CHARACTERIZATION OF ION SORPTION ON METAL SULFIDE MINERALS USING MACROSCOPIC AND SPECTROSCOPIC APPROACHES

A DISSERTATION

SUBMITTED TO THE DEPARTMENT OF GEOLOGICAL AND ENVIRONMENTAL SCIENCES AND THE COMMITTEE ON GRADUATE STUDIES OF STANFORD UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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ABSTRACT

Sorption describes the partitioning of ions between solids and solution. It can occur through the formation of different surface complexes or precipitates, each regulating solute concentrations to a different extent. Consequently, the mechanism of ion retention is a critical factor in determining the transport and fate of ions in the environment. This research examines the sorption mechanism of arsenic, molybdenum, and zinc within mineral and soil suspensions. The work is divided into sections covering (i) the fundamental reaction mechanisms of arsenite and molybdate with sulfide mineral suspensions, and (ii) As(III) and Zn(II) sorption on soils.

Arsenite sorption to sphalerite (ZnS), galena (PbS), amorphous iron sulfide (FeS), and pyrite (FeS₂) was investigated as a function of solution composition. Sorption of As to each solid followed a Langmuir isotherm, with some deviation indicative of precipitation observed at elevated As(III) solution activities. Arsenite sorption increased with pH, with a sharp pH edge between pH 5 and 6. The pH effect differs markedly from that of arsenite sorption on (hydr)oxide minerals and suggests that ligand exchange removes arsenite-bound hydroxyls groups rather than conventional surface ligand exchange. X-ray absorption spectroscopy (XAS) was used to show the conversion of the first coordination shell around arsenic(III) from oxygen to sulfur. The thioarsenate complex formed on ZnS and was likely a $\text{As}_3\text{S}_3(\text{SH})_3$ trimer, which is common in basic, highly sulfidic solutions. Similar polynuclear thioarsenate complexes formed on PbS, while arsenite sorption on FeS and FeS₂ resulted in the reduction to As(-I) and the formation of an FeAsS-like surface precipitate. Arsenite sorption to each of these sulfide minerals was relatively irreversible, except for As(III) sorbed to PbS, which formed
relatively labile complexes presumably due to the poor lattice match of thioarsenite to the surface.

Similar FeAsS-like surface precipitates initially were formed for As(III) retained in a sulfide–rich estuarine soil from Pescadero, CA, converting to orpiment (As$_2$S$_3$) over several weeks. This conversion was most apparent for samples prepared with the highest As solution concentrations, i.e., those most likely to exceed the solubility product of orpiment. Therefore, both sorption to iron sulfide minerals and the precipitation of arsenic sulfides probably occur in other highly sulfidic environments.

Molybdate and tetrathiomolybdate sorption to pyrite was investigated using both solution and spectroscopic techniques. Molybdate sorption was reversible and followed a Langmuir isotherm, with significant sorption only at low pH (pH<5). Tetrathiomolybdate sorption was similar to that of molybdate, although the effect of pH was less pronounced and sorption was irreversible on the time-scales of these experiments. X-ray absorption spectroscopy revealed that molybdate formed a bidentate-mononuclear sorption complex on FeS$_2$. Tetrathiomolybdate coordination changed significantly during adsorption; the Mo-S bond distance changed from 2.20 Å in tetrathiomolybdate to about 2.4 Å upon sorption, and was accompanied by the formation of a Mo-Fe shell at about 2.65 Å. These Mo-S and Mo-Fe distances indicate the formation of a Mo-Fe-S cubane on the FeS$_2$ surface, in which the Mo is triply coordinated to surface-bound sulfur atoms.

Zinc was often sequestered in a contaminated wetland as ZnS, ZnCO$_3$, ZnO and adsorbed Zn species. The fractions of ZnS and ZnCO$_3$ were highest under flooded conditions in which reduction occurred, while adsorbed Zn species occurred only under
oxic conditions (dry or shallow water depths). Zn speciation was effectively described by changes in the depth of the overlying water column, and rapid changes in water column depth were accompanied by correspondingly fluctuations in Zn speciation.

These data illustrate the wide variety of sorption species that can occur in natural matrices. Labile inner-sphere sorption complexes such as MoO$_4^{2-}$ adsorbed to FeS$_2$ may effectively regulate concentrations at low levels; however, facile desorption prevents such surface species from being effective means of reducing transport or bioavailability. In contrast, strongly retained surface complexes can be retained over geological time scales. For example, the Mo-Fe-S cubane formed on FeS$_2$ is comparable to that found in black shales. Solid phases such as the FeAsS-like surface precipitate or As$_2$S$_3$ are thought to be the most stable phases for trace metal sequestration; however, these data show both the rapid oxidation of FeAsS and the rapid transformation of solid Zn phases in response to environmental perturbations. Regardless, these experiments show that sorption to sulfide minerals may control both the short and long-term fate of many chalcophiles in reducing environments.
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Chapter 1. Introduction

OVERVIEW

Toxic elements ideally partition strongly from aqueous solutions onto the solid phase, lowering their aqueous concentrations and thereby minimizing transport and biological risk. Contaminant solubility in the environment is normally controlled by a combination of precipitation and adsorption reactions; thus, a mechanistic understanding of these processes is imperative to ascertain their environmental fates. This research examines the fate of arsenic, zinc, and molybdenum in several different types of environments representative of an estuarine soil rich in sulfides (As), a sulfide-rich marine environment (Mo) and of a terrestrial wetland (Zn). Arsenic and zinc have caused significant environmental contamination and health problems while molybdenum is an important micronutrient required for nitrogen fixation. Each of these elements are chalcophiles; their retention in anoxic soils and sediments is often attributed to their reaction with sulfide minerals. The mechanism of this interaction is unclear. Consequently, this research focuses on the mechanisms of arsenic, zinc, and molybdenum sorption on metal sulfide minerals and within sulfide-rich soils. The research presented in this thesis illustrate the varied mechanisms responsible for As, Mo and Zn sequestration in sulfidic environments and also provides insight into the surface reactivity of sulfide minerals.

ENVIRONMENTAL CHEMISTRY OF ARSENIC, MOLYBDENUM AND ZINC

Arsenic. Arsenic contamination has resulted in widespread environmental problems in many areas including Taiwan (Chen et al., 1994) and Bangladesh (Nickson et al., 1998).
Anthropogenic sources of arsenic contamination include sulfide ore smelting and disposal (e.g., Harrington et al., 1998; Pain et al., 1998), and use in agricultural chemicals, wood preservation, and the burning of fossil fuels enriched in arsenic. Arsenic also enters the environment through natural mineral weathering, volcanic outgassing, and through processes such as acid mine drainage.

Sorption reactions mitigate the hazards of As by maintaining dissolved concentrations at low levels. Arsenic speciation (Fig. 1) has a profound effect on its sorption behavior. In well oxygenated natural waters, As(V) as arsenate, AsO\(_4^{3-}\), is the dominant species (see reviews by Cullen and Reimer, 1989; Korte and Fernando, 1991; Smith et al., 1998). Arsenate may substitute in sulfate or phosphate minerals (e.g., Huggins et al., 1997; Foster et al., 1998; Savage et al., 2000), and forms strong complexes on Fe and Al (hydr)oxides (e.g., Anderson et al. 1976; Waychunas et al., 1993; Manning and Goldberg, 1996; Fendorf et al., 1997; Hiemstra and Van Riemsdijk, 1999). Under slightly reducing conditions, As(V) is reduced to arsenite, H\(_3\)AsO\(_3\) (Masscheleyn et al., 1991), which sorbs less strongly to Al (hydr)oxides (Manning and Goldberg, 1996). Often the reductive dissolution of Fe(III) minerals precedes As reduction, releasing sorbed As(V) into solution (Cummings et al., 1999; Nickson et al., 2000). Arsenic can react with sulfide under highly reducing conditions to form orpiment (As\(_2\)S\(_3\)), arsenopyrite (FeAsS) or other sulfide phases (Belzile, 1988; Sullivan and Aller, 1996). Organoarsenicals also form in reducing environments, although these species generally constitute only a fraction of the arsenic in the environment (Andreae and Klumpp, 1979; Anderson and Bruland, 1991).
The redox stratification in ocean sediments (Cutter, 1991; Sullivan and Aller, 1996) exemplifies the effects that arsenic speciation has on solution concentrations (Fig. 2). Similar trends are observed in freshwater lakes (Aggett and O’Brien, 1985; Moore et al., 1988; Balistieri et al., 1994) and rivers (Johannesson et al., 2000). In oxidized surface sediments, iron (hydr)oxides scavenge arsenate from oxic water columns and become enriched in this element. As depth increases, the redox potential typically decreases, causing reductive dissolution of iron (hydr)oxides. The increase in porewater Fe(II) is accompanied by arsenic release. Iron concentrations decrease below the anoxic boundary by the formation of sulfide minerals. Arsenic concentrations are similarly reduced, presumably through association with iron sulfides or through the formation of neat sulfide minerals. Selective extractions have shown that As in anoxic zones is highly pyritized (e.g., Huerta-Diaz and Morse, 1992; Cooper and Morse, 1996). Unfortunately, differentiating adsorption from precipitation is not possible with these techniques (e.g., Belzile et al., 1989; Cooper and Morse, 1998; Holmes, 1999). Arsenic may be sequestered in the sediments as an arsenic sulfide solid (Sadiq, 1990; Sadiq, 1997); however, sorption on sulfide minerals may also occur. Arsenic sulfides have been identified in lake sediments (Soma et al., 1994), but the identity of the sulfide species could not be determined explicitly. Sulfosalts rims formed around sulfide mineral grains when reacted with As or Sb (Elhaddad and Moh, 1992), also suggesting that As is retained by sulfide mineral surfaces. Research presented here investigates the potential role of such reactions in As(III) retention.

**Molybdenum.** Molybdenum has many biologically important functions. Molybdenum is present in nitrate reductase and in nitrogenase, potentially limiting primary productivity
(Vitousek and Howarth, 1991; Howarth et al., 1999). Under oxic and suboxic conditions, Mo(VI) is the most stable oxidation state and forms the molybdate ion, \( \text{MoO}_4^{2-} \), which is isostructural with sulfate. Molybdate does not appreciably sorb to most (hydr)oxides and aluminosilicates (Xie and MacKenzie, 1991; Goldberg et al., 1996; Rietre et al., 1999; Wu et al., 2000); consequently, it usually is available for biological uptake. Reduced Mo, Mo(IV), is primarily found as molybdenite, MoS\(_2\), the major ore of molybdenum. Reduction of Mo(VI) is favored in sulfidic environments, though seldom observed for kinetic reasons (Helz et al., 1996). Rather, thiomolybdate species, \( \text{MoO}_x\text{S}_{4-x}^{2-} \), are formed in sulfidic environments (e.g., Helz et al., 1996; Erickson and Helz, 2000). While molybdenum adsorbs weakly to (hydr)oxide minerals, it adsorbs appreciably to sulfidic soils and sediments (Bertine, 1972; Bertine and Turekian, 1973; Emerson and Huested, 1991; Amrhein et al., 1993; Crusius et al., 1996; Morford and Emerson, 1999; Johannesson et al., 2000). The mechanism of Mo sorption in these systems is largely a matter of conjecture; it may involve simple surface complexation to iron sulfides or pyrite, coprecipitation with iron sulfides, or the formation of molybdenum sulfides.

Despite the empirical evidence suggesting that many trace metals and metalloids react strongly with sulfide surfaces, little molecular-scale work has been done to determine the nature of the interactions between anions and sulfide minerals. In one of the few molecular-scale studies, Helz and others (1996) examined Mo in black (sulfide-rich) shale and determined that Mo was primarily associated with sulfides. Its incorporation was not as discrete sulfide minerals, but was adsorbed on or coprecipitated with iron sulfides. Furthermore, Mo was not reduced to Mo(IV), suggesting that molybdenum reduction (or the formation of MoS\(_2\)) was not required for enrichment.
While these data (Helz et al., 1996) suggest that arsenic sorption to sulfide minerals may be important, additional research is needed to explain the As and Mo partitioning in the environment. Therefore, the work described in this thesis addresses the shortcomings in our current understanding of As and Mo sorption.

**Zinc.** Zinc sorbs strongly to iron (hydr)oxides (Benjamin and Leckie, 1981; Stahl and James, 1991a) and manganese oxides (Loganathan and Burau 1973; Zasoski and Burau, 1988; Stahl and James, 1991b) in aerated natural systems. Under reducing conditions, Zn partitions to sulfide minerals (Kornicker and Morse, 1991; Huerta-Diaz et al., 1998) and carbonates (Morse, 1986; Zachara et al., 1988; 1991). Previous XAS studies of Zn in natural soils identified metal hydroxide and primary sulfide solid phases with lesser quantities of adsorbed Zn (Hesterberg et al., 1997; O’Day et al., 1998). The presence of both oxidized and reduced Zn phases suggests that seasonal changes in the soil redox status may indirectly influence Zn adsorption, though reductive dissolution of iron and manganese (hydr)oxides, or the elevation of sulfide or carbonate concentrations, followed by subsequent precipitation. However, in complex systems little information is available concerning the response of sorbed Zn to changes in redox potential. Therefore, this research examines the effect of seasonal redox cycling on Zn speciation.

**ION PARTITIONING ON SURFACES**

Sorption describes the partitioning of molecules between solution and solids. Such reactions control the solution concentrations of molecules in the environment, thereby affecting their availability and mobility. Much of what we know about sorption reactions is based on macroscopic measurements (e.g., Davis and Kent, 1990). Although
the models derived from such macroscopic data are useful for the characterization of phase partitioning, they provide no mechanistic insight into the sorption process (Sposito, 1986) and are therefore inherently limited in their applicability. A molecular-level understanding of such phenomena is vital to predict sorption properties under conditions different from those of the calibrating data set. Thus, knowledge of fundamental sorption mechanisms can be applied to describe chemical partitioning in complex natural systems, permitting the estimation of important environmental variables such as bioavailability and mobility. Furthermore, mechanistic information will help define conditions that promote (or limit) desorption.

Sorption can occur through a variety of mechanisms, including adsorption in outer- and inner-sphere complexes and precipitation. Outer-sphere adsorption is an electrostatic, non-specific attraction of an ion to a charged interface. Inner-sphere adsorption occurs through the formation of one or more chemical bonds between the surface and the adsorbate. Precipitation refers to the formation of a solid that has a defined composition and a three-dimensional structure. Precipitation can be heterogeneous (i.e., influenced by the presence of an interface) or it can be homogeneous (determined by the solubility of a pure mineral). Outer-sphere sorption depends only on the weak electrostatic attraction between an ion and surface. Consequently these complexes are both rapidly retained and displaced. Inner-sphere sorption requires both the loss of water molecules from the hydration sphere and subsequent formation of a chemical bond. The formation of a chemical bond stabilizes inner-sphere complexes relative to outer-sphere complexes and generally imparts kinetic limitations to sorption.
and, notably, desorption. Thus, each sorption mechanism imparts a unique reactivity, and consequently a different environmental fate, for the adsorbate.

Several spectroscopic techniques are useful for characterizing sorption mechanisms. One of the most powerful techniques is x-ray absorption spectroscopy (XAS), which is an element specific probe of the local structural environment of the adsorbate that can be performed in complex matrices such as soils and sediments (see reviews by Fendorf et al., 1994; Brown et al., 1995; Conradson, 1998). X-ray absorption near-edge structure (XANES) spectroscopy provides information about the oxidation state and coordination environment of the adsorbate. Extended x-ray absorption fine-structure (EXAFS) spectroscopy augments this information by providing structural information, including the atomic number (Z), coordination number (N), and interatomic distance (R) of the absorbing element. Combined, these spectroscopic techniques can be used to differentiate the mechanisms of ion retention, thereby providing insight into their environmental fate.

While sorption processes are relatively well chronicled for aluminosilicates and metal (hydr)oxides, far less research has been used to create models that describe adsorption on sulfide minerals. In fact, only rudimentary models of adsorption to sulfide minerals are available (Balsley et al., 1996; Balsley et al., 1998; Gärd et al., 1995), and few molecular-scale studies (Soma et al., 1994; Forsling and Sun, 1997; La Force et al., 2000) have examined the structure of the sorption complex to determine the validity of the models. This research provides a microscopic understanding of the sorption process on sulfide minerals. By using XAS and other spectroscopic techniques to characterize the mechanism of ion sorption within pure suspensions, as well as to reduced soil
suspensions, we can begin to create a mechanistically accurate model of ion ion retention on sulfide minerals, and, hence, within anoxic soils and sediments.

**OBJECTIVES AND TASKS**

This research is intended to provide an understanding of trace element sorption processes on sulfide minerals and in soils and sediments that undergo (periodic) reduction. This research is divided into several sections, each examining ion sorption in different geological media with a focus on the sorption of several environmental contaminants including arsenic, molybdenum, and zinc. My thesis specifically addresses: (i) the particular limitations of the current knowledge concerning the mechanism of As(III) and Mo(VI) sorption on selected sulfide minerals; (ii) the stability of sorbed As(III) and Mo(VI); and (iii) the importance of these sorption mechanisms in a sulfidic environments. Additionally, (iv) the mechanism of Zn retention is examined for contaminated soils and subsurface media that undergo periodic reduction.

**EXPERIMENTAL CONCLUSIONS**

This thesis is organized into a collection of independent studies. Chapter 2 investigates solution variables that control arsenite sorption to ZnS and PbS substrates and examines the structure of the resultant surface complexes using spectroscopic methods. As(III) partitioned strongly to PbS and ZnS, forming an inner-sphere surface complex. The local structural environment of arsenic changed from oxygen to sulfur coordination upon sorption, indicative of a reaction mechanism involving coordination to the surface sulfhydryl functional groups. Thioarsenites were the dominant surface
complexes. Arsenite sorbed to ZnS formed an As$_3$S$_3$(SH)$_3$ trimeric species. A similar species is likely formed on PbS; however, the As-S bond distances are elongated on PbS relative to those observed for As in solution due to the increased separation between S-containing functional groups. Facile desorption of As(III) was observed for PbS but not ZnS.

An investigation of As(III) sorption to FeS and FeS$_2$ is described in Chapter 3. Iron sulfide minerals are ubiquitous in reduced soils and sediments; thus, sorption of As to these minerals is of particular interest. Arsenite adsorbed strongly to iron sulfides, conforming to a BET isotherm indicative of a mechanism involving surface precipitation, and was enhanced at neutral and higher pH—distinct from As(III) sorption to iron hydroxides. Sorbed As was reduced to an oxidation state of As(-I), forming both As-S and As-Fe bonds. The coordination environment of sorbed As is similar to that of both arsenian FeS$_2$ and FeAsS. However, As-Fe shells of sorption samples were more comparable to those of FeAsS. Based on these observations, it is concluded that an FeAsS-like precipitate formed on both FeS and FeS$_2$.

While investigations of As(III) sorption to pure mineral suspensions indicate strong partitioning of As to sulfide minerals, the importance of sulfide minerals in complex natural matrices is less clear. Therefore, As(III) sorption to salt marsh soils is investigated in Chapter 4. The chosen salt marsh, a portion of the Pescadero Estuary, is a tidally submerged salt marsh that contains sulfide minerals. Arsenic(III) sorption to these soils was highest at high pH; however, appreciable As sorbed at all pH. The extent of sorption varied somewhat depending on the location of sampling, with sorption most extensive in highly reduced portions of the wetland. Spectroscopic investigations of the
As-loaded soils revealed a FeAsS-like precipitate that converted to orpiment as conditions became more reducing. Thus, both sorption and precipitation mechanisms may be responsible for As sequestration in sulfidic marine environments.

Molybdate and tetrathiomolybdate are enriched in anoxic sediments through an unknown process. Chapter 5 examines one possible means of this enrichment, sorption to FeS₂. Both MoO₄²⁻ and MoS₄²⁻ sorption to FeS₂ are described by a Langmuir isotherm, with sorption enhanced under moderately acidic conditions. Molybdate sorbed to FeS₂ as a bidentate, mononuclear complex. It was only weakly retained, however, and quickly desorbed in response to changing solution composition. Tetrathiomolybdate sorbed irreversibly, forming a Mo-Fe-S cubane structure on the FeS₂ surface. Molybdate is converted to thiomolybdate only at elevated sulfide activities. These results suggest that conversion is required for Mo enrichment within sediments, consistent with the observation that Mo enrichment is typically isolated to highly sulfidic environments. Therefore, sorption of thiomolybdate species may play an important role in the enrichment of Mo in anoxic environments.

