorption spectroscopy (XAS) is a synchrotron-based technique for probing element-specific local bonding structures and oxidation states. For a thorough reference on XAS, see the review by Brown et al. (Brown et al. 1988). An absorption edge is a sharp increase in absorption of X-rays that occurs over a narrow range of energy, which is due to excitation of an electron from a deep core state, such as a K-shell electron. The energy at which this excitation occurs depends on the element and its oxidation state. The spectrum near the absorption edge is called X-ray Absorption Near Edge Structure (XANES). The pre-edge region can contain features related to weak electronic transitions. At energies above the absorption edge, low-frequency oscillations due to weak backscattering with nearby atoms are observed. This region of the spectrum is referred to as Extended X-ray Absorption Fine Structure (EXAFS) (Figure 2.1). XANES edges can be used to determine oxidation state of the target element in certain cases because of differences in electronic shielding. Arsenite and arsenate have distinct edges at 11,871 eV and 11,875 eV, respectively, and these regions of the spectrum can be effectively used to determine As oxidation state in solid phases such as sediments. The EXAFS region can be used to identify local bonding structure, such as bond distances, coordination number, and the identity of nearest neighbor atoms. The EXAFS spectrum is extracted from the total spectrum and weighted to enhance the oscillations at higher energy. A Fourier transform is performed to de-convolute the signals from different backscattering atoms. Bond distances and elemental information can be extracted from the Fourier transformed signal.

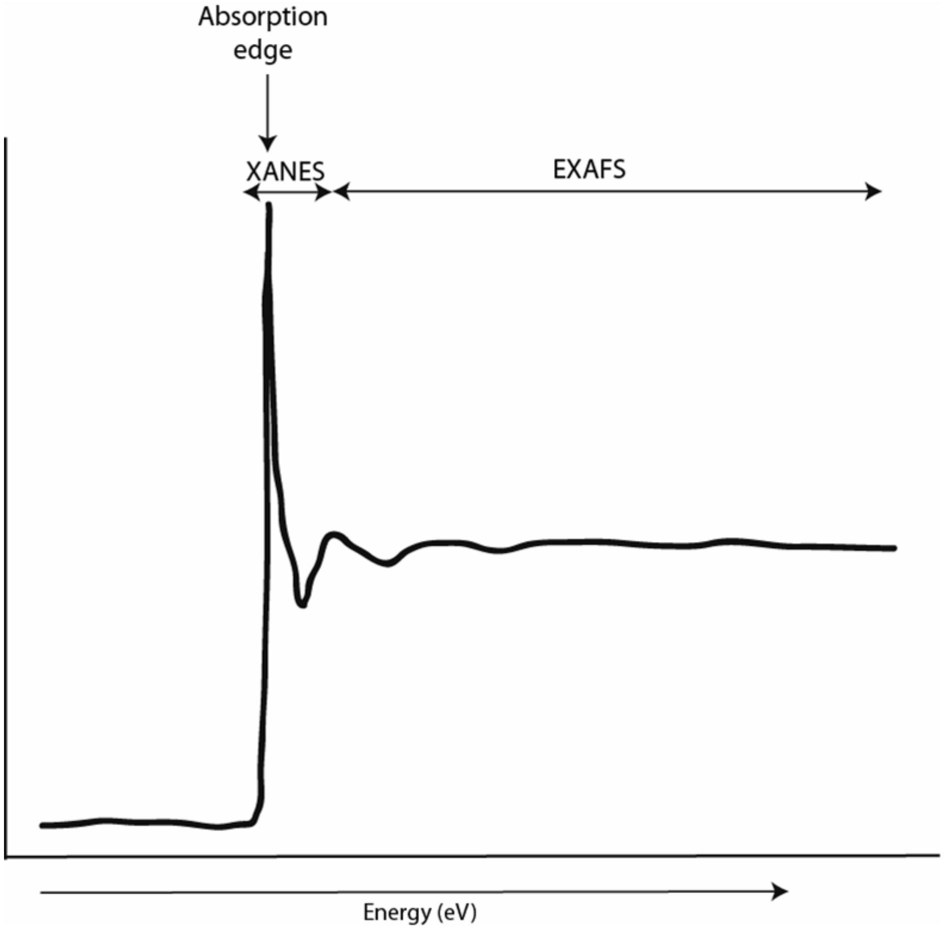

Figure 2.1. Schematic diagram of a normalized XAS spectrum, depicting the absorption edge and the XANES and EXAFS regions. The y-axis has arbitrary units for a normalized spectrum.

Many spectroscopic studies have been performed on As(III) and As(V) adsorbed onto HFO, and all confirm that inner sphere complexation is dominant. Local bonding environments of As(III) and As(V) have been determined by analyzing EXAFS spectra.

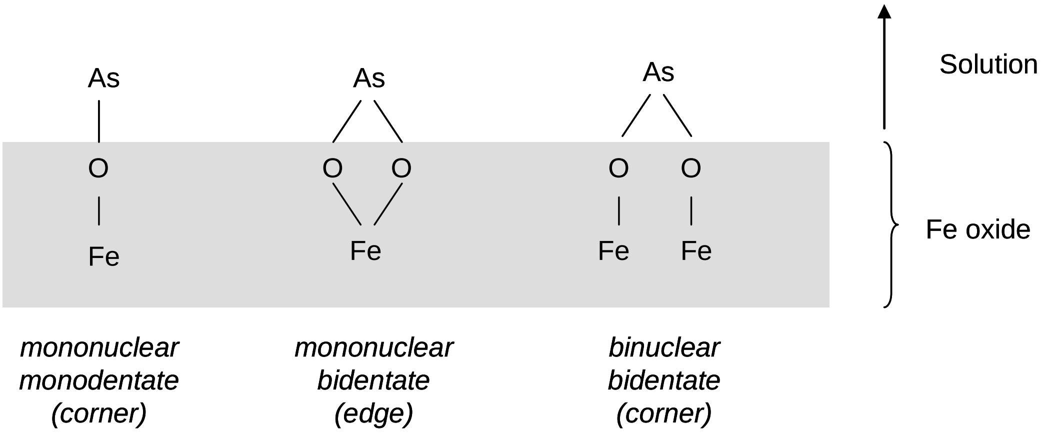

Figure 2.2. Schematic diagram of configurations of As adsorbed onto an Fe oxide surface. Adapted from Cornell and Schwertmann (Cornell and Schwertmann 1996).

There are several possible molecular configurations of As adsorption: mononuclear monodentate, mononuclear bidentate (edge-shared), and binuclear bidentate (corner-shared) (Figure 2.2, 2.3). EXAFS studies have shown that As(V) is primarily adsorbed as binuclear bidentate complexes, with average As-Fe bond lengths between 3.26 Å and 3.3 Å (Waychunas et al. 1993; Sherman and Randall 2003). Waychunas and co-workers proposed a monodentate mononuclear complex that became increasingly abundant as As surface coverage decreased (Waychunas et al. 1993). However, this surface species has been challenged on the basis of thermodynamic instability and crystal growth poisoning effects (Manceau 1995; Sherman and Randall 2003). A mononuclear bidentate complex has been hypothesized by Manceau (Manceau 1995), but this structure has also been questioned due to calculated thermodynamic instability (Waychunas et al. 1995; Sherman and Randall 2003). Arsenite is adsorbed predominantly as binuclear bidentate complexes with an average As-Fe bond length of 3.3 Å, although there is evidence for less-important mononuclear bidentate complexes (Manning et al. 1998;

Ona-Nguema et al. 2005). No mononuclear monodentate complex has been observed for As(III). Binuclear bonding for both As(III) and As(V) has been supported by FTIR studies (Sun and Doner 1996).

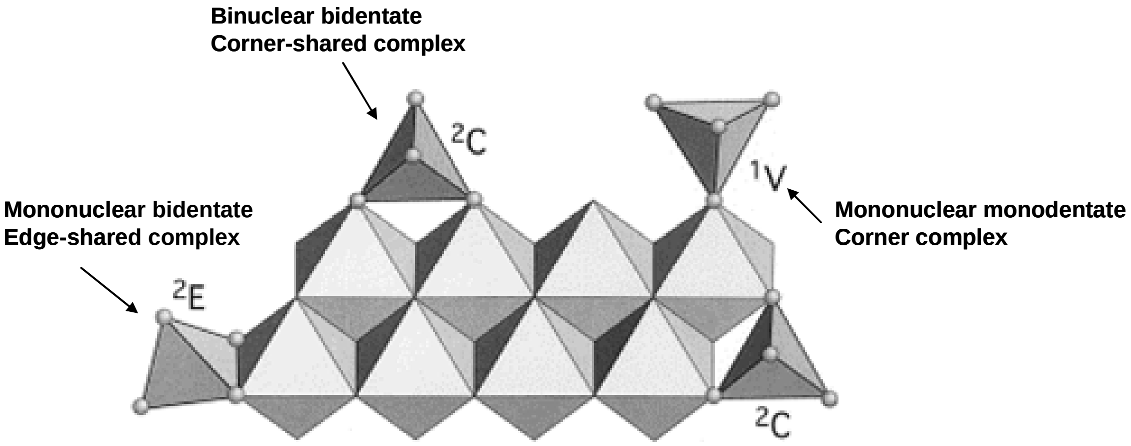

Figure 2.3. Diagram of molecular configurations of As adsorbed onto an Fe oxide surface showing a mononuclear bidentate edge complex (^{2}E), a binuclear bidentate corner complex (^{2}C), and a mononuclear monodentate corner complex (^{1}V). Figure from Sherman and Randall, 2003. Reprinted with permission from Elsevier.