An additional study (Chapter 6) was undertaken to examine the conversion of sorbed Zn species in response to periodic reduction. Zinc speciation was quantified over time in a contaminated wetland in the Coeur d’Alene mining district of northern Idaho. Seasonal flooding had a large impact on Zn speciation—sorbed Zn species and ZnO present in dry summer months were replaced with ZnS and ZnCO₃ as water levels increased in winter and spring. Zn speciation over the entire wetland was correlated to water depth, and individual sampling locations responded rapidly to environmental
changes. These results illustrate the dynamic nature of Zn cycling, even for solid phases often assumed to be stable.

This research illustrates the complexity of trace element sequestration reactions that can occur on sulfide mineral surfaces. Arsenic(III) and Mo(VI) sorb to sulfide minerals in a variety of ways, producing both labile surface complexes and relatively stable surface precipitates. A rich diversity of chemistry is observed for ion sorption on sulfide minerals, ranging from typical anion behavior for molybdate sorption on FeS₂ to sorption more typical of cations for arsenite on simple sulfides (PbS and ZnS). An appreciation of this rich chemistry is required to determine how As, Mo, and other chalcophiles may react within the environment.

Several collaborators participated in this work. Bruce Manning assisted with the studies of As(III) sorption to PbS. Cynthia Chen helped to characterize the wetlands of Pescadero slough, and provided assistance with numerous solution studies. The expertise of George Helz predicates much of the work examining molybdenum and sulfur chemistry and was essential to the experiments concerning Mo sorption on FeS₂. Matt La Force and Colleen Hansel both contributed to the examination of Zn sequestration within a seasonally reduced wetland, which has recently been published (Bostick et al., 2001). The assistance of all of these individuals is greatly appreciated.

REFERENCES


Figure 1. The Eh-pH stability diagram for As. This diagram was calculated using an arsenic and sulfur concentrations of 1 µM and 10 µM, respectively.
Figure 2. Pore water Fe and As concentrations as a function of sediment depth in a core from the Amazon Fan. Based on data from Sullivan and Aller (1996).
Chapter 2.

Arsenite Adsorption on Galena (PbS) and Sphalerite (ZnS)
ABSTRACT

Arsenite, As(III), sorption on galena (PbS) and sphalerite (ZnS) was investigated as a function of solution composition and characterized using x-ray absorption spectroscopy (XAS). Adsorption conformed to a Langmuir isotherm except at the highest surface loadings, and it was not strongly affected by changes in ionic strength. Arsenite sorbed significantly only at pH greater than 5 for PbS and pH 6 for ZnS, behavior distinct from its adsorption on other substrates. Arsenite adsorption on PbS and ZnS resulted in the conversion from As-O to As-S coordination. Arsenite does not adsorb through ligand-exchange of surface hydroxyl or sulfhydryl groups, rather hydroxyls on arsenite undergo ligand exchange with surface-bound sulfhydryl moieties. Rather, it forms a polynuclear arsenic sulfide complex on ZnS and PbS consistent with the As$_3$S$_3$(SH)$_3$ trimer found by Helz et al. (1995) in sulfidic solutions. This complex was unstable in the presence of oxidizing agents and synchrotron light—it quickly converted to As(V) which was largely retained by the surface. These data illustrate the complexity of As(III) adsorption to even simple sulfide minerals.
INTRODUCTION

Arsenic is a toxic metalloid that contaminates soils, sediments, and groundwaters; it can originate from a variety of sources including the oxidation of arsenopyrite or arsenian pyrite from sulfide ore-bearing zones, mines and other sites (e.g. Pain et al., 1998; Nickson et al., 1999; Savage et al. 2000). Arsenate, As(V), present under aerobic conditions is often reduced to arsenite, As(III), in anaerobic environments (see Cullen and Reimer, 1989). Solubility and bioavailability are in part controlled by adsorption processes—in oxidized environments As(V) adsorbs strongly to iron and aluminum (hydr)oxides (e.g., Anderson et al. 1976; Waychunas et al., 1993; Manning and Goldberg, 1996; Fendorf et al., 1997; Hiemstra and Van Riemsdijk, 1999). In contrast, arsenic adsorbs much more weakly in reduced (anaerobic) systems due to the reductive dissolution of the iron minerals and weak retention of As(III) on aluminum (hydr)oxides. Arsenic released into solution in such a manner is responsible for the considerable environmental problems present in Bangladesh today (Acharyya et al., 1999; Chowdury et al., 1999; Nickson et al., 2000). In these reduced environments, sulfide minerals may control As solubility through precipitation or adsorption mechanisms (e.g. Aggett and O’Brien, 1985; Balistrieri et al., 1994; Moore et al., 1994; Sullivan and Aller, 1996). Extraction data suggest that As associates primarily with iron monosulfides or pyrite (Huerta-Diaz and Morse, 1992; Cooper and Morse, 1996); however, arsenic sulfide precipitation or other retention mechanisms may also control As solubility in these environments (Sadiq, 1990; 1997).

Our objective in this study is to define the retention mechanism for As(III) on two sulfide minerals common in reducing environments, galena (PbS) and sphalerite (ZnS).
Both PbS and ZnS occur in sulfide ores, often from solutions rich both in arsenic and sulfide. They both have well defined cleavage surfaces, as well as high symmetry that simplify the consideration of their surface functional groups. Moreover, the stability of ZnS and PbS make them less prone to redox alterations that plague research with pyrite and other iron sulfides. Previous research on PbS and ZnS has focused on the acid-base properties of the surface functional groups (Liu and Huang, 1992; Rönnegren et al., 1992, Rönnegren et al., 1994). While the adsorption of cations to simple sulfides has been examined (e.g., James and Parks, 1975; Moignard et al., 1977; Park and Huang, 1989; Kornicker and Morse, 1991), relatively few studies of anion adsorption on sulfide minerals have been conducted (e.g. Gärd et al., 1995; Forsling and Sun, 1997). Accordingly, this study addresses the mechanisms of anion retention on both ZnS and PbS. Additionally, adsorption on ZnS and PbS may serve as a model for reactions involving more complex iron sulfide minerals ubiquitous in anoxic environments.

Here we employ the combination of solution-phase techniques with X-ray absorption spectroscopy (XAS) to examine both the structure and adsorption characteristics of As on PbS and ZnS. The bulk adsorption study identifies the macroscopic variables, such as arsenite and sulfide concentrations, pH, suspension density, and ionic strength, that control As(III) adsorption. Coupled with XAS, which identifies the structure of the adsorbed As species, a more complete description of arsenite adsorption to PbS and ZnS is ascertained.
MATERIALS AND METHODS

Reaction Conditions

Precautions were taken to minimize the oxidation of mineral surfaces and reagents during all experiments. Oxygen was excluded from the reactions using a glove box equipped with a mixed H₂/N₂ atmosphere (5% H₂) and a Pt catalyst, which maintained O₂ concentrations below the minimum detection level of approximately 1 ppm. All reagents and solutions were prepared fresh prior to use; solutions were prepared with degassed, deionized water. Additionally, suspensions were poised with sulfide when appropriate to maintain a reducing environment.

Materials

All chemicals used were of analytical grade. Suspensions were prepared using commercially available synthetic minerals (>99% purity) obtained from Strem Chemical. Sulfide minerals were stored under nitrogen and washed to remove oxidized surface species. Minerals were first washed with water, then with a 0.01 M sulfide solution (pH 7) to reduce any remaining oxidized products, and then washed again with water to remove residual sulfide and oxidized products.

The surface area was 2.93 m²/g for ZnS determined with a 3 point BET isotherm using N₂(g) as the adsorbate. The PbS exhibited a slightly higher surface area, 4.31 m²/g. Washing decreased the surface area by about 10%, suggesting that the treatments removed some colloidal material. X-ray photoelectron spectroscopy (XPS) was performed to characterize surface oxidation products formed before and after cleaning. XPS was performed on a SSI S-Probe equipped with a monochromatized Al K₀ source.
The instrument was operated at a resolution of approximately 0.7 eV and a spot size of about 0.5 mm. Spectra were calibrated using the energy of bulk ZnS (161.2 eV; Kartio et al., 1998) and PbS (160.7 eV; Wittsock et al., 1996). Scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS) was further used to characterize the solid phases.

**Solution-Phase Experiments**

Several experiments were performed to determine the bulk adsorption characteristics of arsenite on sulfide mineral suspensions. The effect of arsenic concentration, suspension density, pH, ionic strength and sulfide concentration on As sorption, were examined. Stock solutions were made for each of the reagents; 1 mM As(III) as NaHAsO$_2$, 10 mM sulfide as Na$_2$S·9H$_2$O, Arsenite concentrations in the mineral suspensions (1 g/L) of PbS or ZnS varied between 0 and 100 µM As(III). Samples kept at pH 7 were buffered with 0.002 M MOPS, while 0.002 M acetate and 0.002 M borate buffers were used at pH 4 and 9, respectively. Ionic strength was varied between 0.005 M and 0.5 M with NaCl, and added sulfide was varied between 0 and 2 mM using sulfide stock.

For adsorption envelope experiments, the pH of a 1 g/L ZnS or PbS suspension was initially adjusted to between 2 and 3 with 0.1 M HCl, and then As(III) was added to create a 50 µM As solution. Following equilibration for 0.5 h, a sample was taken and the pH measured. The pH was then varied using a small volume of 0.1 M NaOH, re-equilibrated, and re-sampled. This procedure was repeated until the pH reached about 11.
Similar experiments were performed using suspensions in which the initial pH was high (about 11) and titrated to near 3 with 0.1 M HCl.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed on the residual solutions to determine the extent of adsorption and to quantify the release of Pb, Zn or S into solution. Graphite furnace atomic absorption spectroscopy was also occasionally used to determine solution composition. The extent of adsorption was determined by difference.

**X-ray Absorption Spectroscopy**

X-ray absorption spectroscopy (XAS) was performed at the Stanford Synchrotron Radiation Laboratory on beamlines 4-1 or 4-3. The storage ring operated at 3.0 GeV and at currents between 50 and 100 mA. Spectra were taken with a Si(220) double-crystal monochromator with an unfocused beam. Incident and transmitted intensities were measured with 15-cm N₂-filled ionization chambers. Sample fluorescence was measured with a Stern-Heald type detector and a 6 µx Ge filter. For more dilute samples, the fluorescence signal was measured using a 13-element Ge detector oriented 45 degrees off the sample and orthogonal to the incident radiation. The beam was detuned approximately 50% to reject higher-order harmonic frequencies and to prevent detector saturation.

X-ray absorption spectra were collected from –200 to +1000 eV about the K-edge of As (11,867 eV). At least 5 spectra were collected for each sample and averaged for analysis. Internal calibration was achieved with sodium arsenate between the second and third ionization chambers; its inflection point was set at 11874 eV.
Analysis of XAS data was performed using WinXAS (Ressler, 1997). The X-ray absorption near-edge structure (XANES) spectra were collected to determine the oxidation state and coordination environment of the adsorbed As. For XANES analysis, the background was subtracted and the jump height normalized to unity for comparison. No smoothing of the raw spectra was done to preserve spectral line-shapes, although derivative spectra were smoothed 5% to minimize spectral noise. Experimental spectra were compared with the spectra of other common As species, including arsenate (Na₂HAsO₄), scorodite (FeAsO₄·2H₂O), arsenite (NaHAsO₂), realgar (AsS), orpiment (As₂S₃), and arsenopyrite (FeAsS). The As fraction that was oxidized to As(V) during analysis was estimated by fitting linear combinations of both a sample that had not yet oxidized (As(III) sorbed to PbS) and a sample that had undergone complete oxidation (As(V) on PbS). The oxidized standard was prepared by reacting a 1 g/L PbS suspension with 50 μM As(V) at pH 7 (28 μmol/g adsorbed); this sample underwent reduction during analysis so only the initial scan was used as a standard.

Extended x-ray absorption fine structure (EXAFS) spectroscopy allowed for the local structural environment of adsorbed As to be investigated in greater detail. Following spectral averaging, the background was subtracted from the spectra using a polynomial function; the resulting spectral jump heights were normalized to unity. A six-point cubic spline function that followed the envelope of the decaying spectrum was used to isolate the EXAFS spectral contribution (the χ(k) function). The energy (eV) scale was transformed to k-range using 11,185 eV as the energy of the As K edge (E₀). The χ(k) spectrum was then weighted by k³ in order to amplify the upper k-range and Fourier-transformed without smoothing to produce a radial structure function (RSF) using a k-
range of approximately 3 to 10 Å⁻¹. Distinct shells of the RSF function were then back-transformed to isolate the spectral contributions of each atomic shell. Final fits were completed using unfiltered k-weighted χ(k) spectra.

The WinXAS software package was used for EXAFS data analysis using phase and amplitude functions derived using FEFF 7.02 (Zabinsky et al., 1995; Rehr et al., 1991). The element (Z), coordination number (CN), distance (R), and the Debye-Waller factor (σ²) for each shell were determined by fitting the experimental spectrum. The Debye-Waller factor is effectively the variance in the bond length, and is a measure of the disorder of the coordination environment. Single and multiple scattering paths were considered, although no multiple scattering paths were required for fitting. The accuracy of these phase and amplitude functions were confirmed by comparing fits of orpiment, arsenate, and arsenite with known structures. For fitting, all variables were fit independently except E₀ and σ², which were constrained initially to minimize the number of variables. Once the filtered spectra were fit, the resulting parameters were combined and refit to the unfiltered χ(k) spectrum without constraints. The accuracy of the fits was estimated using the χ² statistical parameter, for which smaller values correspond to the best fits. Each fit had a reduced χ² of about 4000 for unsmoothed k³χ(k) spectra, and approximately 300 using RSF’s. By comparison with model compounds, the interatomic distances can be determined within 0.02 Å and the coordination number within 30% for the first shell and less accurate for more distant shells. Elements of similar atomic number (Z±2) cannot be distinguished due to similarities in the phase and amplitude functions, although differences in local structure (i.e. interatomic distances) may help to determine more information about which element is present.
Chromatography

High performance liquid chromatography (HPLC) was used to verify the oxidation state of the arsenic following sorption to PbS. A 0.025 M MOPS buffer was made and adjusted to pH 7 with 1 M NaOH and HCl. Suspensions (1g/L) were prepared by adding PbS in the MOPS buffer and adding As(III) to yield a final concentration of 20 µM. The resulting suspension was kept well stirred throughout the reaction period. Aliquots (5 mL each) were taken from this suspension and filtered (0.2 µm) periodically over 144 h prior to analysis. After 144 hours, the experiment was stopped, the suspension centrifuged (5000 rpm for 15 min) and the solution discarded. The solids were then resuspended in 100 mL of 10 mM phosphate buffer (pH 7) and shaken on a reciprocating shaker for 1.5 h to desorb residual As. All solutions were analyzed for both As(V) and As(III) by high performance liquid chromatography-hydride generation atomic absorption spectrophotometry (HPLC-HGAAS) (Manning and Martens, 1997).

Computational Methods

The structure and spectra of potential arsenic surface complexes was determined using density functional theory. Such computational methods are useful for determining the structure and spectra of a range of adsorption complexes (see Tossell and Vaughan, 1992), and are advantageous when comparing the spectra of unknowns with that of a wide variety of possible surface complexes, particularly for complexes that are not synthetically available. Adsorption complex structures were determined using density-functional calculations in PC Spartan Pro, with a perturbed Becke-Perdew basis set and
full numerical polarization. The density functional basis set used works well for determining the equilibrium geometry of transition metal complexes and typically reproduces bond lengths within 0.01 Å and energies of formation within 0.1 kcal/mol (Hehre et al., 1998).

FEFF 8 (Ankudinov et al., 1998) was used to determine the X-ray absorption spectra of As sorbed to galena and sphalerite using the geometry predicted by density functional methods. These calculations employed full self-consistent field corrections and full multiple scattering (up to 8 legs), which are particularly useful for calculating accurate XANES spectra. A Debye-Waller factor of 0.005 Å² was used for all paths based on the typical disorder for this and other As systems (Waychunas et al., 1993; Manning et al., 1998); no correction was made for thermal disorder as the Debye temperature was unknown for these complexes.

RESULTS AND DISCUSSION

Characterization of the Solid Phases

The surfaces of PbS and ZnS both contain sulfide ions that can oxidize in the presence of air. Consequently, their surfaces were examined to determine redox alterations. Washed ZnS and PbS each had S 2p spectra characteristic of unoxidized phases (Fig. 1). However, oxidized products, principally polysulfides, were also identified on PbS. Thus, the washing procedure, which presumably removed sulfate and much of the polysulfide, was not completely effective at removing all oxidized surface products. The ZnS surface was much less oxidized than the PbS surface. No oxidized sulfur species were identified by XPS, although this technique is only moderately surface
sensitive and, consequently, cannot be used to rule out limited surface oxidation. Little or no signal from O 2s electrons was apparent for ZnS, also indicative of a relatively unoxidized surface. In contrast, the oxidation of PbS was even detected by EDS. The EDS of PbS contained significant O contamination, indicative of an oxide or sulfate phase, while the EDS of ZnS particles were free of oxygen.

It should be noted that neither conventional-source XPS nor EDS is surface sensitive; these techniques examine about the first 20 monolayers of the surface. Despite these limitations, they are useful for characterizing surface oxidation. Synchrotron-based XPS, in which photoelectron energies are tuned to the minimum escape depth, would be useful to further determine both oxidation products and to provide more insight into the structure of the hydrated mineral surfaces.

**Macroscopic Characterization of Adsorption**

Arsenite adsorption on PbS and ZnS was described by a Langmuir isotherm at low coverages and a BET isotherm at higher coverages (Fig. 2). For both PbS and ZnS, sorption was weakest at pH 4 and stronger at higher pH. Adsorption to ZnS increased about 50% between pH 7 and 9, while adsorption to PbS was relatively unaffected by the pH change. The Langmuir isotherm describes adsorption to a finite number of adsorption sites and has been used extensively to describe the adsorption of anions (Stumm and Morgan, 1996). Deviation from the Langmuir isotherm at higher solution concentrations suggests that the maximum surface coverage is exceeded and that adsorbate-adsorbate interactions become significant. This deviation from the Langmuir isotherm at high
surface loading is described by a BET isotherm, suggesting the formation of polymeric complexes or a surface precipitate.

We used the adsorption maximum of the Langmuir equation to estimate the site density of PbS and ZnS. This adsorption maximum was determined without using data for the highest As(III) loadings. For PbS at pH 7, the adsorption maximum was 26 µmol/g, corresponding to a surface coverage of 6.0 µmol/m². The adsorption maximum for ZnS (17 µmol/g) was similar when normalized to surface area, 5.8 µmol/m². The resulting site densities, 3.6 and 3.5 sites/nm² for PbS and ZnS respectively, are consistent with values observed for arsenite adsorption on iron hydroxides (Dzombak and Morel, 1990; Hiemstra and Van Riemsdijk, 1999).

Surface precipitation may occur at high As(III) activity. One possible surface precipitate is arsenic sulfide, which is often proposed to explain As retention in sulfidic environments (Aggett and O’Brien, 1985; Sadiq, 1990). We examined the importance of these sulfide mineral precipitates in adsorption to PbS and ZnS by adding sulfide to suspensions. Sulfide additions did not stimulate As(III) retention on either PbS or ZnS (Fig. 3), in fact additional sulfide inhibited As retention. Therefore, precipitation of arsenic sulfides is not likely occurring on PbS and ZnS. The inhibitory role of sulfide may result from competition for surface sites or a change in surface chemical properties. Additional research is needed to elucidate the role of sulfide in these reactions.

Adsorption of As(III) varied with pH, increasing with increasing pH (Figures 2 and 4). For PbS, very little As(III) was adsorbed below pH 5, with adsorption increasing markedly between pH 5 and 7. ZnS exhibited similar behavior, although the adsorption edge was between pH 4 and 5. Adsorption and desorption edges were also compared to
determine whether equilibrium was established during a reaction. Arsenite adsorption to PbS was reversible (Fig. 4), indicating that any surface complex formed is relatively labile. Thus, surface precipitation mechanisms, which are typically much slower than observed here, are probably not responsible for sorption when As(III) loadings are at or below 50 µmol/g. Arsenite adsorption to ZnS was hysteretic at low pH (Fig. 4), implying that the As(III) surface complex formed on ZnS is more stable than that on PbS.

The effect of pH on As(III) sorption to PbS and ZnS is distinct from that on metal (hydr)oxides. Arsenite adsorption on metal (hydr)oxides is typically described by a diffuse pH envelope in which retention is greatest at circumneutral pH and lowest at high pH (Dzombak and Morel, 1990; Hiemstra and Van Riemsdijk, 1999). In contrast, As(III) increases with pH and has a well-defined adsorption edge on PbS and ZnS; similar behavior has been seen for As(III) adsorption to FeS and FeS₂ (Zouboulis et al., 1993). These differences have important implications for As(III) adsorption on metal sulfides. First, they establish that the sulfide mineral surfaces are not appreciably oxidized because they react distinctly from metal (hydr)oxides. Secondly, they imply that As(III) sorption on PbS and ZnS does not occur simply through the same ligand exchange reaction as postulated for As(III) on metal (hydr)oxides.