2.2.1.4 Competitive effects on As adsorption

The presence of other adsorbing ions can significantly impact the adsorption of As onto HFO. Arsenic adsorption can be affected by electrostatic, steric, or competitive effects. Phosphate has the greatest effect on sorption of As, due to similarities in molecular structure and surface complexation chemistry. Phosphate competes directly with As for surface sites and effectively inhibits both As(III) and As(V) sorption (Liu et al. 2001; Dixit and Hering 2003) (Figure 2.4). Phosphate sorption is more pH dependent than As(V) sorption, and As(V) may be slightly more strongly adsorbed than phosphate (Jain and Loeppert 2000; Hongshao and Stanforth 2001; Liu et al. 2001; Violante and Pigna 2002; Antelo et al. 2005). The order of sorbate addition affects the extent of sorption, particularly in the case of phosphate and As. The sorbate added first will adsorb to a greater extent than the competing sorbate (Hongshao and Stanforth 2001; Liu et al. 2001). Phosphate effects of As sorption will be discussed in more detail in Chapter 3.

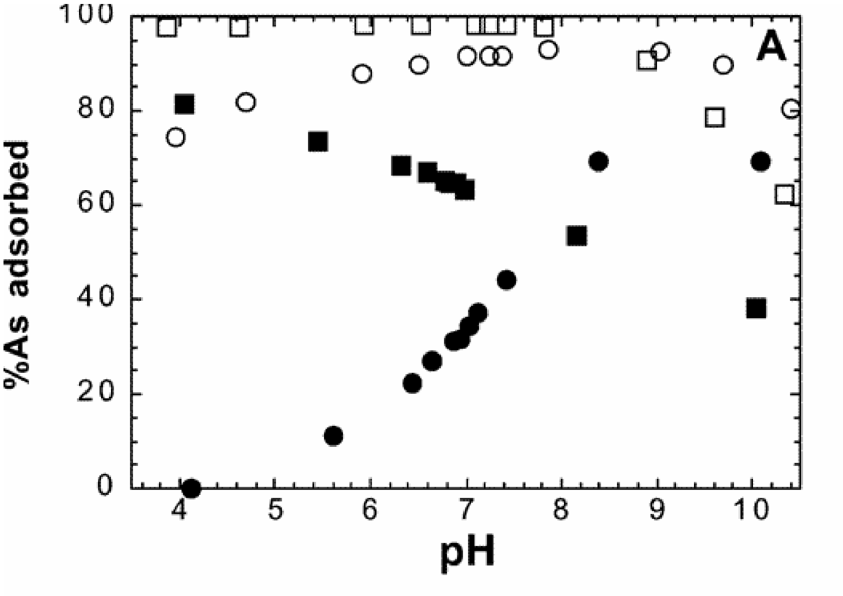

Figure 2.4. As(III) (circles) and As(V) (squares) adsorption envelopes on HFO (0.03 g/L) in the presence of 100 µM phosphate (shaded symbols) and absence of phosphate (open symbols). The total As concentration was 10 µM. Reprinted with permission from Dixit and Hering, 2003. Copyright 2003 American Chemical Society.

Sulfate (H_2SO_4) appears to adsorb to different HFO surface sites than As, and may not directly compete for surface sites in the same way as phosphate (Jain and Loeppert 2000). Sulfate has a very slight affect on As(V) adsorption, but can decrease

As(III) adsorption below pH 7.5 (Wilkie and Hering 1996; Jain and Loeppert 2000; Meng et al. 2000).

The adsorption edge of silicate (H_4SiO_4) is qualitatively similar to that of As(III), with broad maximum adsorption between pH 8-10 (Swedlund and Webster 1999). Silicate decreases As(III) and As(V) adsorption, with a greater effect on As(III) at high silicate concentrations and at pH>8. Silicate forms a polymer on the surface of HFO at high concentrations, resulting in large Si:Fe ratios (>0.1) (Swedlund and Webster 1999; Holm 2002). This surface polymer may inhibit As sorption through steric and/or electrostatic effects. In an experiment by Meng et al., Ca^{2+} or Mg^{2+} counteracted the effect of silicate on As sorption, indicating that a change in surface potential may be at least partially responsible for the inhibition of As adsorption by silicate (Meng et al. 2000). In another study by Wilkie and Hering, Ca^{2+} increased As(V) adsorption onto HFO, most likely due to electrostatic effects (Wilkie and Hering 1996). High concentrations of silicate can also form colloidal Si-Fe(III) polymers that can increase the Fe(III) mobility at high pH (Meng et al. 2000), but the relevance of this effect in natural systems in probably minimal.

The concentrations of carbonate (dissolved CO_2 as H_2CO_3 and its acid dissociation products) in groundwater can be elevated due to microbial respiration and carbonate mineral dissolution. The effect of carbonate concentrations due to atmospheric equilibration (~0.07 mM) on As adsorption is minimal (Fuller et al. 1993; Meng et al. 2000; Arai et al. 2004; Radu et al. 2005). However, higher concentrations (10% $CO_{2(g)}$ = 22 mM dissolved inorganic C) suppressed As(V) adsorption and caused significant amounts of As(III) to desorb in column studies with As(III) pre-equilibrated onto goethite-coated sand (Radu et al. 2005). High concentrations of carbonate affected As(III) sorption more than As(V) (Radu et al. 2005), even though As(V) was hypothesized to be more affected based on surface charge effects (Appelo et al. 2002). Leaching of As from solids by the addition of bicarbonate salts was found to be dependent on both pH and carbonate concentration, with greatest leaching at high carbonate concentrations and at very low or very high pH values (Kim et al. 2000; Anawar et al. 2004). When directly compared to phosphate, carbonate was a much weaker inhibitor of As adsorption (Radu et al. 2005), although it may still be important in groundwater with high carbonate concentrations. Carbonate forms only a very weak complex with As(III) in solution, and As sorption inhibition is likely due to surface effects (Neuberger and Helz 2005).

Carbonate adsorption onto Fe(III) oxide surfaces is most likely a combination of inner and outer sphere complexes (van Geen et al. 1994, Su and Suarez 1997, Villalobos and Leckie 2000, Villalobos and Leckie 2001, Bargar et al. 2005). Arsenic adsorption inhibition is probably due to electrostatic effects from specifically adsorbed carbonate. Carbonate adsorption is highly dependent on pH with maximum sorption on goethite at pH 6 (van Geen et al. 1994). Bicarbonate (HCO_3^-) appears to have a greater affinity for surface complexation than $H_2CO_3^*$ or CO_3^{2-}. Ternary complexation with adsorbed carbonate may also be possible and can affect surface electrostatics (e.g., Na-CO_3-Fe oxide) (Villalobos and Leckie 2001).

Organic carbon may also affect surface complexation of As, and will be discussed in section 2.4.2.

2.2.2 As mineral phases

The partitioning of As between dissolved and solid phases can be controlled by As mineral precipitation as well as adsorption. Arsenite forms insoluble precipitates with sulfide, such as orpiment (As_2S_3), realgar (AsS), and arsenopyrite (FeAsS) in reducing environments (Cullen and Reimer 1989; Nordstrom and Archer 2003); precipitation can be microbially mediated (Newman et al. 1997; Nordstrom and Archer 2003). However, Haiwee Reservoir is non-sulfidogenic, and As-S-Fe mineral formation is unlikely. Scorodite ($FeAsO_4{\cdot}2H_2O$) precipitates only in very acidic environments such as acid mine drainage (Langmuir et al. 2006). Jia et al. observed a ferric arsenate precipitate that formed on the surface of HFO at low pH (pH 3-4), but sorption dominated the As-Fe association at circumneutral pH (Jia et al. 2006). Thus, sorption processes are dominant at Haiwee Reservoir.

2.2.3 Reductive Dissolution of Fe phases

There are four general pathways for Fe(III) dissolution: proton-assisted (acid), ligand-promoted acid, reductive, and ligand-promoted reductive dissolution (Afonso et al. 1990). Ligands such as oxalate can promote the dissolution (either reductive or non-reductive) of Fe(III) oxides. However, reductive dissolution is the most important pathway in the natural environment (Cornell and Schwertmann 1996). Reductive dissolution is driven by the reduction of Fe(III) in the solid phase to the more soluble Fe(II). The dissolution of the solid Fe(III) oxide can potentially release adsorbed trace elements into the porewaters. Reductive dissolution has been observed to release As into aquifers in Bangladesh (Nickson et al. 1998; Nickson et al. 2000; Acharyya 2002; Bose and Sharma 2002; Swartz et al. 2004) and the United States (Peterson and Carpenter 1986; Welch and Lico 1998; Cummings et al. 2000; Welch et al. 2000; Kneebone et al. 2002), as well as into lake sediment porewaters in New Zealand (Aggett and O'Brien 1985) and Switzerland (Azcue and Nriagu 1994). The co-incident increase in dissolved As and Fe concentrations is a strong indicator that reductive dissolution of Fe(III) phases is a likely mechanism of As mobilization. Arsenic mobilization is controlled by the ability of Fe(III) oxides in the subsurface to re-adsorb As as reductive dissolution proceeds (Welch et al. 2000; Swartz et al. 2004; Pedersen et al. 2006) and by the presence of competing ions.

There are both abiotic and biotic pathways for the reductive dissolution of Fe(III). Lovely and co-workers compared the reduction of HFO by three strains of bacteria (a sediment isolate GS-15, *Clostridium pasteurianum*, and *Escherichia coli*) to chemical reduction by a number of different organic compounds, some of which are likely to be found in a natural sedimentary environment. Microbial reduction was faster and more extensive than chemical reduction at neutral pH, suggesting that microorganisms are primarily responsible for Fe(III) reduction in non-sulfidogenic sediments (Lovely et al. 1991). Roden noted that chemical reduction rates vary by three orders of magnitude while bacterial rates are more constant even between different strains, and extrapolation of laboratory chemical rates of compounds such as ascorbate to environmental conditions should be done with caution (Roden 2003). However, it is useful to compare the differences in mechanisms between chemical and biological reductive dissolution, noting that both pathways could be important under a variety of environmental conditions.