The effect of ionic strength (I) on adsorption is useful for broadly discriminating between inner- and outer-sphere mechanisms. Outer-sphere adsorption typically decreases with increasing I due to the competitive effects of the background electrolyte while ions retained as inner-sphere complexes are typically unaffected. Arsenic(III) sorption increased slightly with increasing I (Fig. 5); thus, As(III) most likely forms an inner-sphere complex although spectroscopic data is needed to confirm this conclusion.
This is not surprising since the surface of these sulfides is negative above pH 3 (Bebie et al., 1998) and thus should not form electrostatic bonds with the neutral or anionic As(III) species. Additionally, enhanced adsorption with increasing ionic strength suggests the possible co-adsorption of As with the electrolyte, although the reason for the slight increase with ionic strength is not known.

Little or no Pb or Zn was released into solution following sorption of arsenite and only small quantities of sulfur (as sulfide) at low ionic strength. Up to 5 µM Pb, Zn and S were released in the high ionic strength experiments, suggesting dissolution of PbS and ZnS. Some Zn, Pb and S were also released during the pH envelope experiments due to dissolution at extremely acidic pH. However, the quantity of Pb released was always substantially less than As adsorption. Thus, As adsorption is not described by exchange with Pb.

**Photo-oxidation of Adsorbed Arsenic**

Oxidation state changes could result from As adsorption or sample degradation caused by reaction with oxidized surface species. XANES spectroscopy offers a probe of such alterations. The XANES spectra of adsorbed As changes considerably during analysis (Fig. 6). For example, the spectra of 14 µmol/g of As on PbS initially have a single prominent edge feature with an inflection point near 11,869.5 eV, similar to other As(III) species. However, with progressive scans, an additional spectral feature at 11,874 eV, characteristic of arsenate, As(V), becomes prominent. An isosbestic point indicative of a binary (two-component) system suggests that these two species are the only ones present. Oxidation was quantified using linear combinations of both As(III) and As(V).
adsorbed on PbS (Table 1). Initially, most (85%) of the As was adsorbed as As(III); however, by scan 6 (about 180 min) the spectrum was 75% As(V). This trend in oxidation was observed for all samples regardless of As coverage. In fact, oxidation was most pronounced for samples that contained the highest As loading.

Arsenite oxidation was confirmed using EXAFS spectroscopy (Fig. 6b). The initial scan of 14 µmol/g As on PbS indicates that the As is coordinated primarily to S at a distance of 2.48 Å (Table 1). A small spectral feature due to arsenate (an As-O shell at 1.70 Å) is also observed. After 110 min, the As-S shell CN decreased to 1.7 and the arsenate CN increased to 2.3, indicative of extensive oxidation. Although EXAFS spectroscopic results are comparable to those obtained by XANES analysis, poor spectral quality and inherent accuracy of coordination numbers determined by EXAFS limits their quantitative comparison.

Arsenic oxidation on PbS was also detected chromatographically (Fig. 7; Table 2). After 144 h, a small fraction of As(V) was present in solution. Displacement of surface-associated As with phosphate reveals appreciable (~70%) oxidation to As(V). Thus, the extent of oxidation observed chromatographically was significantly less than was observed by XAS, for which oxidation was complete within a few hours. It must be noted, however, that the recovery of adsorbed As species was small and it is unknown if As(III) or As(V) is preferentially desorbed by phosphate addition.

Arsenite oxidation on PbS could arise from a variety of sources. Small quantities of both sulfate and elemental sulfur were noted for both galena and sphalerite (Fig. 1). Interestingly, initial XANES spectra showed only a small (although measurable) fraction of As(V), regardless of the amount of time in the glovebox prior to XAS analysis.
Oxidation proceeds rapidly only during exposure to the X-ray source. Such photo-oxidation has been observed for several arsenic sulfide species (e.g., Zhou et al., 1992), and explains the enhanced oxidation rate observed by XAS compared to HPLC-HGAAS analysis. Metal thiolates are nucleophiles that lower the absorption energies of the surface (Diaz et al., 1999), which in turn promotes oxidation induced by light or thermal energy. The electronic structure of thioarsenites also makes them particularly susceptible to metal-ligand charge transfer (Zhou et al., 1992). Although photo-oxidation is likely, it requires an oxidant to proceed. Several oxidants may be responsible, including oxidized sulfur species that are detected by XPS, and O$_2$ introduced during analysis. However, in each case only a small fraction of oxidant is required to oxidize the arsenic—if sulfate is assumed to be the oxidant, only 25% of a monolayer of sulfate would be required to oxidize all adsorbed As (a 4 As : 1 SO$_4^{2-}$ ratio). Such small quantities of oxidants are hard to exclude.

Arsenite oxidation was not observed on ZnS. The only spectral feature detected using XANES spectroscopy had an absorption edge of 11869.8 eV (Fig. 8). There are two prominent differences between PbS and ZnS that may explain their variation in reactivity towards oxidation. The XPS and SEM-EDS analyses indicate that ZnS was significantly less oxidized than PbS; therefore, there are fewer oxidants available to react with As(III) (Fig. 1). Additionally, if photochemical processes are responsible for oxidation, then the ZnS should react less favorably than PbS due to its increased band gap relative to that of PbS (0.35 eV for PbS vs. 3.6 eV for ZnS; Weast, 1988).
Local Structure of Adsorbed Arsenic

Adsorption on sulfide minerals may influence the local coordination environment of As. XANES spectroscopy provides information about the coordination environment indirectly—it probes changes in oxidation state that can then be correlated to changes in coordination environment. EXAFS spectroscopy allows these changes to be quantified.

For As(III) on ZnS, XANES spectra were analyzed without any modification; however, spectral processing was often required to examine the local structure of adsorbed (unoxidized) surface species on PbS. For As(III) on PbS, spectral acquisition was limited to a single scan (about 15 minutes) for XANES analyses to minimize oxidation, during which time only a small amount of oxidation occurred. This provided sufficient data quality for XANES analysis but was insufficient for EXAFS analysis. Consequently, several spectra were averaged and spectral subtraction was used to isolate the unoxidized portion of a spectrum.

A large change in the local chemical environment of As is revealed by the XANES spectra. The As absorption edge of the adsorbed As(III) on PbS is shifted lower by 1.5 eV relative to solution phase arsenite, which has an absorption edge of 11,871 eV (Fig. 8). Arsenite adsorbed to ZnS has a similar edge positioned near 11,869.8 eV. The red-shift of adsorbed As(III) likely results from the ligand exchange of oxygen for sulfur—the decrease in ligand electronegativity lowers the excitation energy. In fact, the adsorption edge matches that of orpiment, an As(III) mineral in which As is triply coordinated to S.

For EXAFS analysis of As(III)-reacted PbS samples, spectral subtraction was required to remove the oxidized As(V) component. EXAFS spectra were averaged to get
a composite that contains contributions of both oxidized and unoxidized components. EXAFS spectra of the oxidized surface species were obtained by averaging the last three scans, typically after 3 to 4 hours of reaction. EXAFS spectra of the unoxidized surface species were obtained by difference between the two averages, weighted until little or no oxygen contribution was observed in subsequent EXAFS spectra. Following renormalization, these residual spectra were used to determine the structure of the unoxidized surface complex.

The As local structure observed by the EXAFS spectroscopy of As(III) on PbS (Fig. 9) and ZnS (Fig. 10) also reveals As-S interactions (Table 1). For As adsorbed on PbS, As is coordinated to 3 S at a distance of about 2.4 Å. This As-S distance is somewhat longer than is observed in orpiment, which has an As-S bond length of 2.2 Å, indicating that the structure of adsorbed As is different than the local structure of As in orpiment. An As-As shell is also apparent in the spectra of As(III) on PbS at a distance of about 3.6 Å, which is longer than the disordered As-As shell between 3.2 and 3.5 Å in orpiment (Mullen and Nowacki, 1972; Helz et al., 1995). Thus, orpiment is not found, but a phase (or phases) with a similar number of As-S bonds (3) is present.

The spectra of As(III) adsorbed to PbS did not change appreciably with surface coverage (Fig. 9). Each sample contained a Pb-S shell at about 2.5 Å, and a As-As shell at 3.65 Å. The similarities in spectra for all coverages suggest that one site-type predominates, although smaller fractions of other surface complexes surely are present. The As-As shell was pronounced even at surface coverages less than 10% of a monolayer coverage, suggesting surface clusters even at low coverage.
Arsenite adsorbed on ZnS contains shorter As-S and As-As distances than those observed for PbS (Fig. 9). The As-S bond distances were near 2.25 Å, while As-As distances were 3.35 Å, both of which are contracted by about 0.2 Å relative to PbS. The shells also were somewhat more ordered (a smaller Debye-Waller factor) for As(III) adsorbed on ZnS.

Possible Mechanisms of As Adsorption

The macroscopic data suggest that As(III) is adsorbed on ZnS and PbS surfaces dominantly as inner-sphere complexes. Typically, adsorption to sulfide minerals is modeled as a process analogous to oxide minerals, with adsorption occurring at the hydroxylated metal surface sites. These processes assume that the surface is hydroxylated and have no surface sulfhydryl groups to interact with ions in solution. For example, carbonate adsorption is thought to occur through ligand exchange on hydroxyl surface sites of sulfide minerals (Gärd et al., 1995).

\[
\equiv Me - OH + HCO_3^- \Leftrightarrow Me - OHCO_2^0 + OH^- \tag{1}
\]

which can be rewritten for As(III) sorption, assuming that protonation of the surface complex is the same as in solution (Equation 2; Raven et al., 1998).

\[
\equiv Me - OH + As(OH)_3 \Leftrightarrow Me - OHAs(OH)_2^+ + OH^- \tag{2}
\]

Similar reactions are postulated for iodide sorption on cinnabar (Balsley et al., 1996; 1998).

Proposed sorption reactions can be tested by examining proton stoichiometry. Equations 1 and 2 each assume the evolution of one hydroxide ion and thus should be favored at low pH. In contrast, As(III) adsorption to PbS and ZnS increases with pH (Fig. 3). This difference suggests that Equation 2 is a poor representation of the
adsorption reaction. XAS data also provide evidence of a distinct adsorption process for As(III) on PbS and ZnS. Equation 2 preserves the oxo coordination of As(III); XAS data show that the coordination of As changes from oxo to sulfido upon adsorption. Precipitation could also explain the formation of As-S bonds; however, the reversibility of adsorption, coupled with the different interatomic distances observed for the surface complex compared to known arsenic sulfide complexes, leads us to reject this possibility. Therefore, it appears that arsenic sulfide complexes are formed when As(III) adsorbs to PbS and ZnS.

Several polymeric arsenic sulfide complexes are known to be stable in solution and many such complexes have been postulated to explain increased As(III) solubility in sulfidic solutions (Helz et al., 1995; Spycher and Reed, 1989; Webster, 1990; Tossell, 2000). The most important of these complexes in slightly sulfidic solutions is $\text{AsO(SH)}_2^-$ with $\text{As}_3\text{S}_3(\text{SH})_3$ and its conjugate base more prevalent at higher sulfide activities. Other solution complexes have been postulated (e.g., Mironova et al., 1990), including the $\text{As}_2\text{S}_2(\text{SH})_2$ dimer; however, their existence is not well established and distinction between them is difficult using only macroscopic observables. Of these, the monomeric species can be disregarded because its structure is not consistent with the sulfur coordination observed by XAS; the dimer can similarly be disregarded (Helz et al., 1995). In contrast, the $\text{As}_3\text{S}_3(\text{SH})_3$ complex is consistent with the surface complex observed here.

Unfortunately, no standards are available to study the structure of these arsenic sulfide complexes explicitly, necessitating computational methods. The structure of the complexes was calculated using density functional theory and the resultant geometries
The As trimer (As$_3$S$_3$(SH)$_3$) contains similar bond lengths and angles to those observed on ZnS; the As-S and As-As interatomic distances of 2.25 and 3.35 Å, respectively, are within 0.02 Å of that observed for ZnS. In fact, the As trimer has a very similar calculated EXAFS spectrum to that observed for As(III) adsorbed to ZnS (Fig. 10). Based on these structural similarities, the As(III) surface complex on ZnS is likely to indeed be the thioarsenite trimer.

The As trimer may also form on PbS, although the As-S and As-As bond distances are longer than those of the protonated As trimer. Part of this discrepancy can be explained by the variability in the As-S and As-As bond lengths of the protonated and deprotonated trimeric complex. The As trimer is a relatively strong acid (Helz et al., 1995) and the deprotonated trimer, As$_3$S$_3$(SH)$_2$S$^-$, assumes a much more planar structure; consequently its internal As-S bonds expand to over 2.3 Å, similar to those observed for As(III) on PbS (Table 4). The As-As distances calculated for As$_3$S$_3$(SH)$_2$S$^-$ are also similar to those of As(III)-adsorbed PbS, further suggesting the trimer may be present both on the ZnS and PbS surfaces.

The coordination environment of As on both mineral sulfides is also consistent with structural constraints imposed by the surfaces. The (111) surface of ZnS is the most common and it contains nearly identical sulfur coordination to that observed for the As trimer. If As occupies the tetrahedral sites above the sulfur plane that are coordinated to Zn in the bulk crystal (Fig. 11a), then little or no distortion is necessary to form the measured As-S bond distances. The structure of As adsorbed to PbS is less consistent with the crystallographic considerations (Fig. 11b). Constraints based on the EXAFS-derived interatomic distances allow PbS to adsorb As(III) only on the (111) plane with As
in the tetrahedral sites normally vacant in the bulk structure. The longer As-S distance can be explained due to the increased distance between the surface sulfur atoms and the planar arrangement of sulfur atoms at the galena surface. Alternatively, the As trimer could bind end-on to the surface—such a complex would not be constrained by surface structure. Thus, crystallographic considerations suggest the presence of an adsorbed trimeric As species on ZnS; the nature of the As trimer adsorbed to PbS is less clear.

The combination of these data allows us to postulate a chemical reaction that is consistent with the solution data presented above. The complete chemical reaction must exhibit increased adsorption with pH, form a reversible surface complex, not evolve Pb, Zn, and little sulfide, and be inhibited by sulfide. The reaction must also form the surface As species $\text{As}_3\text{S}_3(\text{SH})_3$ or $\text{As}_3\text{S}_3(\text{SH})_2\text{S}^-$, suggested by XAS. The following reaction for As(III) adsorption to a generic metal sulfide ($\text{MeS}$), where Me is either Pb or Zn, is consistent with these considerations assuming that the surface is sulfhydryl-terminated.

$$9 \equiv \text{MeSH} + 3\text{As(OH)}_3 \Leftrightarrow 9 \equiv \text{MeO}^- + \text{As}_3\text{S}_3(\text{SH})_3 + 3\text{H}_2\text{S} + 9\text{H}^+ \quad [3]$$

If the Me sites were not completely deprotonated, the reaction would be the following:

$$9 \equiv \text{MeSH} + 3\text{As(OH)}_3 \Leftrightarrow 9 \equiv \text{MeOH} + \text{As}_3\text{S}_3(\text{SH})_3 + 3\text{H}_2\text{S} \quad [4]$$

Reaction 3 is strongly pH dependent—Me hydrolysis and the acidity of the As trimer and $\text{H}_2\text{S}$ contribute to the observed pH dependence. These reactions evolve sulfide, which can recombine with the Me sites according to the following reaction:

$$3 \equiv \text{MeOH} + 3\text{H}_2\text{S} \Leftrightarrow 3 \equiv \text{MeSH} + 3\text{H}_2\text{O} \quad [5]$$

The combination of reactions 4 and 5 yields the net reaction below.

$$6 \equiv \text{MeSH} + 3\text{As(OH)}_3 \Leftrightarrow 6 \equiv \text{MeOH} + \text{As}_3\text{S}_3(\text{SH})_3 + 3\text{H}_2\text{O} \quad [6]$$
If recombination is complete as suggested by Equation 6, then sulfide additions would not influence adsorption because it is not a reactant or product. Our data show that sulfide inhibits As adsorption, thus some intermediate reaction between reactions 3, 4 and 6 probably occurs as a result of incomplete deprotonation of surface hydroxyls or exchange of surface hydroxyls with bisulfide in solution.

It should be noted that these reactions serve only as a guideline to understanding the mechanism of As(III) adsorption to these mineral phases. Additional reaction products undetected using these methods may be present; thus, the reaction stoichiometry is only approximate. Despite these limitations, the reactions are consistent with the key observations that As adsorption on PbS and ZnS is greatest at higher pH and forms a polynuclear arsenic sulfide complex.

**CONCLUSIONS**

Adsorption of As on PbS and ZnS involves a complex mechanism. An inner-sphere complex forms on the mineral surface; however, the As(III) surface complex on PbS is labile. Interestingly, As(III) adsorption increases sharply with pH, which is distinct from As(III) adsorption on iron oxides, indicating that the adsorption mechanisms differ. Spectroscopic data corroborates the difference between As(III) adsorption on sulfides versus that on oxides. The formal oxidation state of the arsenic is unchanged by adsorption, although the edge shifts to lower energies due to sulfur coordination. Surface sulfhydryl groups are present and are the reactive species in arsenite adsorption; their presence needs to be considered to accurately determine the mechanism of ion adsorption in other systems. Conventional ligand exchange mechanisms with surface hydroxyl or
sulfhydryl groups can be ruled out because they preserve the oxo-coordination of arsenite and XAS results show that adsorbed As is sulfur-coordinated. Rather, ligand exchange of hydroxyl groups on arsenite for surface-bound sulfhydryl groups results in the formation of sulfide complexes similar to $\text{As}_3\text{S}_3(\text{SH})_3$ clusters observed in solution (Helz et al., 1995). These clusters oxidize on the PbS surface by reaction with residual oxidants on the sulfide mineral but form stable inner-sphere complexes on ZnS. Thus, adsorption on sulfide minerals may be an effective means of reducing As concentrations in natural environments.

REFERENCES


Table 1. Oxidation state of 20 µM As(III) adsorbed to 1 g/L PbS at pH 7 (14 µmol/g). The As(III) and As(V) fractions, as well as the coordination number (CN) and interatomic distance (R), were determined using XANES and EXAFS spectra in Figure 6.

<table>
<thead>
<tr>
<th>Scan No.</th>
<th>Time (min)</th>
<th>As(III)</th>
<th>As(V)</th>
<th>As-S</th>
<th>As-O</th>
<th>As-S</th>
<th>As-O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>-------</td>
<td>CN</td>
<td>R (Å)</td>
<td>CN</td>
<td>R (Å)</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>85</td>
<td>15</td>
<td>3.3</td>
<td>2.48</td>
<td>1</td>
<td>1.70</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>66</td>
<td>34</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>45</td>
<td>55</td>
<td>-</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>110</td>
<td>38</td>
<td>62</td>
<td>1.7</td>
<td>2.48</td>
<td>2.3</td>
<td>1.69</td>
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<tr>
<td>5</td>
<td>145</td>
<td>31</td>
<td>69</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>180</td>
<td>25</td>
<td>75</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2. Oxidation state of 20 µM As(III) adsorbed to 1 g/L PbS (at pH 7) as determined by HPLC-GFAAS.

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>As(III) µM</th>
<th>As(V) µM</th>
<th>As sorbed percent</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>6.01</td>
<td>ND</td>
<td>69.5</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
<td>5.78</td>
<td>ND</td>
<td>71.1</td>
<td>-</td>
</tr>
<tr>
<td>48</td>
<td>0.065</td>
<td>ND</td>
<td>99.6</td>
<td>-</td>
</tr>
<tr>
<td>144</td>
<td>ND</td>
<td>ND</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>144-PO₄³⁻ extract b</td>
<td>0.33</td>
<td>1.49</td>
<td>-</td>
<td>9.1</td>
</tr>
</tbody>
</table>

(a): Below detection limits.
(b): A 1:10 dilution of a 10 mM PO₄³⁻ extractant solution added to suspension after 144 hours.
Table 3. Local structure for As(III) adsorbed to PbS and ZnS. Fits of samples adsorbed to PbS reflect the subtraction of the oxidized As(V) component. The coordination number (CN) is typically accurate to within ±1, interatomic distance (R) within ± 0.02 Å; $\sigma^2$ represents the variance in R. For all of the media, $E_0$ was set at ≈ 11870 eV.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atoms</th>
<th>CN</th>
<th>R (Å)</th>
<th>$\sigma^2$ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 µmol/g As(III) on PbS</td>
<td>As-S</td>
<td>3.32</td>
<td>2.51</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>As-As</td>
<td>2a</td>
<td>3.65</td>
<td>0.007</td>
</tr>
<tr>
<td>16 µmol/g As(III) on PbS</td>
<td>As-S</td>
<td>2.84</td>
<td>2.50</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>As-As</td>
<td>2a</td>
<td>3.66</td>
<td>0.005</td>
</tr>
<tr>
<td>20 µmol/g As(III) on PbS</td>
<td>As-S</td>
<td>3.42</td>
<td>2.51</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>As-As</td>
<td>2a</td>
<td>3.65</td>
<td>0.007</td>
</tr>
<tr>
<td>36 µmol/g As(III) on PbS</td>
<td>As-S</td>
<td>3.21</td>
<td>2.52</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>As-As</td>
<td>2a</td>
<td>3.68</td>
<td>0.008</td>
</tr>
<tr>
<td>62 µmol/g As(III) on PbS</td>
<td>As-S</td>
<td>2.66</td>
<td>2.52</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>As-As</td>
<td>2a</td>
<td>3.68</td>
<td>0.007</td>
</tr>
<tr>
<td>14 µmol/g As(III) on ZnS</td>
<td>As-O</td>
<td>0.79</td>
<td>1.76</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>As-S</td>
<td>2.25</td>
<td>2.23</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>As-As</td>
<td>1.63</td>
<td>3.35</td>
<td>0.003</td>
</tr>
</tbody>
</table>

(a): Fixed during fitting.
Table 4. Interatomic distances determined using density functional theory for selected arsenic sulfide complexes.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\text{As-S}^a$</th>
<th>$\text{As-S}^b$</th>
<th>As-O</th>
<th>As-As</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(SH)$_3$</td>
<td>-</td>
<td>2.23</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AsS(OH)(SH)$^-$</td>
<td>-</td>
<td>2.11, 2.26</td>
<td>1.81</td>
<td>-</td>
</tr>
<tr>
<td>As(OH)(SH)$_2$</td>
<td>-</td>
<td>2.25</td>
<td>1.82</td>
<td>-</td>
</tr>
<tr>
<td>As$_2$S$_2$(SH)$_2$</td>
<td>2.25</td>
<td>2.23</td>
<td>-</td>
<td>3.01</td>
</tr>
<tr>
<td>As$_3$S$_3$(SH)$_3$</td>
<td>2.24</td>
<td>2.23</td>
<td>-</td>
<td>3.34</td>
</tr>
<tr>
<td>As$_3$S$_3$(SH)$_2$S$^-$</td>
<td>2.31 (2.25-2.47)$^c$</td>
<td>2.11, 2.26</td>
<td>-</td>
<td>3.45</td>
</tr>
</tbody>
</table>

(a): Internal (bridging) As-S bonds.
(b): External (As=S$^-$ and As-SH) As-S bonds.
(c): Average value, with range in parentheses.
Figure 1. S 2p XPS of the PbS (a) and ZnS (b) used in these experiments. Washing removed much of the sulfate associated with the surface; however, residual polysulfide was present at the surface of PbS.
Figure 2. Adsorption isotherms of As(III) on 1 g/L PbS (a) and ZnS (b) as a function of pH.
Figure 3. Effect of sulfide addition on 55 μM As(III) sorption to 1 g/L PbS at pH 7.
Figure 4. The adsorption envelopes for 50 µM As(III) on 1 g/L PbS (a) and ZnS (b).
Figure 5. Effect of ionic strength on the adsorption of 55 µM As(III) sorption to 1 g/L PbS at pH 7.
Figure 6. XAS of 20 μM As reacted with 1 g/L PbS at pH 7 (14 μmol/g) over successive scans. The XANES spectra (a) shows the average of all scans and each of the first 6 individual scans that were collected. The EXAFS spectra show both the (b) k-weighted \( \chi(k) \) spectra, and (c) the RSF functions for scans 1 and 4. Each scan takes approximately 0.5 hours to complete.
Figure 7. Representative HPLC-HGAAS chromatograms of standard solutions and As(III)-treated PbS showing (a) 20 ppb As(III) standard, (b) 20 ppb As(V) standard, (c) As(III)-PbS reaction solution at t = 48h (no dilution), and (d) replicate injections of 10 mM PO$_4^{3-}$ buffer extract of As(III)-treated PbS (1:10 dilution).
Figure 8. Representative XANES spectra of As(III) adsorbed on ZnS and PbS compared to several As standards.
Figure 9. The k-weighted $\chi(k)$ spectra (a) and corresponding RSF’s (b) of As(III) adsorbed on PbS as a function of As(III) surface loading. The spectral component due to oxidized species has been subtracted for ease of interpretation.
Figure 10. The k-weighted $\chi(k)$ spectrum (a) and RSF (b) of As(III) adsorbed on ZnS. The calculated spectrum of $\text{As}_3\text{S}_3(\text{SH})_3$ (c) is shown for comparison.
Figure 11. The proposed structure of the As trimer on the [111] ZnS (a) and [111] PbS (b) surfaces. The light atoms are sulfur, the black atoms are As, and the gray atoms are Pb or Zn.

a: (111) ZnS with trimer

b: PbS (111) with trimer
Chapter 3.

Arsenite Sorption on FeS and FeS$_2$
ABSTRACT

Arsenite sorption to iron sulfide (FeS) and pyrite (FeS$_2$) was investigated as a function of total arsenic concentration, suspension density, sulfide concentration, pH, and ionic strength. Arsenite partitioned strongly to both FeS and FeS$_2$ under a range of conditions. Sorption obeyed a Langmuir isotherm at low surface coverages, with a calculated site density of near 2.6 and 3.7 sites/nm$^2$ for FeS and FeS$_2$ respectively. The maximum surface loading was exceeded at elevated As concentrations, suggesting surface precipitation was important under such conditions. X-ray absorption spectroscopy (XAS) confirmed the presence of surface precipitates at all coverages. Sorbed As was coordinated to both sulfur and iron at distances of 2.35 and 2.4 Å, respectively, characteristic of a decrease in As coordination in arsenopyrite (FeAsS). The absorption edge of sorbed As was also shifted relative to arsenite and orpiment (As$_2$S$_3$), revealing As(III) reduction and a complete change in As local structure. The resulting surface complex was susceptible to oxidation, possibly influencing the stability of As sorbed to sulfide minerals in the environment. Sulfide additions inhibit sorption despite the formation of a sulfide phase. Surface precipitation of As on FeS and FeS$_2$ supports the empirical correlation of arsenic uptake with pyrite and other iron sulfides.

INTRODUCTION

Arsenic is an element whose toxicity and bioavailability is controlled largely through sorption processes (Cullen and Reimer, 1989; Korte and Fernando, 1991). Under oxic conditions, As is primarily found as arsenate, As(V), which adsorbs strongly to Fe and Al (hydr)oxides (e.g., Anderson et al. 1976; Waychunas et al., 1993; Manning and
Goldberg, 1996; Fendorf et al., 1997; Hiemstra and Van Riemsdijk, 1999). Adsorbed arsenic species are released into solution under slightly reducing conditions through the reductive dissolution of the Fe (hydr)oxides and subsequent release of arsenate (Cummings et al., 1999; Nickson et al., 2000; Zobrist et al., 2000). Arsenate reduction to highly-toxic arsenite, As(III), may accompany its release into solution, potentially leading to widespread environmental contamination (Nickson et al., 1998; Acharyya et al., 1999; Langner and Inskeep, 2000).

Arsenic concentrations typically decrease under anoxic conditions in ocean sediments (Cutter, 1991; Sullivan and Aller, 1996), freshwater lakes (Aggett and O’Brien, 1985; Balistrieri et al., 1994), and rivers (Moore et al., 1994, Johannesson et al., 2000). The uptake of arsenic in anoxic environments is strongly correlated with the formation of iron sulfide minerals including pyrite. Selective extractions suggest that As is highly pyritized (e.g., Huerta-Diaz and Morse, 1992; Cooper and Morse, 1996); however, the contributions of precipitation, coprecipitation, and adsorption mechanisms on sulfide minerals has not been resolved (e.g., Belzile et al., 1989; Cooper and Morse, 1998; Holmes, 1999). Arsenic sulfides have also been identified in contaminated lakes (Soma et al., 1994) and wetlands (LaForce et al., 2000). Although the formation of discrete arsenic sulfides, such as orpiment (As$_2$S$_3$), realgar (AsS) or arsenopyrite (FeAsS), has been proposed to explain As uptake in anoxic environments, arsenic solubility seldom conforms to that of pure mineral sulfides (Sadiq, 1990; Sadiq, 1997). Thus, the specific mechanism of As retention in anoxic systems is not well understood despite the empirical relationship between the presence of sulfide minerals and arsenic solubility.
The surface chemistry of pyrite and other iron sulfide minerals has received considerable attention. Surface termination may lead to the formation of unsaturated surface groups that react with water or dissolved sulfide under environmental conditions (Guevremont et al., 1998b). Such defects occur at under-coordinated surface atoms (Rosso et al., 1999) or surface Fe or S sites partially stabilized by disproportionation, and are highly reactive (Guevremont et al., 1997; Uhlig et al., 2001). Disproportionation reactions result in a wide variety of surface species, including Fe(III) sulfides and polysulfides, even on pristine surfaces (Nesbitt and Muir, 1994; Herbert et al., 1998; Nesbitt et al., 1998). The defect structures control surface oxidation by serving as centers for electron transfer (Guevremont et al., 1997; Guevremont et al., 1998a; Bostick et al., 2000a). Cation sorption reactions may also involve defects and redox processes such as the oxidation and disproportionation of the surface (e.g., Bancroft and Hyland, 1990; Xie et al., 1996; Bostick et al., 2000b). For example, the adsorption of Ag$^+$ on pyrite involves sulfur disproportionation and redox processes (Hiskey et al., 1987; Scaini et al., 1995).

$$FeS_2 + 8Ag^+ + 4H_2O \rightleftharpoons Fe^{2+} + Ag_2S + 6Ag^0 + SO_4^{2-} + 8H^+ \quad [1]$$

Other adsorption reactions may also occur. Surface protons may exchange with cations in solution according to traditional surface complexation or ion exchange (James and Parks, 1975; Kornicker and Morse, 1991).

$$m(\equiv S - H) + Me^{2+} \leftrightarrow (\equiv S)_m - Me^{2m} + mH^+ \quad [2]$$

Metal cations may exchange with insoluble sulfides through a replacement reaction (Gaudin et al., 1959; Pugh and Tjus, 1987; Park and Huang, 1989).

$$Me^{2+} + ZS \leftrightarrow MeS + Z^{2+} \quad [3]$$
Such replacement reactions are favored when the resulting sulfide is less soluble than the initial sulfide mineral; they are thus important for soluble sulfide minerals such as iron sulfide. These examples illustrate the rich diversity of cation adsorption reactions that are possible on iron sulfide minerals.

Anion adsorption on sulfide minerals has received less attention. Anion sorption to sulfide minerals is typically modeled as an exchange reaction with surface hydroxyl and sulfhydryl groups (Gärd et al., 1995; Balsley et al., 1996; Forsling and Sun, 1997; Balsley et al., 1998). Disproportionation or other redox transformations may also couple with anion sorption on sulfide surfaces; however, the extent of oxidation and reduction during anion sorption is not well documented.

Sulfide or sulfide minerals appear to regulate As levels in anoxic environments. Some macroscopic studies of arsenic sorption have been performed on sulfide minerals (Grigorev et al., 1976; Grigorev and Pushkarev, 1986; Zouboulis et al., 1993; Hasany et al., 1999). The mechanism of arsenic retention, however, has not been described. Accordingly, we characterize arsenite sorption on FeS and FeS$_2$ using both traditional solution-phase methods and spectroscopic techniques. Solution-phase data provide information about the variables that control As sorption to sulfide minerals. Spectroscopic techniques, such as x-ray absorption spectroscopy (XAS) and x-ray photoelectron spectroscopy (XPS) can identify the structure and oxidation state of sorbed As, providing information needed to better estimate the importance of sulfide phases to As regulation in the environment.
MATERIALS AND METHODS

Materials

All chemicals used were of analytical grade. Iron sulfide minerals were obtained from Strem Chemical (>99% purity) and were identified as troilite and pyrite by X-ray diffraction. These minerals oxidize readily; therefore, care must be taken to prevent oxidation and preserve, as best as possible, the integrity of the sulfide surface. Consequently, the following procedures were used to prevent oxidation. Reactions were performed in a mixed H₂/N₂ atmosphere (10% H₂) with a Pt catalyst that maintained O₂ concentrations below 1 ppm. Additionally, minerals were stored under nitrogen and the surfaces were carefully cleaned prior to use. Minerals were first washed with water, then a 0.01 M sulfide solution (pH 7) to reduce any remaining oxidized species, and then washed again with water to remove residual sulfide and other products. Sulfide treatment created similar surfaces to acid treatment for FeS₂ and was superior to acid for FeS, which dissolved in the strong acid solution.

Surface area was determined with a three-point BET isotherm using N₂ as the adsorbate. The surface area of FeS and FeS₂ were 3.2 and 41 m²/g respectively. X-ray photoelectron spectroscopy (XPS) was used to characterize the extent of surface oxidation as described below. Scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS) was further used to characterize the solid phases; fewer fine-grained material in washed samples were noted.

Solution-Phase Experiments

Several parameters, including concentration of As(III), mineral, and sulfide, pH, and ionic strength, can influence the extent of As(III) sorption on FeS and FeS₂.
Therefore, FeS and FeS$_2$ suspensions (1 g/L) were reacted with arsenite (0 to 250 µM As(III) initial concentration) under a wide range of conditions to determine their effect on As sorption. Arsenic and sulfide were added using 10 mM stock solutions, As(III) as NaHAsO$_2$, sulfide as Na$_2$S·9H$_2$O. Adsorption isotherms were performed at pH 4, 7 and 9 by buffering 1 g/L mineral suspensions with 0.002 M acetate, MOPS, or borate to maintain sample pH. Ionic strength was varied between 0.005 M and 0.5 M with 1.0 M NaCl, and initial total sulfide concentration set between 0 and 2 mM.

The effect of pH on sorption was investigated by adjusting the pH of FeS$_2$ and FeS suspensions (1 g/L) containing As(III). The initial suspension pH was adjusted to between 2 and 3 (with 0.1 M HCl and 0.1 M NaOH) and then the As(III) stock solution was added to create a 50 µM As(III) solution. A sample of the suspension was filtered (0.2 µm pore size) and the pH measured following 0.5 h equilibration at each pH. This procedure was repeated until the pH reached about 11. Similar experiments were performed using suspensions in which the initial pH was high (about 11) and titrated to near 3 with HCl. Residual solutions were analyzed for total Fe, As, and S using a Thermo Jerrell Ash IRIS inductively coupled plasma-optical emission spectrometer (ICP-OES). The extent of sorption was determined by difference between initial and final As concentrations. Selected residual solids were sealed in Kapton film to prevent oxidation, stored under nitrogen, and analyzed by XAS or XPS within 1 d of their preparation.

**Flow-Cell Experiments**

Flow-cell experiments were performed to study the effect of residence time on As sorption to FeS$_2$. These experiments employed a small (1-cm in diameter and 0.1-cm
length) disk through which a solution containing As(III) and sulfide solutions were passed (Fig. 1). The disk was placed directly into the synchrotron beam to permit in situ XAS analysis without oxidation of the column materials. Solutions were pumped through the column using a peristaltic pump operating at a flow rate between 0.10 mL min\(^{-1}\) and 1.0 mL min\(^{-1}\), corresponding to residence times between 15 and 150 sec. Residence times were significantly shorter than reaction times of As(III) sorbed to FeS\(_2\) in batch experiments; thus, these experiments permit the study of kinetics and short-lived intermediates.

Arsenic(III) solution concentrations were set at 25 \(\mu\)M. Care was taken to avoid orpiment (As\(_2\)S\(_3\)) saturation; sulfide concentrations were kept at 0.5 \(\mu\)M. The pH was maintained at 7 using 0.002 M MOPS added directly to As(III) solutions. The disk equilibration process was monitored by XAS. Spectra were collected prior to reaction with arsenite solution and consecutively following flow of the As(III) solution. Final spectra were obtained once no changes were apparent in the adsorption edge of these rapid scans. The equilibration time was quite rapid, about 15 to 30 min was typically sufficient.

A small volume of As solution was present that potentially could influence the observed spectrum of sorbed As(III). Blanks were thus run in the presence of solution prior to column packing to ensure that solution-phase As did not contribute to the spectrum. Controls were also run without As in solution to identify contaminants in the mineral suspensions. Additional blanks were examined to test for the presence of As in the column or column housing. All blanks were devoid of As edges; thus, spectra collected in flow cell experiments were representative of arsenite sorbed on FeS\(_2\).
X-ray Absorption Spectroscopy

X-ray absorption spectroscopy was performed at the Stanford Synchrotron Radiation Laboratory on beamlines 4-1, 4-3, or 9-3. The storage ring operated at 3.0 GeV and at currents between 50 and 100 mA. Spectra were taken with a Si(220) double-crystal monochromator with an unfocused beam. Incident and transmitted intensities were measured with 15-cm N2-filled ionization chambers. Sample fluorescence was measured with either a Stern-Heald or 13-element Ge detector orthogonal to the incident beam and using a 6 µx Ge filter. The beam was detuned approximately 50% to reject higher-order harmonic frequencies and to prevent detector saturation. Spectra were internally calibrated by placement of a sodium arsenate standard between the second and third ionization chamber; its inflection energy was set at 11,874.0 eV.

X-ray absorption spectra were collected from –200 to +1000 eV about the K-edge of As (11,867 eV). At least 5 spectra were collected for each sample and averaged for analysis. The WinXAS software (Ressler, 1997) was used to analyze XAS data. For x-ray absorption near-edge structure (XANES) analysis, the background was subtracted and the jump height normalized to unity for comparison. No smoothing of the raw spectra was done to preserve spectral line-shapes, although derivative spectra were smoothed 5% to decrease spectral noise. Experimental spectra were compared with those of other common As species, including arsenate (Na2HAsO4), scorodite (FeAsO4·2H2O), arsenite (NaHAsO2), realgar (AsS), orpiment (As2S3), arsenian pyrite (As-substituted FeS2) and arsenopyrite (FeAsS).
XANES spectroscopy provides information about the oxidation state and coordination environment of the adsorbed As. Although XANES spectroscopy also provides some information about the local structural environment of sorbed As, extended x-ray absorption fine-structure (EXAFS) spectroscopy is needed to determine the specific nature of this coordination. The $\chi(k)$ (EXAFS) spectrum was isolated by subtracting the background, normalizing the edge height, and fitting a seven-point cubic spline function that followed the envelope of the decaying spectrum. The spectrum was converted from energy to momentum space ($k$-space) using an $E_0$ of 11,885 eV. The $\chi(k)$ spectrum was then weighted by $k^3$ in order to amplify the upper $k$-range and Fourier-transformed without smoothing to produce a radial structure function (RSF) using a $k$-range of approximately 3 to 10 Å$^{-1}$. Individual shells were isolated through Fourier filtering for analysis; however, final fits were always performed on raw (unfiltered and unsmoothed) spectra.

The element (Z), coordination number (CN), distance (R), and the Debye-Waller factor ($\sigma^2$) for each shell were determined by fitting the experimental spectrum using phase and amplitude functions derived using FEFF 8 (Rehr et al., 1991; Zabinsky et al., 1995; Ankudinov et al., 1998). The accuracy of these phase and amplitude functions were confirmed by comparing fits of orpiment, arsenate, and arsenite with known structures. Both single and multiple scattering paths were considered, although no multiple scattering paths were required for fitting. The $E_0$ was constrained to the same value for all shells; however all other parameters were varied during fitting. The accuracy of the fits was estimated using the $\chi^2$ statistical parameter, for which smaller values correspond to the best fits. Each fit had a reduced $\chi^2$ of about 4000 for
unsmoothed $k^3\chi(k)$ spectra and approximately 300 using RSF’s. This procedure is reasonably accurate for the determination of interatomic distances (within 0.02 Å); however, considerable errors in coordination environment (30% for the first shell and less accurate for more distant shells) result due to the high correlation of CN and $\sigma^2$. Therefore, the coordination numbers were constrained for As-S and As-Fe shells. The identification of different elements is made based on both differences in the phases and amplitude functions of different atom pairs and local structure (i.e. interatomic distances).