2.2.3.1 Chemical Mechanisms

Chemical reductants include H_2S and various organic compounds, such as ascorbate and humic acids (Hering and Stumm 1990; Schwertmann 1991; Rochette et al. 2000; Thamdrup 2000). Reductive dissolution is thought to occur through a series of reaction steps: adsorption of the reductant, electron transfer to the Fe(III), and release of Fe(II) from the lattice (usually the rate-limiting step). Fe(II) is more readily released from the crystal lattice because the binding energy is less for Fe(II) than Fe(III). In addition, surface protonation near the sorption site of the reductant can accelerate dissolution (Suter et al. 1991). Organic compounds that are not involved in electron transfer can either accelerate or inhibit reduction. If sorption of the organic compound polarizes the Fe bonds making the Fe(II) bond easier to break, reduction will occur at a faster rate. On the other hand, large organic compounds on the Fe(III) oxide surface may sterically hinder adsorption of the reductant, thus decreasing the reduction rate (Schwertmann 1991). The reaction pathway can be additionally complicated by catalysis of the dissolution and subsequent mineralogical transformations of the parent Fe(III) phase by Fe(II) (Zinder et al. 1986; Schwertmann 1991; Suter et al. 1991; Benner et al. 2002; Hansel et al. 2005; Pedersen et al. 2005; Pedersen et al. 2006). The effect of Fe(II) on secondary mineral formation will be discussed in more detail in section 2.2.3.3. Photoreduction has been observed for Fe(III) oxides, but is unlikely to be important in Haiwee Reservoir sediments, where iron reduction does not occur at the surface of the sediment.

Adsorbed oxyanions, such as As(V), have been shown to inhibit the reductive dissolution in laboratory studies with ascorbic acid as a reductant and in ligand-promoted dissolution. This could be due to a decrease in surface protonation and/or reductant sorption because of steric or electrostatic effects at the oxide surface (Bondietti et al. 1993; Biber et al. 1994; Kraemer et al. 1998; Eick et al. 1999; Pedersen et al. 2006).

2.2.3.2 Biological Mechanisms

Bacterial Fe(III) reduction can be carried out by a genetically and metabolically diverse group of microorganisms. Bacteria can generally utilize many electron acceptors, usually coupled to organic carbon or H_2 oxidation. The sequence of electron acceptors follows decreasing $p\varepsilon$: O_2, nitrate, Mn oxides, Fe(III) oxides, sulfate, and methane (fermentation) (Stumm and Morgan 1996). Fe(III) reduction may be responsible for a significant fraction of total organic carbon mineralization in sediments (Thamdrup 2000).

The mechanism of enzymatic reduction is not well known. Some organisms require direct contact with an Fe(III) oxide surface, while others may synthesize electron shuttle compounds or use naturally-occurring humic acids to transfer electrons between the cell and the Fe(III) oxide surface (Thamdrup 2000). Some cells may produce reactive oxygen species such as superoxide to mediate Fe(III) dissolution (Fujii et al. 2006). Natural Fe(III) chelators may also accelerate microbial Fe reduction without requiring direct cellular contact with the solid phase (Jones et al. 2000; Royer et al. 2002). Rates of bacterial Fe(III) reduction are highest with a poorly crystalline Fe(III) phase, and decrease with increasing crystallinity (Roden and Zachara 1996), confirming the observation that amorphous Fe(III) oxides are the most bioavailable.

2.2.3.3 Secondary mineral transformation

Fe(II) adsorption onto Fe(III) oxides is unique in that electron transfer into the Fe(III) oxide results in migration of the electron (and effectively the Fe(II)) into the bulk mineral. This migration was observed by Mössbauer spectroscopy and isotopic exchange experiments (Williams and Scherer 2004; Pedersen et al. 2005). Fe(II) can destabilize the bulk mineral, allowing mineral transformations to take place more readily.

In the presence of Fe(II), HFO can transform to numerous other Fe(III) oxides such as goethite (α-FeOOH), lepidocrocite (γ-FeOOH), and hematite (Fe_2O_3), as well as other Fe(II) or mixed Fe(II)-Fe(III) minerals such as magnetite (Fe_3O_4), siderite ($FeCO_3$), vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$), and green rusts. The rate of transformation increases with increasing Fe(II) concentrations (Hansel et al. 2005; Pedersen et al. 2006). At low Fe(II) concentrations, goethite and lepidocrocite formation is catalyzed by increased local dissolution of the Fe(III) oxide because of Fe(II) destabilization of the Fe(III) oxide surface. Magnetite formation is more favorable at higher Fe(II) concentrations, and proceeds through solid state conversion or surface nucleation. At high rates of Fe(II) production, siderite can form if there is an adequate concentration of carbonate and vivianite with high concentrations of phosphate (Figure 2.5).

The mineralization process is complicated by the presence of anions, such as chloride, sulfate or carbonate (Figure 2.5). Phosphate, silicate, carbonate, Ni, Co, and Ca can favor the formation of green rusts and vivianite. While there are several forms of green rust, formation of carbonate green rust ($[Fe^{II}_4Fe^{III}_2(OH)_{12}]^{2+} \cdot [CO_3, nH_2O]$) is more favorable than the sulfate analogue (Ona-Nguema et al. 2004). The structure has layers of Fe(II) and Fe(III) octahedra, with water and anions such as carbonate intercalated in the interlayers. Green rusts have been observed as a microbially-induced biomineralization product of HFO in laboratory incubations (Fredrickson et al. 1998). Just as HFO is metastable with respect to the formation of goethite and hematite, green rusts are metastable with respect to magnetite and siderite. Green rusts are formed in an early stage of biomineralization. Phosphate, As(V), silicate and Co stabilize green rusts by preventing re-crystallization into goethite, siderite, and magnetite (Zachara et al. 2002; Bocher et al. 2004).