**X-ray Photoelectron Spectroscopy**

X-ray photoelectron spectroscopy (XPS) was performed on a Surface Science Instruments S-Probe equipped with a monochromatized Al K$_\alpha$ source (1486 eV). The resulting kinetic energies were between 400 and 1300 eV, corresponding to a mean free path of about 10-20 monolayers; thus, only limited surface sensitivity is achieved in these experiments. The instrument was operated at a resolution of approximately 0.7 eV and a spot size of about 0.5 mm. Both clean solids and selected As-sorbed FeS and FeS$_2$ samples were analyzed to determine the integrity of the sulfide surface and changes that result from sorption. Samples were prepared by drying under nitrogen, followed by mounting the resulting powders on double-sided carbon tape. Survey scans were used to determine the average composition of the surface. The thickness of the adventitious carbon coating was estimated to be between 10 and 20 Å using C content and an escape depth of 20 Å. Detailed scans of the S and Fe edges provided information about the oxidation of the surface, and the formation of several surface products. The binding energies were calibrated using the S 2p$_{3/2}$ spectral line of bulk pyrite and FeS.
respectively. The difference between S 2p$_{3/2}$ and S 2p$_{1/2}$ was fixed at 1.18 eV and their peak area ratio set at 2 to minimize the number of variables used in fitting. Fe spectra were fit with Fe(II)-S and Fe(III)-S multiplets in accordance with convention (e.g., Uhlig et al., 2001). Peak widths were not constrained; however, they were similar to those reported by others. Peaks were identified by comparison with literature values (Karthe et al., 1993; Herbert et al., 1998; Nesbitt et al., 1998; Uhlig et al., 2001).

RESULTS AND DISCUSSION

Solid Phase Characterization

The S 2p spectra of cleaned FeS and FeS$_2$ contain two principal peaks (Fig. 2), at 161.0 and 162.2 eV for FeS and 162.6 and 163.8 eV for FeS$_2$; the doublets are attributed to the 2p$_{3/2}$ and 2p$_{1/2}$ electrons of bulk FeS and FeS$_2$, respectively (e.g., Knipe et al., 1995; Herbert et al., 1998; Nesbitt et al., 1998). The prevalence of the bulk FeS and FeS$_2$ peaks indicates that much of the surface is free of oxidation; however, small signals attributed to other sulfur species are suggested by the fitting (Table 1). For pyrite, a small spectral feature is found at a shift of -1.1 eV from the bulk pyrite peak, a feature attributed to sulfide (S(-II)-Fe) presumably formed through the stabilization of broken disulfide bonds (e.g., Nesbitt et al., 1998; Uhlig et al., 2001). Peaks somewhat larger than the S(-II)-Fe peaks are present at higher bonding energy than bulk pyrite, indicative of oxidation products such as elemental sulfur or polysulfides. Sulfide as well as elemental sulfur and polysulfide are commonly formed on “pristine” pyrite through disproportionation reactions; however, the excess polysulfide indicates that surface oxidation has occurred at least to a limited extent. Polysulfide is also identified on FeS,
which also contains spectral features attributed to thiosulfate and sulfate at higher binding energies (166.7 and 169.1 eV). The presence of these oxidized sulfur species indicates that the FeS surface is more oxidized than that of pyrite.

The Fe 2p spectra also contain evidence of surface oxidation (Fig. 3). The FeS₂ spectrum contains three distinct chemical environments, Fe(II)-S, Fe(III)-S, and Fe(III) oxides (Table 2). The Fe(III) oxide peak is very small, consistent with the limited extent of oxidation on the FeS₂. The FeS spectrum contains these features and a small feature diagnostic of Fe(III) sulfates. The Fe(II) and Fe(III)-S peaks are multiplets, typically found on both pyrite (Uhlig et al., 2001) and mackinawite (Herbert et al., 1998) surfaces. The Fe(III)-OH and Fe(III)-SO₄²⁻ feature, similar in binding energy to FeOOH and jarosite, are often found on oxidized iron sulfide surfaces (e.g., Karthe et al., 1993). While Fe(III) sulfates are commonly found on FeS₂ surfaces (e.g., Karthe et al., 1993), they are not detected or are small features in these spectra presumably due to cleaning procedures. Both Fe and S were detected in cleaning solutions at concentrations up to 30 µM, confirming that the surface oxidation products are removed. While these data clearly show that the surfaces of FeS and FeS₂ are somewhat oxidized, oxidation may have occurred at least partially during XPS sample preparation, which involves drying the samples. Oxidation of FeS and FeS₂ surfaces may influence As(III) sorption, potentially altering the redox state of adsorbed As.

**Macroscopic Sorption Characteristics**

Sorption isotherms provide information about the interactions of the mineral and adsorbed species. Arsenite sorption was strongest at higher pH, with pyrite having similar sorption maxima at pH 7 and 9, both of which are much greater than sorption at
pH 4 (Fig. 4). A similar trend was also observed for As(III) sorbed on FeS although sorption affinity increased with pH over the entire pH range examined.

At low concentrations, sorption resembled a Langmuir isotherm (Fig. 4), typical of anion adsorption in which a finite number of sites of similar energy react until all of the sites are occupied (the monolayer capacity). Adsorption was enhanced at higher As activities, indicative of adsorbate-adsorbate interactions and cannot be described by a Langmuir isotherm (Fig. 4). Sorption beyond the monolayer capacity indicates that a three-dimensional structure such as a polymeric cluster or surface precipitate form and is described by a BET isotherm. Deviation from the Langmuir isotherm is most notable in the case of FeS, which exhibits linear sorption above the adsorption maximum.

The monolayer capacity depends on the surface area of the solid and is diagnostic of the surface site density. We estimate the surface site density with the portion of the adsorption isotherms that appear to be unaffected by precipitation mechanisms. For FeS₂ at pH 7, the adsorption maximum was 231 µmol/g, which corresponds to a surface coverage of 5.6 µmol/m². The As(III) surface coverage on FeS was similar (4.4 µmol/m²) but smaller in magnitude (14 µmol/g) due to its lower surface area. The adsorption maxima yield an average site area of 2.6 and 3.7 sites/nm² for FeS and FeS₂ respectively, similar to the site densities (1-3 sites/nm²) typically observed for arsenite adsorption on iron hydroxides (Dzombak and Morel, 1990; Hiemstra and Van Riemsdijk, 1999). Similarities between site densities suggest that adsorption processes may control As(III) binding at lower As concentrations; however, surface precipitation or polynuclear surface complex formation is likely at higher concentrations.
The As(III) sorption isotherms for FeS and FeS\textsubscript{2} were affected by pH (Fig. 4). The pH envelopes for As(III) on FeS and FeS\textsubscript{2} also indicate that sorption increases with increasing pH (Fig. 5). Minimal As(III) was sorbed on FeS below pH 6, with sorption increasing markedly between pH 6 and 8. Arsenite sorption on FeS\textsubscript{2} exhibited a similar adsorption edge but was shifted to lower pH (between 4 and 5.5). Similar edge positions have been observed previously for FeS\textsubscript{2} (Zouboulis et al., 1993) and are different from those observed for As(III) sorbed on iron (hydr)oxides (Fig. 5). Arsenite sorption on metal (hydr)oxides is typically described by a diffuse pH envelope in which sorption is greatest at circumneutral pH and lowest at high pH (Dzombak and Morel, 1990; Hiemstra and Van Riemsdijk, 1999). The characteristic differences between sorption to these metal sulfides and metal (hydr)oxides implies that sorption occurs through a fundamentally different mechanism than occurs on iron (hydr)oxides.

Anion sorption on hydroxides occurs through ligand exchange of surface hydroxyl groups with an anion in solution (Anderson et al., 1976):

\[ 2 \equiv Fe – OH + As(OH) \Leftrightarrow Fe_2 – O_2 As(OH) + 2H_2O \]  \[ [1] \]

The reaction of multiple surface groups results in the formation of multi-dentate surface complexes. Similar adsorption mechanisms have been proposed for anions on sulfide minerals. For example, iodide adsorption on sulfide mineral surfaces is thought to involve the exchange of surface hydroxyls groups (Balsley et al., 1996; Balsley et al., 1997):

\[ \equiv Hg – OH + I^- \Leftrightarrow Hg – I + OH^- \]  \[ [2] \]
Although the resultant OH\(^-\) stoichiometry varies significantly, such ligand-exchange reactions often evolve hydroxyl groups (or consume H\(^+\)) with sorption; consequently, these models (Equations 1 and 2) predict that sorption is most pronounced at low pH.

We can examine the effect of pH on sorption to better constrain the type of surface reaction that occurs on the surface. Arsenite sorption on FeS and FeS\(_2\) increases at higher pH (Fig. 5); therefore, a different surface reaction that ligand exchange (exemplified by Equation 1) is needed to describe As(III) sorption to iron sulfide minerals. Electrostatic (outer-sphere) sorption mechanisms can be disregarded based on their pH dependence (Fig. 5) and lack of ionic strength dependence (Fig. 6). Outer-sphere sorption of anions is favored at low pH (when the surface is positively charged); however, the surfaces of iron sulfide minerals are negatively charged above pH 2-3 (Bebie et al., 1998) and are not expected to form electrostatic sorption complexes with neutral anionic arsenite. Outer-sphere sorption mechanisms also are inconsistent with the observed hysteresis in sorption and desorption (Fig. 5); the lag in desorption suggests a slow process more compatible with the formation of strong, inner-sphere complexes. Thus, it appears As(III) sorbs to FeS and FeS\(_2\) through in an inner-sphere mechanism distinct from those of surface hydroxyl exchanges.

Sulfide additions may influence As(III) sorption to FeS\(_2\) by stimulating the precipitation of stable arsenic sulfides such as orpiment. Sulfide additions would stimulate the precipitation of arsenic sulfides, thereby lowering solution As concentrations. While these solid phases may indeed be the most stable thermodynamically, the addition of sulfide to the system inhibits sorption rather than promotes it (Fig. 7). Thus, arsenic sulfides are unlikely to explain As sorption in these
experiments. Inhibition could occur through competitive adsorption of sulfide and arsenite anions to reactive surface sites. Alternatively, sulfide (sorbed or in solution) could be a reaction product in the operative sorption mechanism, thereby inhibiting sorption directly.

**Arsenic Speciation**

Spectroscopic techniques such as XAS supplement the information gleaned from solution phase experiments by providing specific information about the oxidation state and local structure of sorbed As(III). Such information is vital for constructing a reasonable model of sorption reactions. Arsenite reacted with FeS and FeS\(_2\) have similar shape and both have an inflection point near 11,868 eV (Fig. 8), significantly lower than the arsenite ion (11,871 eV). Spectra were similar over As loadings ranging from well below monolayer coverage to the highest As loadings examined, implying that a similar As complex is formed over a wide range of As concentrations. The edge position of sorbed As is intermediate between AsS (11,869 eV) and FeAsS (11,867 eV); the shift in edge position implies that As(III) has undergone extensive reduction. Unfortunately, XANES spectroscopy cannot discriminate well between different arsenic sulfide species because they have similar edge positions. Consequently, additional information was needed to fully characterize the structure of sorbed As on FeS and FeS\(_2\).

Although samples initially were reduced, additional scans collected of As(III) sorbed to iron sulfides showed increasing evidence of oxidation (Fig. 9). Oxidation was marked by the presence of a spectral feature at 11,874.2 eV—a similar edge position to that of arsenate. After 1 to 2 h, oxidation was complete and little of the residual signal remained. Samples were typically only oxidized to a limited extent prior to placement in
the synchrotron beam. Therefore, it appears that exposure to the X-ray beam facilitates arsenic oxidation in these samples.

Sulfur coordination of As is confirmed by EXAFS spectroscopy. The EXAFS spectrum of As(III) sorbed on FeS and FeS$_2$ at pH 4 shows some oxidation; nevertheless, the principal feature is comprised of both As-S and As-Fe shells at about 2.4 Å (Fig. 10). Such bond lengths are similar to As-Fe and As-S in arsenopyrite (2.35 and 2.37 Å respectively); however, the second shell As-Fe distances, pronounced for FeAsS, are absent for As(III) sorbed on FeS and FeS$_2$. The lack of second-shell features suggests the presence of significant structural disorder. Arsenic substituted in pyrite also contains both As-S and As-Fe coordination, but bond lengths are shorter (Savage et al., 2000) than those observed for As(III) on FeS$_2$. Importantly, the local structure of sorbed As species differs from both orpiment and realgar, both of which lack As-Fe coordination and have shorter As-S bond distances than are observed here. Although none of the selected standards match the spectrum of As(III) on FeS or FeS$_2$, the As-S and As-Fe coordination shell suggests that an FeAsS-like phase is formed. Structural disorder may account for the lack of the second As-Fe shell, a feature common in surface precipitates and freshly precipitated As$_2$S$_3$ (Helz et al., 1995).

EXAFS spectra of sorbed As usually exhibited oxidation over time (Fig. 10). Oxidation was mild for pH 4 samples and extensive for samples prepared at neutral and higher pH. The As-S shell near 2.4 Å, characteristic of sorbed As(III) at pH 4, is also present at pH 7; however, a single As-O shell near 1.70 Å, characteristic of arsenate, dominates the spectra. Although an As-Fe shell may be present in pH 7 samples, spectra were of insufficient quality to resolve As-S and As-Fe features. Minor As-Fe or As-As
spectral features are also observed at 3.35 Å, presumably from a combination of the pristine and oxidized surface species.

The stability of low pH samples may be attributed to the dissolution of surface-bound oxidants or a decreased oxidation rate (McKibben and Barnes, 1986). The dissolution of potential oxidants such as Fe(III) species and polysulfides are known to occur at lower pH. In fact, acid treatments are commonly used to remove oxidized products from pyrite surfaces.

Sulfide was added as a redox buffer to prevent oxidation; however, sulfide was inefficient at preserving reduced As species except at concentrations above 0.5 mM. Arsenic sulfide precipitation was expected in such solutions as they are significantly oversaturated with respect to orpiment. Indeed, the EXAFS spectra of these sulfide-rich suspensions confirm the presence of As$_2$S$_3$ (Fig. 11). The spectra contain an As-S shell at 2.23 Å and weak As-As shells between 3.2 and 3.5 Å, which are consistent with the spectra of amorphous As$_2$S$_3$ (Helz et al., 1995).

**Chemical Intermediates**

Batch reactions contain evidence for the conversion of arsenite to a sulfide surface complex and its subsequent oxidation. Flow experiments offer the potential to examine the intermediates that form prior to arsenic sulfide surface complexes. Additionally, the residence time of As in flow experiments can be maintained below the time required for As oxidation. The EXAFS spectra of As sorbed on FeS$_2$ in column experiments appear in Fig. 12. Generally, these spectra contained As-O and As-S coordination in the first shell and the clear presence of an As-Fe second shell. Similar increases were noted for
As(III) sorbed on FeS\textsubscript{2} at pH 6 and 9. The As-O distance was somewhat shorter than for arsenite in solution (1.73 Å compared to 1.77 Å for arsenite), suggesting that the As(III) coordination shell is somewhat altered from normal solution. An As-Fe shell at 2.81 to 2.85 Å is also noted in the spectra, consistent with arsenite adsorption in a mononuclear, bidentate complex on pyrite. Arsenite coordination is initially conserved in these intermediate surface complexes; however, the As-S coordination number increases with increasing residence time (decreasing flow rates). The 2.23 Å As-S distance is similar to As-S distances observed in orpiment and realgar and considerably shorter than those of As(III) adsorbed in bulk experiments. First-shell As-Fe bonds, observed for bulk samples, are not seen in these samples; however, it is unlikely that we would resolve such shells since they are small and out-of-phase relative to the As-S shell. An increase in the intensity of the As-Fe shell (at 2.81 Å) occurs concurrent with the increase in As-S shell intensity, suggesting that increased reaction times also contribute to the bidentate arsenite complex. Thus, increased residence times leads to formation of both the bidentate arsenite complex noted above and the arsenic sulfide complex measured under bulk conditions.

It should be mentioned that the surface species identified in batch experiments might also be a kinetic product that would eventually give way to the formation of more stable species, crystalline surface precipitates of FeAsS, As\textsubscript{2}S\textsubscript{3}, or scorodite. Suspensions not prepared with additional sulfide are particularly sensitive to subsequent reactions. Such suspensions are far from equilibrium and mineral dissolution may contribute to the formation of arsenic sulfide minerals. Alternatively, the continual reduction of iron and sulfide in anoxic environments may also influence the structure of sorbed As(III).
Iron and Sulfur speciation

Despite the limitations in spectral analyses imposed by sample oxidation, arsenic(III) reduction to arsenic sulfide surface species is readily apparent by XAS. The spectra contain significantly different structures than solution-phase arsenite—the oxygen coordination of arsenite is replaced by both As-S and As-Fe shells in the first coordination sphere, thereby forming reduced As species. Such reduction must be paired with the oxidation of Fe(II), S(-II) or S(-I), potentially identified by XPS.

Sulfur 2p spectra indicate a loss in the intensity of the S(-II) spectral feature (Fig. 1). The fractional area of the S(-II) species decreases from about 0.13 on untreated FeS$_2$ to 0.05 on As-reacted FeS$_2$. The fractional area of S(-II) feature on FeS also decreases, from 0.67 to 0.55 following reaction with arsenite. An increase in the fractional area of the polysulfide surface components is also noted by the XPS; this could be due to the paired oxidation of sulfur species that would accompany As reduction. Iron 2p spectra also contain some evidence of oxidation (Fig. 2). The intensity of both the Fe(III)-S and Fe(III)-OH peaks increase through sorption.

The changes in the S and Fe XPS data are consistent with the reaction of As(III) with surface sulfide. Additional oxidized Fe and S species may have been released into solution during sorption, thereby going undetected by XPS; however, only a small quantity (less than 3 µM) of S and even less Fe was released during sorption (probably oxidized species). Additionally, the changes in S and Fe XPS spectra were minor and could be a result of either surface oxidation during reaction or preparation. Small differences in spectral normalization also may impart errors on the quantification of
minor species. Better surface sensitivity may help to resolve these problems by focusing only on the interfacial S and Fe species most affected by As sorption.

**CONCLUSIONS**

Arsenite sorption on FeS and FeS$_2$ results in the formation of an FeAsS-like surface precipitate. Both Fe and S must be incorporated into the surface precipitate; thus, the iron sulfide mineral surface is consumed as a consequence of sorption. Such a precipitation mechanism of arsenite influences the retention characteristics of arsenic profoundly. Arsenite sorption is minimal at low pH, in contrast to its behavior on most (hydr)oxide mineral surfaces. Additions of sulfide inhibit As(III) sorption despite the formation of a sulfidic precipitate at the mineral surface, possibly by inhibiting mineral dissolution or competitive sorption. These differences need to be considered when evaluating the potential of sulfide minerals to sequester As in natural environments.

The high affinity of arsenite for sulfide minerals may regulate As solution concentrations in reducing environments through the formation of FeAsS-like phases in slightly sulfidic solutions and through the formation of As$_2$S$_3$ in highly sulfidic zones. Thus, thermodynamic equilibrium with arsenic sulfide minerals is achieved only in the presence of appreciable sulfide concentrations (Sadiq, 1997). The association of As with pyrite suggested by selective extraction (Huerta-Diaz and Morse, 1992; Cooper and Morse, 1996) is apparent because FeAsS formation occurs on FeS and FeS$_2$ mineral surfaces. In both cases, arsenic precipitates as stable, insoluble sulfide phases on the surface of iron sulfide minerals, suggesting that sorption may be an effective and relatively irreversible process that can successfully regulate As concentrations in
reducing environments. However, iron, arsenic, or sulfide oxidation may lead to the release of oxidized As species, as process similar to the reductive dissolution of arsenate adsorbed to iron (hydr)oxides. The effect of these roxidation processes needs to be examined to determine the long-term stability of As sequestered by iron sulfide minerals.

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Table 1. Binding energy shifts for sulfur 2p$_{3/2}$ spectra of the cleaned and As(III)-reacted FeS and FeS$_2$ used in these experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Species$^\dagger$</th>
<th>$E$ (eV)</th>
<th>$\Delta E$ (eV)$^\ddagger$</th>
<th>Relative Intensity</th>
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<td>0.14</td>
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<td></td>
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<td>169.1</td>
<td>8.1</td>
<td>0.09</td>
</tr>
<tr>
<td>As-reacted FeS$_2$</td>
<td>S(-II)-Fe</td>
<td>161.2</td>
<td>-1.4</td>
<td>0.05</td>
</tr>
<tr>
<td>43 µg/g</td>
<td>FeS$_2$ (bulk)</td>
<td>162.6</td>
<td>-</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>Polysulfide</td>
<td>163.8</td>
<td>1.2</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>$S_2O_3^{2-}$</td>
<td>166.8</td>
<td>4.2</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>$SO_4^{2-}$</td>
<td>169.0</td>
<td>6.4</td>
<td>0.06</td>
</tr>
</tbody>
</table>

$^\dagger$ Peaks identities were determined based on the data of Herbert et al. (1998), Nesbitt et al. (1998) and Uhlig et al. (2001). $^\ddagger$ The difference in line energy from bulk material.
Table 2. Binding energies for Fe 2p3/2 spectra of cleaned and As(III)-reacted FeS and FeS2 used in these experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Species†</th>
<th>E (eV)</th>
<th>ΔE (eV)‡</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cleaned FeS</td>
<td>Fe(II)-S multiplet¥</td>
<td>706.4</td>
<td>-</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>Fe(III)-S multiplet</td>
<td>709.5</td>
<td>3.1</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Fe(III)-OH</td>
<td>711.3</td>
<td>4.9</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>Fe(III)-SO4</td>
<td>712.8</td>
<td>6.4</td>
<td>0.14</td>
</tr>
<tr>
<td>Cleaned FeS2</td>
<td>Fe(II)-S multiplet</td>
<td>707.2</td>
<td>-</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Fe(III)-S multiplet</td>
<td>709.3</td>
<td>2.1</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Fe(III)-OH</td>
<td>711.3</td>
<td>4.1</td>
<td>0.07</td>
</tr>
<tr>
<td>As-reacted FeS</td>
<td>Fe(II)-S multiplet</td>
<td>706.4</td>
<td>-</td>
<td>0.43</td>
</tr>
<tr>
<td>21 µg/g</td>
<td>Fe(III)-S multiplet</td>
<td>709.4</td>
<td>3.1</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>Fe(III)-OH</td>
<td>711.5</td>
<td>5.1</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>Fe(III)-SO4</td>
<td>712.8</td>
<td>6.4</td>
<td>0.08</td>
</tr>
<tr>
<td>As-reacted FeS2</td>
<td>Fe(II)-S multiplet</td>
<td>707.2</td>
<td>-</td>
<td>0.68</td>
</tr>
<tr>
<td>43 µg/g</td>
<td>Fe(III)-S multiplet</td>
<td>709.2</td>
<td>2.0</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>Fe(III)-OH</td>
<td>711.2</td>
<td>4.0</td>
<td>0.10</td>
</tr>
</tbody>
</table>

† Peaks identities were determined based on the data of Karte et al. (1993), Herbert et al. (1998), Nesbitt et al. (1998) and Uhlig et al. (2001). ‡The difference in line energy from bulk material. ¥ Fe-S multiplets are composed of a principal peak (the energy given) and up to three other peaks of decreasing intensity at higher energy.
Table 3. Arsenic local structure for As(III) adsorbed to FeS and FeS₂. The coordination number (CN) is typically accurate to within ±1, the interatomic distance (R) within ± 0.02 Å; σ² represents the variance in R. For all of the media, E₀ was ≈ 11869 eV.

<table>
<thead>
<tr>
<th>Sample</th>
<th>As-O CN</th>
<th>R (Å)</th>
<th>σ² (Å²)</th>
<th>As-O CN</th>
<th>R (Å)</th>
<th>σ² (Å²)</th>
<th>As-Fe CN</th>
<th>R (Å)</th>
<th>σ² (Å²)</th>
<th>As-Fe/As CN</th>
<th>R (Å)</th>
<th>σ² (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenian FeS₂</td>
<td>-</td>
<td>-</td>
<td>1 f</td>
<td>2.25</td>
<td>0.008</td>
<td>3 f</td>
<td>2.32</td>
<td>0.011</td>
<td>3 f</td>
<td>3.17</td>
<td>0.004</td>
<td></td>
</tr>
<tr>
<td>FeAsS</td>
<td>-</td>
<td>-</td>
<td>1 f</td>
<td>2.34</td>
<td>0.008</td>
<td>3 f</td>
<td>2.37</td>
<td>0.009</td>
<td>1 f, 2 f</td>
<td>3.06, 3.20</td>
<td>0.007</td>
<td>0.007</td>
</tr>
<tr>
<td>As₅S₃</td>
<td>-</td>
<td>-</td>
<td>3 f</td>
<td>2.24</td>
<td>0.004</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1 f, 2.5 f</td>
<td>3.19, 3.56</td>
<td>0.010</td>
<td>0.009</td>
</tr>
<tr>
<td>13 µmol/g As(III) on FeS, pH 4</td>
<td>-</td>
<td>-</td>
<td>1 f</td>
<td>2.33</td>
<td>0.007</td>
<td>3 f</td>
<td>2.39</td>
<td>0.009</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>40 µmol/g As(III) on FeS₂, pH 4</td>
<td>-</td>
<td>-</td>
<td>1 f</td>
<td>2.35</td>
<td>0.008</td>
<td>3 f</td>
<td>2.40</td>
<td>0.009</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>6 µmol/g As(III) on FeS, pH 7</td>
<td>3.5</td>
<td>1.69</td>
<td>0.003</td>
<td>1 f</td>
<td>2.37</td>
<td>0.005</td>
<td>3 f</td>
<td>2.41</td>
<td>0.010</td>
<td>2 f</td>
<td>3.35</td>
<td>0.007</td>
</tr>
<tr>
<td>36 µmol/g As(III) on FeS₂, pH 7</td>
<td>3.0</td>
<td>1.72</td>
<td>0.004</td>
<td>1 f</td>
<td>2.40</td>
<td>0.008</td>
<td>3 f</td>
<td>2.38</td>
<td>0.013</td>
<td>2 f</td>
<td>3.35</td>
<td>0.009</td>
</tr>
<tr>
<td>41 µmol/g As(III) on FeS₂, pH 7, 0.5 mM sulfide</td>
<td>1.0</td>
<td>1.71</td>
<td>0.006 f</td>
<td>2.30</td>
<td>2.23</td>
<td>0.006 f</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1 f, 2.5 f</td>
<td>3.21, 3.53</td>
<td>0.012, 0.013</td>
</tr>
<tr>
<td>27 µmol/g As(III) on FeS₂, pH 7, 1 mM sulfide</td>
<td>-</td>
<td>-</td>
<td>2.9</td>
<td>2.23</td>
<td>0.006 f</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1 f, 2.5 f</td>
<td>3.19, 3.55</td>
<td>0.008, 0.010</td>
<td></td>
</tr>
<tr>
<td>50 µM As(III) on FeS₂ column, pH 9, 0.1 mL min⁻¹ flow rate</td>
<td>2.5</td>
<td>1.73</td>
<td>0.006 f</td>
<td>1.0</td>
<td>2.23</td>
<td>0.006 f</td>
<td>0.75</td>
<td>2.81</td>
<td>0.006 f</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>50 µM As(III) on FeS₂ column, pH 9, 1.0 mL min⁻¹ flow rate</td>
<td>2.7</td>
<td>1.73</td>
<td>0.006 f</td>
<td>0.6</td>
<td>2.23</td>
<td>0.006 f</td>
<td>0.5</td>
<td>2.81</td>
<td>0.006 f</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

(f): fixed during fitting.
Figure 1. Flow cell design illustrating the placement of the FeS$_2$ disk in the synchrotron beam.
Figure 2. The sulfur $2p_{3/2}$ spectra of cleaned and As(III)-reacted FeS and FeS$_2$. 
Figure 3. The Fe 2p$_{3/2}$ spectra of cleaned and As(III)-reacted FeS and FeS$_2$. 
Figure 4. Sorption isotherms for As(III) on 1 g/L FeS (a) and FeS$_2$ (b) at varying pH values.
Figure 5. Sorption envelopes for 55 µM As(III) on 1 g/L FeS (a) and FeS₂ (b).
Figure 6. Effect of sulfide addition on As(III) sorption to 1 g/L FeS$_2$ at pH 7.
Figure 7. Effect of ionic strength on As(III) sorption to 1 g/L FeS and FeS$_2$ at pH 7.
Figure 8. XANES spectra of As standards and As(III) sorbed on FeS and FeS$_2$. 

- $\text{AsO}_4^{3-}$
- $\text{H}_3\text{AsO}_3$
- $\text{AsS}$
- $\text{As}_2\text{S}_3$
- $\text{FeAsS}$
- arsennian $\text{FeS}_2$
- 38 mmol As/g $\text{FeS}_2$
- 21 mmol As/g FeS

E (eV)  
Normalized Absorbance

Normalized Absorbance

11860 11870 11880 11890
Figure 9. XAS spectra of 40 µM As(III) sorbed to 1 g/L FeS₂ at pH 7 (38 µmol/g As) illustrating the sample oxidation that proceeds during analysis. The XANES spectra (a) show the first 7 scans during analysis, and the RSF’s (b) show the initial and 7th scan collected. Each scan takes approximately 0.5 hours to complete.
Figure 10. The k-weighted $\chi(k)$ spectra (a) and corresponding RSF’s (b) of As(III) sorbed on FeS and FeS$_2$ at pH 4 and 7. The low coverage of samples at pH 4 impacts data quality, while samples at pH 7 show a strong As-O shell indicative of oxidation.
Figure 11. EXAFS spectra 25 μM As(III) sorbed to 1 g/L FeS$_2$ at pH 7 poised with 0.5 mM (a) and 1.0 mM (b) sulfide.
Figure 12. EXAFS spectra of FeS$_2$ columns reacted with a solution of 50 µM As(III), and 1 µM sulfide at pH 7 at flow rates of 0.1 mL/min and 1 mL/min flow rates.
Chapter 4.

Arsenite Sorption Within Sediments of a Sulfidic Estuary, Pescadero, California
ABSTRACT

Arsenite sorption on sediments from a sulfidic estuarine salt marsh was characterized as a function of solution composition. Although the extent of sorption varied with sampling locations, several adsorption characteristics were apparent. Sorption generally conformed to a Langmuir isotherm but exceeded predicted trends at extended reaction periods. A fraction of arsenite adsorbed over the entire pH range examined, although it was most extensive at pH greater than 7. Sorption was relatively unaffected by changes in ionic strength. The observed sorption characteristics indicate that arsenite partitions strongly to these sulfidic estuarine soils. X-ray absorption spectroscopy revealed that As-bearing iron sulfide phases were responsible for As partitioning in these sediments. Sorption initially produced an FeAsS-like precipitate similar in structure to those reported for As(III) sorption to iron sulfides, a complex that is highly reactive and oxidizes readily during analysis. Following reaction for 21 d, much of the FeAsS-like precipitate was converted to As$_2$S$_3$. A drop in the redox potential accompanied this conversion, suggesting that sulfide formation may facilitate this conversion. The sorption processes discerned in this study reveal the importance of sulfide minerals in As sequestration within anoxic environments.
INTRODUCTION

Arsenic is a toxic heavy metal that can be released into the environment through the oxidation of sulfide-bearing ores and coal. Redox transformations and adsorption processes control the fate and transport of arsenic in soils, sediments, and groundwater (Cullen and Reimer, 1989; Korte and Fernando, 1991). Arsenate, As(V), formed in oxic conditions, partitions strongly to the solid phase through adsorption on Fe and Al (hydr)oxides (Anderson et al. 1976; Waychunas et al., 1993; Manning and Goldberg, 1996; Fendorf et al., 1997; Hiemstra and Van Riemsdijk, 1999), or the precipitation of insoluble arsenate minerals (Rochette et al., 1998; Savage et al., 2000). Reduction of these minerals under suboxic conditions releases arsenate into solution, leading to contamination of associated waters (Cummings et al., 1999; Nickson et al., 2000). Arsenate is also reduced to arsenite, As(III), under reducing conditions. Arsenite adsorbs strongly to iron (hydr)oxides (Manning et al., 1998; Raven et al., 1998), but adsorbs to aluminosilicates less strongly (Manning and Goldberg, 1997). Dissolved arsenite is of particular concern due to its elevated toxicity (Nickson et al., 1998; Acharyya et al., 1999).

Dissolved arsenic is sequestered in sulfidic environments (Aggett and O’Brien, 1985; Moore et al., 1988; Cutter, 1991; Balistreri et al., 1994; Sullivan and Aller, 1996; Johannesson et al., 2000). Several mechanisms have been proposed to explain As enrichment in these anoxic systems, including orpiment (As$_2$S$_3$) or realgar (AsS) precipitation (Sadiq, 1990; Sadiq, 1997), incorporation into arsenopyrite (FeAsS) or pyrite (FeS$_2$) (Aggett and O’Brien, 1985; Moore et al., 1988) and adsorption on sulfide minerals (Zouboulis et al., 1993; Hasany et al., 1999). Arsenic sorption on sulfide
minerals forms both surface complexes (Grigorev et al., 1976; Grigorev and Pushkarev, 1986; Chapter 2) and surface precipitates (Hasany et al., 1999; Chapter 3), potentially providing a beneficial As sink in sulfide-rich systems.

Much of the previous research on As sequestration in anoxic environments is based on correlations of dissolved As, Fe, and S concentrations or selective extractions (e.g., Huerta-Diaz and Morse, 1992; Cooper and Morse, 1996). While these data have established the importance of sulfidic phases to As sorption, they have not resolved the mechanism of As retention in sulfidic soils and sediments (Belzile et al., 1989; Cooper and Morse, 1998; Holmes, 1999). Spectroscopic approaches such as X-ray absorption spectroscopy (XAS), which provides an element-specific probe of As local structure and oxidation state (Brown, 1990; Fendorf et al., 1994; Conradson et al., 1998), are thus imperative to fully understand reaction mechanisms. Accordingly, we characterize arsenite sorption to soils within a sulfidic salt marsh near Pescadero, California. Sorption to these soils is characterized using batch techniques, while XAS was used to determine mechanisms of As sequestration within the salt marsh.

**MATERIALS AND METHODS**

**Sediment Collection and Handling**

Samples were collected from a salt marsh near Pescadero Slough (Fig. 1). The estuary is located about 60 km south of San Francisco, CA on the Pacific coast of California; it is tidally inundated but protected from wave action by barrier dunes. Sediments in this wetland are derived from fine sediment transported from Pescadero Creek through a lateral salt marsh. The salt marsh sediments have a background As
concentration of about 14 µg/g, typical of other uncontaminated soil and sediments (Nriagu, 1994).

Cores were taken along a transect from the center (core A1) to the eastern margin (core C1) of the marsh using a 3-cm diameter piston coring device (Fig. 1). Cores A1 and B1 were isolated from the lower salt marsh that is subject to daily tidal action (the wettest region), while core C1 is subject to only occasional flooding. A thick biofilm was removed from the samples and the top 5-cm of the core was homogenized and stored at 4°C prior to use. Water content was determined for each of the homogenized cores by measuring the mass of a core subsample before and after drying at 110 °C.

Precautions were taken to minimize oxidation of the sediment and reagents during all experiments. All experiments were performed in a glovebox equipped with a mixed H₂/N₂ atmosphere (5% H₂) that maintained O₂ concentrations below 1 ppm. Sediments were used immediately following extraction and all reagents and solutions were prepared fresh prior to use.

**Solution-Phase Experiments**

Initial investigations showed that sorption reached a relatively constant value within 0.5 h; therefore, sorption experiments were carried out for this duration. Longer reaction times were explored for core A1 (2 g/L suspension density), which was reacted with 55 µM As(III) at pH 4 and 7 over 14 d. For comparison, FeS and FeS₂ suspensions (1 g/L) were reacted with 55 µM As(III) at pH 7 over the same period.

Several experiments were performed to determine the macroscopic sorption characteristics of arsenite within suspensions of each of the three sediment cores. Initial
arsenite concentrations in sediment suspensions (2 g/L dry weight) varied between 0 and
200 µM As(III) using 10 mM As(III) stock solution made with NaHAsO₂. Constant pH
samples were buffered with 0.01 M acetate (pH 4), MOPS (pH 7), or borate (pH 9)
buffers. Ionic strength was varied between 0.01 M and 0.5 M with 1.0 M NaCl.
Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed on
the residual solutions to determine the extent of sorption, which was determined by
difference between initial and final aqueous concentrations.

For sorption envelope experiments, the pH of a 2 g/L sediment suspension was
adjusted to 3 with 0.5 M HCl and then arsenite stock solution was added to yield 50 µM
total As(III). After equilibration for 0.5 h, the pH was measured, and the suspension was
sampled and filtered (0.2 µm pore size). Following sampling, 0.5 M NaOH was added to
increase the pH by about 1 pH unit. This procedure was repeated until the pH was near
11. Parallel sorption envelope experiments were performed using suspensions in which
the initial pH was high (about 11) and titrated to near 3 with HCl.

**X-ray Absorption Spectroscopy**

X-ray absorption spectroscopy was performed at the Stanford Synchrotron
Radiation Laboratory on beamlines 4-3 and 11-2. The storage ring operated at 3.0 GeV
and at currents between 50 and 100 mA. Incident and transmitted intensities were
measured with 15-cm N₂-filled ionization chambers. Sample fluorescence was measured
with a 13-element Ge detector containing a 6 µx Ge filter. The incident beam intensity
was detuned approximately 50% to reject higher-order harmonic frequencies and to
prevent detector saturation. Spectra were internally calibrated with sodium arsenate (to 11,874 eV).

X-ray absorption spectra were collected from –200 to +1000 eV about the As K-edge (11,867 eV). At least 5 spectra were collected for each sample and averaged, they then were analyzed using WinXAS (Ressler, 1997) in combination with Feff 8.0 (Rehr et al., 1991; Zabinsky et al, 1995; Ankudinov et al., 1998). The X-ray absorption near-edge structure (XANES) spectra provides information about the oxidation state and site symmetry of the adsorbed As. XANES spectra were not smoothed to preserve line-shapes; however, first-derivative XANES spectra were smoothed 5% to decrease noise. Spectra were compared to several model compounds including arsenate (as Na₂HAsO₄), scorodite (FeAsO₄·2H₂O), arsenite (as NaHAsO₂), realgar (AsS), orpiment (As₂S₃), arsenian pyrite (Fe(As,S)₂) and arsenopyrite (FeAsS) to determine the structural and oxidation state changes of As.

Extended x-ray absorption fine structure (EXAFS) spectroscopy was also used to determine the coordination environment of sorbed arsenic species. The k³-weighted χ(k) spectrum was isolated using a seven point spline function and an E₀ of 11870 eV. The EXAFS spectrum was then Fourier-transformed without smoothing to produce a radial structure function (RSF) using a k-range of approximately 3 to 11 Å⁻¹. Preliminary fits of Fourier-filtered shells were used as a guide for final fits, which always used unsmoothed k-weighted χ(k) spectra. This fitting procedure yields information about the local structure of sorbed As species, including the coordination number (CN), distance (R), and the Debye-Waller factor (σ²) for each shell. This method yields accurate interatomic distances (within 0.02 Å); however, the CN can only be determined within about 30%
due to the correlation of CN and $\sigma^2$. Differences in phase and amplitude functions and interatomic distances permit the identification of different elements.

Linear combination fitting of XAS data was performed using WinXAS. These fits were performed as described elsewhere (e.g. Foster et al., 1998; Ostergren et al., 1999; Ressler et al., 2000) and are only briefly described here. Linear combination fitting used both normalized XANES spectra without smoothing and smoothed first-derivative spectra over an energy range of 11,860 to 11,890 eV. EXAFS linear combination fitting used k-weighted $\chi(k)$ spectra and a k-range of 4 to 10 Å$^{-1}$.

RESULTS AND DISCUSSION

Site Characterization

Pore water salinity varied depending on the season; however, salinities were generally between 35 and 47 ‰. Seawater has a salinity of about 33 ‰ in this region; the increased salinity of the salt marsh reflects the evaporation from the estuary during periods when the seawater is not actively exchanged. The soil pH for each core was between 4.4 and 5.1, somewhat lower than for seawater or pristine salt marshes, likely due to slight oxidation of sulfide minerals (Anisfeld and Benoit, 1997). Despite evidence of oxidation, the redox potential ($E_h$) of the cores was near –200 mV, indicative of strongly reducing conditions.

Core samples were composed predominantly of quartz, feldspars and organic matter (Table 1). Pyrite (FeS$_2$) also was detected by x-ray diffraction. These minerals were extremely fine grained—nearly all of cores A1 and B1 was clay-sized (<2 µm
diameter). Core section C1 was somewhat more coarse, about 20% of the core was of silt (2-50 μm) or sand-sized particles (50 μm to 2 mm).

Iron K-edge X-ray absorption spectroscopy of the cores revealed that most of the Fe was present as iron sulfide phases including mackinawite; however, a significant FeS$_2$ component was also present (Fig. 2). Iron is coordinated to 4 sulfur atoms at a distance of 2.17 Å. The short Fe-S distance indicates that the Fe is primarily in tetrahedral coordination and consistent with mackinawite, a tetragonal FeS (Lennie et al., 1995). An Fe-Fe shell at 3.37 Å similar to mackinawite is also noted. Griegite, Fe$_3$S$_4$, also has some tetrahedral Fe and may also be present. It should be noted that both the Fe-S and Fe-Fe shells are extremely disordered, partially a result of the poor crystallinity of mackinawite; the presence of additional sulfide phases may also contribute to the observed disorder. Regardless, it is clear that most of the Fe in these sediments is present in sulfide minerals. The prevalence of sulfide mineral phases is supported by the presence of soluble sulfide concentrations greater than 8 μM (Table 1) and the availability of sulfate in porewaters for biological and chemical reduction. Thus, FeS, FeS$_2$ and other sulfidic phases are the principal Fe phases in each of these soil cores.