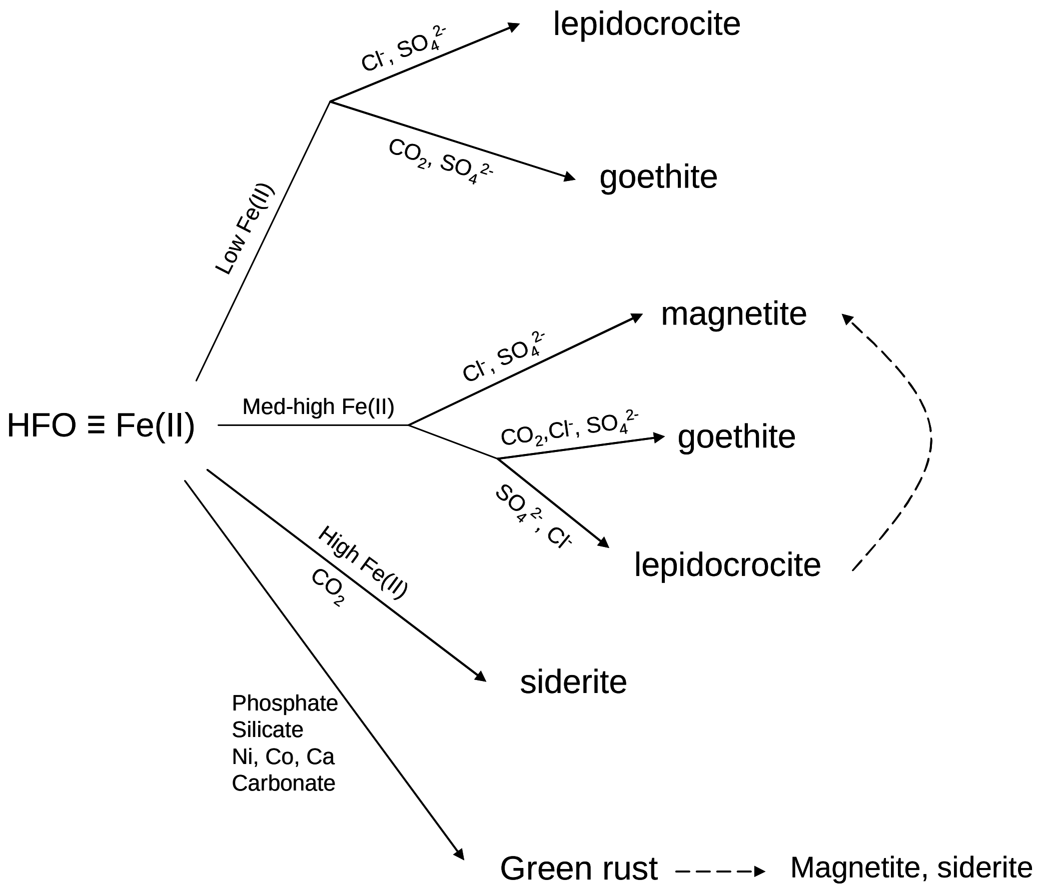

Figure 2.5. Secondary mineral transformations of HFO due to adsorbed Fe(II). Adapted from references: (Fredrickson et al. 1998; Benner et al. 2002; Zachara et al. 2002; Hansel et al. 2003; Hansel et al. 2005; Pedersen et al. 2005; Pedersen et al. 2006). The dashed lines indicate further mineral transformation that can occur spontaneously.

While Fe(II) can be produced by microbial processes, the role of bacteria in secondary mineral transformation is unclear. Many of the same secondary minerals are observed when Fe(II) is added abiotically. However, larger particles are formed in the abiotic Fe(II) reactions compared to biogenically produced Fe(II) transformation products (Hansel et al. 2003). In addition, complete conversion of Fe(III) in Fe(III) oxides to Fe(II) is rarely observed in biological experiments. Secondary mineral precipitation and Fe(II) adsorption may make the Fe(III) oxide less bioavailable for reduction (Urrutia et al. 1999; Hansel et al. 2004; Royer et al. 2004). While mineral transformation is primarily an abiotic reaction involving Fe(II), the rate and extent of Fe(II) production can be biologically controlled.

2.2.3.4 Implications for As mobility

Reductive Fe(III) oxide dissolution is controlled by a complex interplay of many different parameters, such as pH, redox state, mineralogy, biological activity, and solution chemistry. Biologically-mediated reduction depends strongly on the bacterial consortia present in the sediments, as well as substrate availability (e.g., organic carbon) and Fe oxide crystallinity. The rate of dissolution can, in turn, affect the mineral transformation products, which have the potential to sequester As in more crystalline lattice structures or release As to the porewaters as surface binding sites are lost.

2.3 Redox cycling of arsenic

2.3.1 Redox cycling of As by microbes

Bacteria may be one of the most important agents in As cycling in sediments. Both As(V) reduction and As(III) oxidation can be microbially mediated, and have been observed in the environment (Ahmann et al. 1997; Oremland et al. 2002).

The chemical similarity between As(V) and phosphate has important consequences for the biological cycling of arsenic. Bacteria have uptake systems to transport phosphate inside the cell. When there is an ample supply of phosphate, bacteria use the inorganic phosphate transport (Pit) uptake system, which is non-specific and allows As(V) inside the cell. When phosphate levels are low, the more phosphate specific transport (Pst) uptake system is used, which is less likely to transport As(V) inside the cell (Tamaki and Frankenberger 1992). Once As(V) has entered the cell, As(V) reduction can proceed via two different metabolic pathways: respiration and detoxification.

2.3.1.1 Respiratory As(V) reduction

Respiratory As(V) reduction couples the reduction of As(V) to the oxidation of a compound such as organic carbon, a process which conserves energy for the cell and allows for cell growth (Laverman et al. 1995; Newman et al. 1998). Bacteria capable of respiratory As(V) reduction have been isolated from many sediment and aquifer environments and represent a very genetically diverse group of organisms. Thus far, no obligate dissimilatory As(V) reducing bacteria have been found and all isolates are able to utilize other electron acceptors (Oremland and Stolz 2003). Unless the As concentrations are extremely high, such as in Mono Lake (17 mg/L), the contribution of respiratory As(V) reduction is probably negligible with respect to the total mineralization of organic carbon (Oremland et al. 2000; Thamdrup 2000). However, this process can be significant for As redox transformations in sediment. The main pathway for dissimilatory As(V) reduction is the *arrA* pathway, named for the periplasmic ArrA reductase, and is well conserved among a diverse group of organisms (Saltikov and Newman 2003; Malasarn et al. 2004). Further discussion on respiratory As(V) reduction can be found in Chapter 5.

2.3.1.2 As(V) reduction for detoxification

Arsenic toxicity to bacteria cells has been mitigated by the evolution of several detoxification pathways. As mentioned in section 2.1.2.2, some bacteria methylate As to reduce its toxicity. Another pathway is As(V) reduction, which allows As(III) to be actively pumped out of the cell. This pathway, known as *arsC* for the cytoplasmic ArsC reductase, involves an As(III)-specific transporter that requires the consumption of ATP (Cervantes et al. 1994; Rosen 1996). Bacteria can have both the respiratory *arrA* and the *arsC* pathways. In *Shewanella* species strain ANA-3, the *arrA* pathway is activated at a much lower As(V) concentration than the *arsC* detoxification pathway (Saltikov et al. 2003; Saltikov et al. 2005). The rates of As(V) reduction via the detoxification pathway are less than the respiratory pathway, but As(V) reduction for detoxification may still be an environmentally relevant process under certain environmental conditions (Jones et al. 2000; Macur et al. 2004).

2.3.1.3 As(III) oxidation

As(III) oxidation can also be bacterially mediated (Oremland et al. 2002; Oremland and Stolz 2003). Macur et al. observed that microbial As(III) oxidation and

As(V) reduction can co-occur in unsaturated sediments under the same environmental conditions (Macur et al. 2004). In addition, bacterial As(III) oxidation has been shown to catalyze the oxidation of geothermal As(III) in Hot Creek (Wilkie and Hering 1998).

2.3.2 Abiotic As redox chemistry

Oxygen can oxidize As(III), although the kinetics of this reaction are slow except at high pH (>10) (Manning and Goldberg 1997; Swedlund and Webster 1999). Manganese oxides can quickly oxidize adsorbed As(III), and this has been shown to be an active pathway for several synthetic manganese oxides (manganite and birnessite) (Scott and Morgan 1995; Chiu and Hering 2000; Manning et al. 2002) and in natural sediments and clays (Manning and Goldberg 1997; Amirbahman et al. 2006). Green rust may also catalyze As(III) oxidation, although the importance of this reaction in biogenically formed green rust in sediment is unclear (Su and Puls 2004; Su and Wilkin 2005). As(V) reduction by green rust has not been observed (Randall et al. 2001; Ruby et al. 2006). In addition, natural organic carbon can either oxidize As(III) or reduce As(V), and will be discussed in section 2.4.2.

2.4 Effect of organic carbon on arsenic cycling

2.4.1 Source of organic carbon

Sedimentary organic matter is derived from decaying phytoplankton and other plant or animal material. As proteins, lipids, and other components decay, compounds such as melanins, humic acids, and fulvic acids are formed and are commonly found in natural sediments (Stumm and Morgan 1996). Natural organic matter (NOM) is a mixture of many types of functional groups, including phenols, fatty acids, carbohydrates, sugars, and amino acids. NOM can also contain significant amounts of inorganic impurities, such as Fe, Mn, and Al. The organic carbon pool is a substrate for a range of microbial processes, including but not limited to As(V) and Fe(III) reduction.