**Macrosopic Sorption Characteristics**

Arsenite sorption varied somewhat as a function of pH (Fig. 3). Sorption increased gradually over the entire pH range for each of the three cores; however, arsenite sorption on core A1 sediments was greater than cores B1 and C1. Core A1 also was more strongly affected by pH than cores B1 and C1. Chemical and mineralogical differences between the core sections likely cause the observed differences in reactivity.
toward arsenite. Although the sulfide mineral content of each core is high, cores A1 and B1 have low redox potentials indicative of a strongly reducing environment while core C1 contains appreciable quantities of other minerals and a more oxidized redox status. These additional mineral constituents, or the partial oxidation of sulfide minerals may lead to the different sorption characteristics (Anisfeld and Benoit, 1997). Sample oxidation or disequilibrium may also contribute to the observed variation in As sorption. Because of the increased reactivity of core A1, it was used in further experiments examining the effects of arsenic concentration, ionic strength, and sulfide addition.

The sorption envelope of As(III) on core A1 is comparable to that on other potential sorbents (Fig. 3). Arsenite sorption and desorption on Pescadero soils has a similar isotherm shape to that of FeS2 (Zouboulis et al., 1993), with sorption increasing over the entire pH range. The observed pH dependence of As(III) sorption on sulfide minerals is distinct; sorption to aluminum hydroxides and aluminosilicates occurs at acidic conditions (Anderson et al., 1976; Manning and Goldberg, 1996) and iron (hydr)oxides sorb most strongly at circumneutral pH (Dzombak and Morel, 1990; Bowell, 1994). The similarity of sorption envelopes is empirical evidence that FeS2 or other sulfide minerals are important for As retention in these soils. Limited sorption at low pH is also observed for As(III) sorption on these soils, likely a result of sorption on non-sulfidic phases such as aluminosilicate clay minerals, which retain As more strongly than sulfide minerals at low pH.

Arsenite sorption on core section A1 was described by a Langmuir isotherm, consistent with sorption on FeS2 and other substrates (Fig. 4). The maximum surface loading for As(III) on core A1 was 48 µmol/g, or about 0.22 µmol/m² given a surface
area of 217 m$^2$/g. The other cores had similar isotherms but lower maximum surface loadings. This surface loading corresponds to an active site density of 0.13 sites/m$^2$, lower than site densities determined for oxides (1-3 sites/m$^2$; Dzombak and Morel, 1990) and sulfides (2-4 sites/m$^2$; Chapters 2, 3, 5). This is not surprising since the bulk of these salt marsh soils are organic matter and quartz, which react only weakly with As (Anderson et al., 1976; Thanabalasingam and Pickering, 1986). Consequently, minor constituents (only a fraction of the surface area) are probably most important to arsenite sorption.

The effect of ionic strength (I) on As(III) sorption to these sediments helps to further refine the mechanism of retention. Inner-sphere mechanisms including adsorption and precipitation are largely unaffected by ionic strength, while outer-sphere (electrostatic) adsorption is affected by competition with the background electrolyte. Arsenite sorption to these soils is largely unaffected by increases in salt concentration (Fig. 5), although a slight decrease in As sorption is noted for I > 0.1 M. Thus, both the dependence of sorption on ionic strength and the slow desorption process are consistent with the formation of inner-sphere complexes or surface precipitates.

The effect of sulfide additions on arsenite sorption is useful to examine the importance of sulfide mineral precipitation (Sadiq, 1990; Sadiq, 1997) and coprecipitation (Bertine, 1972; Bertine, 1973; Aggett and O’Brien, 1985; Moore et al., 1988). Sulfide mineral formation should be enhanced by the presence of excess sulfide. The addition of sulfide to the suspensions did not result in increased As sorption; in fact, it inhibited As(III) sorption in these sediments (Fig. 6). These results suggest that arsenic sulfide minerals are not formed during short-term sorption experiments; however, As(III)
sorbed to FeS$_2$ forms an FeAsS-like precipitate and is also inhibited by sulfide (Chapter 3).

Iron or sulfur evolution during As sorption also would provide information about the mechanism of sorption. Unfortunately, the background concentration of sulfate is very large and no change in S concentration was apparent. Additionally, the concentration of Fe was relatively low (a few µM or lower) and erratic, probably maintained by either the solubility or oxidation of iron sulfide minerals.

**Sorption Kinetics**

Suspensions in the aforementioned experiments were reacted with As(III) for about 0.5 h prior to analysis of solutions, but sorption continued slowly over extended time periods (Fig. 7). Arsenite sorption to Pescadero sediments at pH 7 was nearly complete within the first minute; however, remaining dissolved As continued to react slowly over several days. This slow reaction continued for up to two weeks. For reactions of core A1 at pH 4, sorption was minimal and reached a constant value within 2 h. The rate of sorption to core section A1 was similar to the observed rate of As(III) sorption to FeS$_2$. In contrast, As(III) sorption to FeS continued for many days until nearly complete sorption was achieved.

Common kinetic models (e.g., first-order, second-order, parabolic diffusion or the Elovich models) failed to adequately described As(III) sorption to Pescadero sediments, FeS or FeS$_2$. Deviation from these kinetic models arises when multiple reactions influence the observed reaction rate; thus, As(III) sorption to these sediments, FeS, and FeS$_2$ probably involves multiple reactions (Sparks, 1989, Sposito, 1994; Sparks, 1998).
The kinetic data suggest that rapid sorption precedes a slower sorption process that continues for greater than 48 h. Two-step reactions are commonly used for sorption processes in soils and sediments (Sparks, 1989). The first reaction probably represents the initial sorption of As on the reactive surfaces of the soil. The second, slower, reaction may be attributed to the subsequent formation of sulfide minerals or diffusion limitations. These distinct processes are confirmed by XAS and will be discussed later.

**Arsenic Oxidation State**

Arsenite was strongly retained by Pescadero sediments. While macroscopic sorption characteristics of As(III) sorption on these sediments is similar to that on FeS and FeS₂, their correlation is insufficient to unequivocally define the sorption mechanism. Therefore, XAS is used to probe the role of sulfide minerals in As retention in Pescadero sediments.

X-ray absorption near-edge structure spectroscopy was used to determine the oxidation state of sorbed As species. Unfortunately, the XANES spectra of 50 µM As(III) sorbed to 2 g/L core A1 for 1 h (13 µmol/g) show the spontaneous oxidation of sorbed As (Fig. 8). Initially, the spectrum contains a combination of both reduced As species (at or below 11,871 eV), and a small As(V) shoulder (11,874 eV). Following three scans, the magnitude of the reduced As peak is considerably lower and the magnitude of the As(V) peak enhanced, indicative of oxidation during analysis. The fraction of As(V) increases from about 35% initially to 98% by scan 3 (after about 1.5 h) as noted by linear combination XANES fitting (Table 2). Arsenic oxidation complicates the detailed spectral analysis of sorbed As species. Spectral subtraction is used to
alleviate interference from As(V) produced during analysis—the As(V) component of the normalized XANES is subtracted to isolate the spectrum of sorbed As species prior to oxidation. Spectral processing is only required for As(III) sorbed to the core sections for 1 h—samples reacted for 21 d were stable.

The XANES spectra of As(III) sorbed to core A1 for 1 h and 21 d are compared with a variety of As-containing reference materials in Figure 9. After reaction for 1 h, the spectrum of sorbed As contains absorption edges at 11,868.9 and 11,871.4 eV (not including the absorption edge of arsenate, which is formed during analysis), corresponding to the adsorption edges of arsenic sulfides and arsenite, respectively. The adsorption edge of the As-S compound is slightly higher than for As(III)-sorbed FeS or FeS₂ (about 11868 eV) and intermediate between the edge of As₂S₃ (11,869.5 eV) and FeAsS (11,867 eV). The identity of the arsenic sulfide phase is thus difficult to determine by XANES spectroscopy. Despite this limitation, it is apparent that much of the arsenic(III) has undergone significant structural changes during sorption, changing from oxygen coordination in arsenite to sulfur coordination within these soils. Thus, sulfide minerals are an important phase for As sequestration in this, and presumably other, anoxic environments.

After As(III) has reacted with the salt marsh sediment for 21 d, only a single absorption edge (at 11,869.4 eV) is clearly defined, indicating that the conversion of residual arsenite to sulfide phases is complete and not susceptible to photooxidation (Fig. 9). The absorption edge of the aged samples is also shifted from the absorption edge of the sample reacted for only 1 h, to an edge very similar to that of orpiment and realgar.
Thus, pure arsenic sulfide minerals appear to form following extended (21 d) reaction times.

EXAFS spectroscopy provides additional insight into the structure of sorbed As. The EXAFS spectra of As(III)-reacted Pescadero sediments contain features attributed to As-O, As-S and As-Fe shells (Fig. 10). The As-O shell between 1.70-1.75 Å is indicative of arsenate and arsenite sorbed to the soil or formed during analysis. The As-S distances near 2.20 Å are indicative of orpiment, consistent with XANES data, while longer As-S distances (> 2.3 Å) are useful to distinguish other sulfide species. Highly reduced As species, including iron As(-I) sulfides and As sorbed to iron sulfides have an As-S shell between 2.3 and 2.4 Å, and also contain an As-Fe shell at a very short distance (2.4-2.5 Å). The As-Fe shell is directly out-of-phase with the As-S shell, making the As-S shell difficult to detect. Second nearest neighbor As-Fe or As-As shells also are diagnostic of the sorption environment, but their use is impaired in these systems by structural disorder and low crystal symmetry.

The spectrum of 13 µmol/g As reacted for 1 h has a large As-O shell at 1.70 Å indicative of As(V) formed by photooxidation. Other spectral features are hard to identify due to interference from this large As-O shell; however, an As-Fe shells at 2.56 Å is noted. The short As-Fe distance is indicative of a direct bond between As and Fe, which occurs in arsenian pyrite, FeAsS, and the FeAsS-like precipitate formed by As sorption on FeS2. As-S shells are not identified, due in part to the aforementioned phase cancellation with the As-Fe shell, and the lack of appreciable quantities of As2S3 in this sample. A small As-Fe shell is also present at about 3.34 Å, slightly longer than second-
shell As-Fe bonds in FeAsS or As sorbed to FeS$_2$. These EXAFS data suggest that much of the unoxidized As is present as an FeAsS-like precipitate or related species.

Samples aged for 21 d have a dominant As-S shell at a distance of 2.20 Å, typical of As$_2$S$_3$, and small As-O and As-Fe shells (Fig. 10). An As-As distance of 3.54 Å is also detected; the similarity of these As-S and As-As shells to the As$_2$S$_3$ structure indicates that much of the sorbed As in aged samples is present as orpiment—a finding also supported by XANES results. An As-Fe shell at a distance of about 2.54 Å is also detected. This shell is not resolved from the As-S shell due to the limited k-range (about 3 to 10 Å$^{-1}$); however, a As-Fe shell improves the fit of the first shell of all samples and is separated from the As-S shell in some samples using an extended k-range (Fig. 11). A 2.54 Å As-Fe shell suggests a reduced FeAsS-like phase, but the fit distance is elongated relative to standards. Additional As-S or second As-As/Fe shells, both of which are lacking, are needed to resolve the identity of this phase.

Spectral fitting suggests that both As$_2$S$_3$ and As(III) sorbed to iron sulfides are present in these samples. Unfortunately, the interpretation of spectral shells is limited by the complexity and convolution of the spectra. The Debye-Waller factors also must be fixed to minimize the number of free-floating parameters in fits, introducing error into the determination of coordination number and the relative abundance of different As phases. Linear-combination fitting of EXAFS spectra offers an alternative quantification method that often requires fewer variables and that is often effective at resolving a range of spectral components (Foster et al., 1998; Ostergren et al., 1999; Ressler et al., 2000). Linear combination fitting benefits from the use of a complete and uniform spectral library, problematic for this system. We used a spectral library, constrained based on
EXAFS fitting results, to sorbed arsenite, arsenate, As$_2$S$_3$ and As sorbed to FeS$_2$. Using these standards, the linear combination fitting indicates that the majority of the 13 µmol/g As reacted for 1 h is composed of arsenate (64%) and As sorbed to FeS$_2$ (27%, Fig. 12). Once these fractions are weighted to account for the formation of As(V) during analysis, the spectrum is composed of about 75% As sorbed to FeS$_2$. In contrast, the largest fraction of the aged samples is As$_2$S$_3$, with minor fractions (5-20%) of As sorbed to FeS$_2$, and arsenite and arsenate. The prevalence of orpiment in aged samples and the conversion of FeAsS-like surface precipitates to orpiment over time was also seen using conventional EXAFS fitting.

**CONCLUSIONS**

Arsenic is thought to partition with sulfide minerals in anoxic soils and sediments. These experiments examined As(III) sorption to salt marsh soils and found retention characteristic of inner-sphere sorption or precipitation. Sulfide minerals were responsible for As sequestration in Pescadero sediments. X-ray absorption spectroscopy showed that arsenite underwent conversion to a sulfur-containing coordination environment. Arsenic was sequestered initially through its reduction to and subsequent precipitation of an FeAsS-like phase. The initial precipitate was highly reactive and readily oxidized during analysis. This reactivity was also reflected in the effect of increased reactions times—orpiment, As$_2$S$_3$, was formed over extended contact times. The fraction of orpiment is greatest in aged samples with the highest As and sulfide concentrations (those with the longest reaction time), consistent with the enhanced precipitation of As$_2$S$_3$ at elevated As or sulfide activities.
Arsenic speciation changes observed by XAS help to explain the two-step reaction sequence observed based on the kinetic data (Fig. 7). The FeAsS-like precipitate is formed rapidly, comprising the bulk of sorbed As within 1 h. Sorption conforms to a Langmuir isotherm (Fig. 3) because the extent of reduction and precipitation depends on the concentration of available reduced iron and sulfur species. Continued reduction leads to the development of As$_2$S$_3$, a stable reaction product not susceptible to photooxidation.

These data allow us to refine our understanding of As cycling in the environment, particularly under anoxic conditions (Fig. 13). Surface reactions of iron sulfide minerals, specifically FeS$_2$, are responsible for the initial attenuation of arsenic in anoxic environments. Previously, it was believed that precipitation or coprecipitation was the predominant mechanism of As retention in such environments Aggett and O’Brien, 1985; Moore et al., 1994). The formation of As$_2$S$_3$ is presumably most important at elevated As(III) and sulfide activities in which the solution is supersaturated with respect to orpiment. In natural systems, where As concentrations are typically very low and sulfide activities are maintained at low to moderate levels by water circulation, adsorption to sulfide minerals may be most important. Regardless, sorption reactions on sulfide minerals are a vital step to the sequestration of As in anoxic environments.

REFERENCES


Table 1. Selected mineralogical and chemical characteristics for three cores (0-5 cm depth) along a transect in a salt marsh near Pescadero, CA.

<table>
<thead>
<tr>
<th>Core</th>
<th>% Sand</th>
<th>% Silt</th>
<th>% Clay</th>
<th>Organic matter (g kg⁻¹)</th>
<th>Mn⁺⁺⁺ (g kg⁻¹)</th>
<th>Fe⁺⁺⁺ (g kg⁻¹)</th>
<th>Soil pH</th>
<th>ΣH₂S (µM)</th>
<th>Mineralogyb</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1</td>
<td>1</td>
<td>98</td>
<td>343</td>
<td>0.03</td>
<td>29.0</td>
<td>4.78</td>
<td>41</td>
<td>Q, P, S, V</td>
</tr>
<tr>
<td>B1</td>
<td>2</td>
<td>1</td>
<td>97</td>
<td>371</td>
<td>0.06</td>
<td>27.5</td>
<td>4.31</td>
<td>30</td>
<td>Q, P, S, V</td>
</tr>
<tr>
<td>C1</td>
<td>9</td>
<td>11</td>
<td>80</td>
<td>280</td>
<td>0.06</td>
<td>23.0</td>
<td>4.26</td>
<td>8</td>
<td>Q, P, S, V</td>
</tr>
</tbody>
</table>

(a): Measured by extraction with dithionate-citrate-bicarbonate.
(b): Mineralogy determined for the <2 µm particle size by powder x-ray diffraction (XRD). Mineral abbreviations: P=plagioclase, S=smectite, V=vermiculite, Q=quartz.

Table 2. Oxidation state changes to 50 µM As(III) adsorbed to 2 g/L samples of core A1 for 1 h (at pH 7) as determined by linear combination XANES fitting.

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>As₂S₃ /other sulfide percent</th>
<th>As(III) percent</th>
<th>As(V)</th>
<th>Residuala</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>38</td>
<td>27</td>
<td>35</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>27</td>
<td>2</td>
<td>71</td>
<td>7</td>
</tr>
<tr>
<td>1.5</td>
<td>2</td>
<td>0</td>
<td>98</td>
<td>6</td>
</tr>
</tbody>
</table>

(a): Residual, a measure of goodness of fit, is defined as the normalized sum of differences between observed and expected spectra, multiplied by 100%.
Table 3. Arsenic local structure for As(III) adsorbed to FeS and FeS$_2$. The $E_0$ was $\approx$ 11869 eV for aged samples, and 11,873 eV for the sample reacted for 1 h.

<table>
<thead>
<tr>
<th>Sample</th>
<th>As-O</th>
<th>As-S</th>
<th>As-Fe/As</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CN$^a$</td>
<td>R (Å)$^b$</td>
<td>$\sigma^2$ (Å$^2$)$^c$</td>
</tr>
<tr>
<td>Arsenian FeS$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeAsS</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As$_2$S$_3$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 µmol/g As(III) on FeS$_2$, pH 4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 µmol/g As(III), 1 h</td>
<td>3.8</td>
<td>1.70</td>
<td>0.004</td>
</tr>
<tr>
<td>8 µmol/g As(III), 3 wk</td>
<td>1.03</td>
<td>1.71</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 µmol/g As(III), 3 wk</td>
<td>1.31</td>
<td>1.71</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23 µmol/g As(III), 3 wk</td>
<td>1.33</td>
<td>1.71</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27 µmol/g As(III), 3 wk</td>
<td>1.73</td>
<td>1.70</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a): Coordination number.
(b): Interatomic distance.
(c): Debye-Waller factor, the variance in R.
(d): Fixed during fitting.
(e): As-As distance.
Table 4. Linear combination fits of k-weighted EXAFS spectra of As(III) sorbed to Pescadero soils.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fractional Species&lt;sup&gt;a&lt;/sup&gt;</th>
<th>As(V)</th>
<th>As(III)</th>
<th>As&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;3&lt;/sub&gt;</th>
<th>As on FeS&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Residual&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>13 µmol/g As(III), 1 h</td>
<td></td>
<td>0.64</td>
<td>0.03</td>
<td>0.06</td>
<td>0.27</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.08)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>(0.17)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>(0.75)&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>8 µmol/g As(III), 21 d</td>
<td></td>
<td>0.05</td>
<td>0.13</td>
<td>0.58</td>
<td>0.24</td>
<td>47</td>
</tr>
<tr>
<td>15 µmol/g As(III), 21 d</td>
<td></td>
<td>0.11</td>
<td>0.08</td>
<td>0.63</td>
<td>0.18</td>
<td>59</td>
</tr>
<tr>
<td>23 µmol/g As(III), 21 d</td>
<td></td>
<td>0.09</td>
<td>0.08</td>
<td>0.69</td>
<td>0.14</td>
<td>61</td>
</tr>
<tr>
<td>27 µmol/g As(III), 21 d</td>
<td></td>
<td>0.14</td>
<td>0.03</td>
<td>0.73</td>
<td>0.10</td>
<td>51</td>
</tr>
</tbody>
</table>

(a): The reference spectra are scorodite (As(V)), sodium arsenite (As(III)), orpiment (As<sub>2</sub>S<sub>3</sub>), and 13 µmol/g FeS<sub>2</sub> (100 µM As, 1 g/L suspension, pH 4) for the As on FeS<sub>2</sub> standard.

(b): Residual, a measure of goodness of fit, is defined as the normalized sum of differences between observed and expected spectra, multiplied by 100%.

(c): Fraction recalculated without As(V) fraction.
Figure 1. Location of Pescadero Slough illustrating the sampling area (a) and sampling transect (b). Pescadero Slough is located about 60 km south of San Francisco, CA. The tick marks are for the UTM coordinates in meters.
Figure 2. Fe K-edge EXAFS spectrum (a) and its Fourier transform (b) of cores A1 and C1 prior to reaction with As. The experimental data (solid line) for each core is fit (dotted line) with an Fe-S shell (CN=4, R=2.17 Å, $\sigma^2=0.013$) and an Fe-Fe shell (CN=4, R=3.37 Å, $\sigma^2=0.020$).
Figure 3. Sorption envelopes of As(III) on selected Pescadero soil cores (a) and Fe mineral standards (b).