2.4.2 Effect on As chemistry

There is some evidence that NOM has redox properties, and can catalyze the reduction of As(V) or the oxidation of As(III), particularly in the presence of a mineral surface such as hematite (Redman et al. 2002; Ko et al. 2004; Bauer and Blodau 2006). However, the redox activity of NOM is highly variable; Bauer et al. found that NOM extracted from peat promoted As(V) reduction, while NOM extracted from wetland sediment catalyzed As(III) oxidation (Bauer and Blodau 2006). It is, therefore, difficult to generalize the effect of organic matter on As redox chemistry, although it may be important in some sediment systems.

Organic carbon has been shown to promote As mobilization in laboratory studies, either due to sorption effects or aqueous complexation (Redman et al. 2002; Bauer and Blodau 2006). Humic and fulvic acids are capable of inhibiting As(III) and As(V) adsorption to Fe(III) oxide surfaces due to steric and/or electrostatic effects (Xu et al. 1991; Grafe et al. 2001; Grafe et al. 2002; Redman et al. 2002; Ko et al. 2004). Natural organic matter can adsorb onto Fe oxide surfaces through functional groups such as carboxylic acids, phenols, and amines or as outer-sphere complexes (Kaiser et al. 1997; Grafe et al. 2002; Buschmann et al. 2006). Organic carbon has also been shown to complex As in solution, although the mechanism is most likely through inorganic impurities such as Fe(III) and Mn(III,IV). Fe(III) stabilized in NOM (dissolved Fe(III) or colloidal Fe(III) oxide particles) can form bridging complexes with As, for the same reasons that As adsorbs to the surface of Fe(III) minerals (Ko et al. 2004; Lin et al. 2004; Ritter et al. 2006). As(V) tends to form stronger complexes than As(III) on a variety of Fe(III)-containing organic substrates (Thanabalasingam and Pickering 1986; Warwick et al. 2005; Buschmann et al. 2006). Phosphate competes with As for NOM complexation, supporting the Fe(III) bridging mechanism (Thanabalasingam and Pickering 1986).

2.5 Early diagenesis in sediments

Sediment diagenetic processes are the biogenic and abiotic changes that occur to alter the sediment during and after deposition (Stumm and Morgan 1996). Diagenesis is driven primarily by the mineralization of organic carbon and the subsequent changes in redox potential with depth. As the sediments become more reducing, the redox equilibrium of various chemical species in the sediment shifts. However, it is important to recognize that the kinetics of these reactions are variable and sensitive to environmental parameters such as microbial activity (Hering and Kneebone 2001). Thus, it is common to observe As(III) and As(V) or Fe(III) and Fe(II) co-occurring under a variety of redox conditions due to kinetic factors.

Sediment diagenesis involves chemical, physical, and biological processes, including 1) deposition, 2) diffusion, 3) reductive dissolution (and other redox changes) and 4) secondary mineral precipitation. At Haiwee Reservoir, fresh, oxidized Fe- and

As- rich floc is deposited on the sediment surface. Organic matter is also deposited through the floc and by settling phytoplankton and plant matter. Organic matter deposition is seasonal, as primary productivity varies with nutrient input and temperature. In addition, sediment compaction decreases porosity with depth, possibly affecting molecular diffusion.

Oxygen is the most favorable electron acceptor, and the diffusion of O_2 into the sediments from the overlying water is balanced by microbial consumption. In many freshwater sediments, the transition from oxic or suboxic to anoxic can occur within a depth interval of millimeters to centimeters (Song and Muller 1999). In suboxic zones, Mn oxides and nitrate are reduced, releasing Mn(II) and nitrite or N_2. Reductive dissolution of Fe oxides and sulfate reduction occur in the more reducing anoxic zones, as discussed in section 2.2.3. Deeper in the sediment column, methane fermentation may occur under very reducing conditions. Trace elements, such as As, may also undergo redox transformations during this process, such as As(V) reduction, as discussed in section 2.3.

As the reductive dissolution of Fe(III) oxides releases Fe(II) and trace elements into the porewater, several chemical processes are possible. Dissolved organic carbon may form aqueous Fe and/or As complexes, or inhibit sorption onto mineral surfaces. Competitively sorbing compounds such as phosphate can be released from the dissolving solid phase or from mineralization of organic matter and affect the partitioning of As on the solid phase. Fe(II) may catalyze the formation of secondary minerals such as green rust, magnetite, and goethite, which can either sequester or mobilize As.

Dissolved Fe(II) and As are subject to molecular diffusion. If Fe(II) diffuses into the suboxic zone, it could be re-precipitated by reaction with O_2 or Mn oxides, resulting in fresh surface sites for As to be re-adsorbed.

The processes governing As mobilization and sequestration are a complex combination of biological, chemical, and physical parameters. The As- and Fe-rich sediment deposited at Haiwee reservoir provides a unique setting to study the biogenic and chemical diagenetic processes that control As partitioning between the solid and dissolved phases in the environment.