(a) 55 µM As(III) on 2 g/L soil

(b) 55 µM As(III) on 1 g/L solids
Figure 4. Sorption isotherms for As(III) on core section A1 and FeS₂ at pH 7.
Figure 5. Effect of sulfide addition on As(III) sorption to 2 g/L Pescadero core A1, FeS, and FeS$_2$ at pH 7.
Figure 6. Ionic strength effects on 50 µM As(III) sorption to 2 g/L Pescadero soil core A1 at pH 7.
Figure 7. Sorption of a 100 µM As(III) to a Pescadero core section A1 and iron sulfide mineral suspensions over time.
Figure 8. Raw (a) and first-derivative (b) XANES spectra of 50 μM As(III) reacted at pH 7 with 2 g/L sediment from core section A1 (13 μmol/g) over successive scans. The shift in the peak indicates that the sample is undergoing oxidation during analysis.
Figure 9. Representative XANES spectra of As(III) adsorbed on Pescadero core A1 compared to several As standards. The spectrum of the A1 core reacted for 1 h has been processed to remove As(V) formed during analysis; however, no correction was necessary for suspensions reacted for 21 d.
Figure 10. The k-weighted $\chi(k)$ spectra (a) and corresponding Fourier transforms (b) of As(III) adsorbed on sediment from core A1 as a function of As(III) surface loading and reaction time. The experimental spectra (solid lines) are fit (dotted lines) with the parameters in Table 3.
Figure 11. EXAFS spectrum of 75 μM As(III) reacted with 2 g/L core A1 (23 μmol/g) for 3 weeks showing the effect of k-range on the radial structure function. The fits of each (dotted lines) use the same fitting parameters (Table 3). The As-Fe shell can be resolved from the As-S shell with an extended k-range.
Figure 12. Linear combination fits (dotted lines) of EXAFS spectra of As(III) sorbed to sediments from core A1 (solid lines). The spectra have been fit with linear combinations of As(V), As(III), As$_2$S$_3$, and As(III) sorbed to FeS$_2$ using the fractions described in Table 4.
Figure 13. Schematic illustration of As cycling that incorporates As transformations in sulfidic environments.
Chapter 5.

Differential Adsorption of Molybdate and Tetrathiomolybdate on Pyrite (FeS₂)
ABSTRACT

Molybdate (MoO$_4^{2-}$) and tetrathiomolybdate (MoS$_4^{2-}$) sorption on synthetic pyrite (FeS$_2$) was investigated as a function of solution composition. Both MoO$_4^{2-}$ and MoS$_4^{2-}$ partitioned strongly on FeS$_2$ under a range of conditions and ionic strengths. Molybdate and tetrathiomolybdate adsorption obeyed a Langmuir isotherm with a calculated site density of 2 to 3 sites/nm$^2$ under acidic and circumneutral conditions, which decreased to less than 1 site/nm$^2$ at pH 9. Although both MoO$_4^{2-}$ and MoS$_4^{2-}$ adsorbed most strongly under moderately acidic conditions, MoO$_4^{2-}$ readily desorbed while MoS$_4^{2-}$ remained adsorbed even at high pH. The reversibility of adsorption for MoO$_4^{2-}$ suggests the formation of either weak inner-sphere or outer-sphere complexes while strong inner-sphere complexes are likely for MoS$_4^{2-}$. X-ray absorption spectroscopy (XAS) was used to determine the structure of the surface complexes. Molybdate formed bidentate, mononuclear complexes on FeS$_2$. For tetrathiomolybdate, the Mo-S distances were elongated relative to tetrathiomolybdate, and Mo-Fe bonds at 2.7 Å were observed. The Mo-S and Mo-Mo distances for tetrathiomolybdate on pyrite are consistent with the formation of Mo-Fe-S cubane-type clusters. The high affinity of MoS$_4^{2-}$ for FeS$_2$, as well as its resistance to desorption, supports the hypothesis that thiomolybdate species are the reactive Mo constituents in reduced sediments and may control Mo enrichment in anoxic marine environments.

INTRODUCTION

Molybdenum has many vital biological functions including nitrogen fixation and nitrogen assimilation. For nitrogen fixation, molybdenum forms the Mo-Fe-S cubane in
nitrogenase that is responsible for the reduction of \( \text{N}_2(g) \) to \( \text{NH}_4^+ \), a critical step of the nitrogen cycle. Molybdenum also forms the active site of nitrate reductase, thereby allowing the incorporation of nitrate-N. These essential ecosystem functions are regulated by the availability of Mo, consequently, processes that control Mo availability are of interest. Molybdenum deficiency is uncommon in near-neutral soils and sediments under typical, oxic, conditions. Under such conditions, molybdenum is stable as either hexavalent molybdate, \( \text{MoO}_4^{2-} \), or octahedral polymolybdate complexes that each react only weakly with aluminosilicates and metal (hydr)oxides (Xie and MacKenzie, 1991; Goldberg et al., 1996; Rietre et al., 1999; Wu et al., 2000; Bourikas et al., 2001). Molybdate reacts more strongly with manganese oxides (Bertine and Turekian, 1973; Calvert and Pedersen, 1993) and some clay minerals at low pH (Goldberg et al., 1996); however, \( \text{MoO}_4^{2-} \) is mobile and available for biological uptake in most systems.

Molybdenum chemistry in reduced (anoxic) environments is more complex. Molybdenum is scavenged in such environments (Emerson and Huested, 1991; Amrhein et al., 1993; Crusius et al., 1996; Morford and Emerson, 1999; Erickson and Helz, 2000; Johannesson et al., 2000), leading to non-conservative behavior in sulfidic sediments (Emerson and Huested, 1991), estuaries (Vandenberg, 1993) and other reduced environments. In some cases, the decrease in soluble Mo concentrations may contribute to Mo deficiencies, potentially limiting productivity (Vitousek and Howarth, 1991; Howarth et al., 1999). The enrichment observed in anoxic sediments is directly correlated to the presence of sulfide—suboxic (sulfide-free, intermediate redox status) environments exhibit no Mo enrichment (Crusius et al., 1996). Consequently, Mo enrichment has been used as a proxy for sulfidic, anoxic conditions during sediment
deposition and genesis (e.g. Shaw et al., 1990; Crusius et al., 1996; Morford and Emerson, 1999; Adelson et al., 2001).

The mechanism of Mo retention in sulfidic environments is not well established. Molybdenum enrichment has often been attributed to the reduction of $\text{MoO}_4^{2-}$ to form molybdenum(IV) sulfide (e.g., Amrhein et al., 1993).

$$\text{MoO}_4^{2-} + 2e^- + 2\text{HS}^- + 6\text{H}^+ \iff \text{MoS}_2 + 4\text{H}_2\text{O}, \quad \Delta G^0 = -314.3 \text{ kJ/mol} \tag{1}$$

Although plausible for some systems, MoS$_2$ rarely precipitates due to kinetic limitations (Helz et al., 1996). Elements such as U, W, and Re are concentrated in sulfidic soils and sediments through the formation of insoluble reduced oxide phases (Colodner et al., 1993; Crusius et al., 1996; Choppin and Wong, 1998; Johannesson et al., 2000); however Mo does not form insoluble oxides. Molybdenum enrichment may also involve simple surface complexation or coprecipitation with iron (di)sulfides including pyrite (Bertine, 1973; Bertine and Turekian, 1973; Thomson et al., 1998). Thiomolybdate species, MoO$_x$S$_{4-x}^{2-}$, may also be important precursors to either precipitation or Mo adsorption in sulfidic environments (e.g., Helz et al., 1996; Erickson and Helz, 2000). Unfortunately, at the present time insufficient data are available to define the process(es) responsible for Mo retention in anoxic sediments and soils.

Sulfide minerals may have a controlling impact on Mo sequestration in anoxic environments. Accordingly, this research examines the role sorption processes involving pyrite plays in the enrichment of Mo within anoxic environments. Both molybdate and tetrathiomolybdate adsorption were examined and surface structures resolved using X-ray absorption spectroscopy (XAS).
MATERIALS AND METHODS

Reagents

All reactions were performed in a glovebox (95% N₂, 5% H₂) that maintained O₂ concentrations below 1 ppm. Synthetic pyrite, FeS₂, was purchased from Strem Chemical (>99% purity). The mineral surface was prepared by washing with water, 0.1 M HCl, and finally with 0.01 M sulfide solutions to remove oxidized surface species. The washed FeS₂ has a surface area of 41.7 m²/g as determined with a 3-point nitrogen BET isotherm. X-ray photoelectron spectroscopy of the resulting mineral surfaces showed no evidence of sulfate, thiosulfate or other oxidized sulfur species, although limited surface oxidation of Fe was apparent regardless of cleaning procedures. The washed material was used immediately to minimize further oxidation.

All other chemicals were of analytical grade. Molybdenum was added to suspensions using 10 mM stock solutions of Na₂MoO₄·2H₂O or (NH₄)₂MoS₄; 10 mM stock solutions of sulfide were prepared using Na₂S·9H₂O. Reagents were stored under nitrogen and used as purchased.

Adsorption Experiments

Adsorption of MoO₄²⁻ and MoS₄²⁻ on FeS₂ was investigated under a wide variety of conditions. A series of FeS₂ suspensions were reacted with MoO₄²⁻ or MoS₄²⁻ (0-100 µM Mo) as a function of suspension density (0.5 to 2 g/L), pH (3 to 11), ionic strength (0.005-0.5 M), and the addition of sulfide (0-2 mM total sulfide). Adsorption isotherms were performed at pH 4, 7 and 9 by buffering 1 g/L mineral suspensions with 0.002 M acetate, MOPS, or borate, respectively, to maintain sample pH.
The effect of pH on sorption was also investigated by adjusting the pH of mineral suspensions containing Mo(VI). Molybdate, 100 µM, was added to a 1 g/L FeS₂ suspension having an initial pH between 2 and 3. The pH was measured after equilibration for 30 minutes, sampled, and then increased with a small volume of 0.5 M NaOH. This procedure was repeated until the pH reached about 11. Similar experiments were performed using suspensions in which the initial pH was high (~ 11) and titrated to pH ~3 with 0.5 M HCl. Suspended solids were removed from subsamples by filtration (0.2 µm pore size) and residual solutions were analyzed for total Fe, As, and S using a Thermo Jerrell Ash IRIS inductively coupled plasma-optical emission spectrometer (ICP-OES). The extent of sorption was determined by difference between initial and final Mo concentrations.

Samples were prepared for XAS by reacting 100 µM molybdate or thiomolybdate with 1g/L FeS₂ at pH 9 under total sulfide concentrations of 0.1, 2 and 5 mM. Sulfide concentrations were chosen to poise the suspensions at a constant redox potential and also served to stabilize either thiomolybdate or molybdate. At pH 9, MoO₄²⁻ solutions are stable at total sulfide concentrations below ~2 mM; MoS₄²⁻ solutions are stable at concentrations above 2 mM (Helz et al., 1996). Following reaction for 3 h, solids were isolated by filtering and sealed in Kapton film, stored under nitrogen, and analyzed within 24 h.

**X-ray Absorption Spectroscopy**

X-ray absorption spectroscopy was performed at the Stanford Synchrotron Radiation Laboratory on beamlines 4-3 and 11-2. The storage ring operated at 3.0 GeV
and at currents between 50 and 100 mA. Spectra were taken with a Si(220) double-crystal monochromator with an unfocused beam. Incident and transmitted intensities were measured with 15-cm N₂-filled ionization chambers. Sample fluorescence was measured with a 13-element Ge detector containing a 6 µm Ge filter. The incident beam intensity was detuned approximately 50% to reject higher-order harmonic frequencies and to prevent detector saturation. Spectra were internally calibrated by placement of a molybdenum metal foil between the second and third ionization chamber.

X-ray absorption spectra were collected from –200 to +1000 eV about the Mo K-edge (20,000 eV). At least 5 spectra were collected for each sample and averaged for analysis. XAS spectra were analyzed using WinXAS (Ressler, 1997) in combination with Feff 8.0 software (Rehr et al., 1991; Zabinsky et al., 1995; Ankudinov et al., 1998). The X-ray absorption near-edge structure (XANES) spectra provides information about the oxidation state and coordination environment of the adsorbed As. XANES spectra were not smoothed to preserve line-shapes; however, first-derivative XANES spectra were smoothed 5% to decrease noise levels. XANES spectra were compared to several model compounds (including MoS₂, MoO₄²⁻ and MoS₄²⁻) to determine the structural and oxidation state changes resulting from sorption and to validate the phase and amplitude functions derived using Feff.

Extended x-ray absorption fine structure (EXAFS) spectroscopy was also used to determine the coordination environment of adsorbed molybdenum species. The k³-weighted χ(k) spectrum was isolated using a seven point spline function and an E₀ of 20,000 eV. The EXAFS spectrum was then Fourier-transformed without smoothing to produce a radial structure function (RSF) using a k-range of approximately 3 to 14 Å⁻¹.
Preliminary fits on Fourier-filtered shells were used as a guide for final fits, which always used unsmoothed k-weighted $\chi(k)$ spectra. This procedure yields information about the local structure of Mo at the pyrite surface, including the coordination number (CN), distance (R), and the Debye-Waller factor ($\sigma^2$) for each shell. Such EXAFS fitting is highly accurate for the determination of interatomic distances (within 0.02 Å); however, larger errors in CN and $\sigma^2$ (up to 30%) result due to their correlation. Differences in phase and amplitude functions and interatomic distances permit the identification of different elements.

**RESULTS AND DISCUSSION**

**Solution-Phase Experiments**

Both one and two-site Langmuir isotherms were used to describe MoO$_4^{2-}$ and MoS$_4^{2-}$ sorption on FeS$_2$. Molybdate and tetrathiomolybdate adsorption on FeS$_2$ conformed most closely to a one-site Langmuir isotherm at pH 4, 7, and 9 (Fig. 1). Freundlich isotherms were less effective at fitting the adsorption data. Fitting the data with two Langmuir sites did not improve the accuracy of fitting at low adsorption densities for all samples except MoS$_4^{2-}$ at pH 7, which contained two distinct adsorption regions (Fig. 2). Anion adsorption reactions commonly obey Langmuir isotherms, reaching an adsorption maximum when surface sites are saturated. Precipitation reactions, which do not exhibit adsorption maxima, are distinct from the observed data, suggesting that molybdenum does not form surface precipitates on FeS$_2$.

Isotherm data can be interpreted to yield information about the affinity and site density of each Mo species for FeS$_2$ (Table 1). The monolayer capacity for MoO$_4^{2-}$ was
130 µmol g\(^{-1}\) at pH 4 and 7, decreasing to 60 µmol g\(^{-1}\) at pH 9. The monolayer capacity for MoS\(_4^{2-}\) ranged between 150 µmol g\(^{-1}\) at pH 4 to 12.1 µmol g\(^{-1}\) at pH 9. The monolayer capacities correspond to site densities for both MoO\(_4^{2-}\) and MoS\(_4^{2-}\) of about 2 sites/nm\(^2\) at pH 4 and 7, and much lower at pH 9. A site density of 2 sites/nm\(^2\) corresponds to 0.5 reactive sites per unit cell, assuming that reactive sites are uniform and on the (100) plane. This suggests that not all disulfide groups on the surface are reactive. Defects and other sites are well recognized for their important roles in adsorption (Guevremont et al., 1997; Guevremont et al., 1998; Bostick et al., 2000). They are also the reactive sites for pyrite oxidation (Sasaki, 1994; Martello et al., 1994; Rosso et al., 1999). These defects are more reactive and their presence may result in the high-energy site suggested by the 2-site Langmuir isotherm for MoS\(_4^{2-}\) at pH 7; however, more data are needed to accurately determine which FeS\(_2\) surface reactive groups react with molybdenum.

Experiments were also performed to examine the effect of pH on adsorption (Fig. 3). Molybdate exhibited an adsorption maximum between pH 5 and 6, with adsorption decreasing sharply as the pH departed from this range. A similar pH of maximum adsorption was noted for molybdate on amorphous iron sulfide (Bertime, 1972) and iron (hydr)oxide (Bibak and Borggard, 1994; Bourikas et al., 2001). Although adsorption was strong between pH 4 and 7, MoO\(_4^{2-}\) was rapidly desorbed through changes in pH (Fig. 3). Reversible adsorption behavior implies that the MoO\(_4^{2-}\) surface complexes are labile, consistent with an outer-sphere or weak inner-sphere complex. In contrast, MoS\(_4^{2-}\) adsorption was greatest under acidic conditions and steadily decreased as pH became more basic (Fig. 3). Tetrathiomolybdate adsorption was considerably less reversible than
MoO$_4^{2-}$; only a fraction of MoS$_4^{2-}$ was released following adsorption even as pH increased to nearly 11. Irreversible adsorption implies inner-sphere thiomolybdate adsorption complexes form on FeS$_2$, although it is not possible to discriminate between adsorption and precipitation based on irreversibility alone.

The effect of ionic strength on sorption was used to confirm the presence of inner-sphere adsorption complexes. Both MoO$_4^{2-}$ and MoS$_4^{2-}$ adsorption were impacted somewhat by increasing the ionic strength of the suspension (Fig. 4); MoO$_4^{2-}$ adsorption was affected by salt additions at all concentrations, while MoS$_4^{2-}$ adsorption was unaffected except at low ionic strengths. Ionic strength changes generally affect outer-sphere complexes; therefore, these data imply that MoO$_4^{2-}$ and MoS$_4^{2-}$ is adsorbed in part as outer-sphere complexes. The negative FeS$_2$ surface charge at pH>3 (Bebie et al., 1998) makes outer-sphere complexes unlikely; however, a small fraction of the species could be bound to oxidized regions of the surface that have positive surface charge at pH 7. Outer-sphere molybdate complexes commonly form on iron (hydr)oxides (Bibak and Borggard, 1994); thus, ionic strength would affect adsorption to a limited extent. Interestingly, the effect of ionic strength was most pronounced when excess sulfide was present in solution (Fig. 3). The reason for this combined effect of ionic strength and sulfide addition is unclear.

Sulfide additions exert a considerable effect on the adsorption of both MoO$_4^{2-}$ and MoS$_4^{2-}$ (Fig. 5). In all cases, the presence of excess sulfide inhibited Mo sorption. Inhibition was most pronounced for the smallest additions of sulfide, as sulfide was incrementally increased its effect became smaller. Inhibition of Mo adsorption implies that sulfide competes for surface sites or is evolved during Mo adsorption. The
precipitation of molybdenum sulfide would also be enhanced by sulfide addition (Equation 1). The opposite trend was observed; thus, precipitation of Mo sulfides is not likely. Precipitation mechanisms are also unlikely given the adherence of adsorption to the Langmuir isotherm. However, spectroscopic confirmation is necessary to validate this conclusion.

**Solid Phase Analysis**

**XANES Spectroscopy**

Macroscopic studies provide information about the influence of solution composition and the affinity of FeS$_2$ surfaces for molybdenum species. Spectroscopic information is also needed to characterize the adsorption mechanism. Here we used X-ray absorption spectroscopy to define the local structure of molybdenum adsorbed on FeS$_2$. XANES spectroscopy is diagnostic of oxidation state and coordination, permitting the differentiation of MoO$_4^{2-}$ and MoS$_4^{2-}$ (Fig. 6). The spectrum of MoO$_4^{2-}$ contains a large pre-edge feature and a main edge position (defined by its inflection point) at 20,016 eV; MoS$_4^{2-}$ does not have a pronounced pre-edge feature and has an edge position 10 eV lower than molybdate in energy. The difference is a consequence of the greater covalency in MoS$_4^{2-}$ and permits the simple differentiation of oxygen and sulfur coordination for Mo(VI). As such, XANES spectroscopy affords the opportunity to discern the conversion of tetrahedral Mo-O coordination in MoO$_4^{2-}$ to octahedral sulfur coordination. Accordingly, we use XANES spectroscopy to characterize the coordination of adsorbed MoO$_4^{2-}$ and MoS$_4^{2-}$ on FeS$_2$. 
The spectrum of molybdate-adsorbed samples contained a pre-edge feature and an edge position of 20,016 eV (Fig. 6), consistent with MoO$_4^{2-}$. Thus, it appears that the structure of MoO$_4^{2-}$ is largely unchanged following adsorption on FeS$_2$. In contrast, MoS$_4^{2-}$ undergoes major structural changes during adsorption (Fig. 7). While spectra lack the presence of a prominent pre-edge feature, the derivative spectra contain two maxima at 20,007 and 20,019 eV, neither of which corresponds to MoO$_4^{2-}$ nor MoS$_4^{2-}$.

**EXAFS Spectroscopy**

Further information regarding the structural environment of Mo on FeS$_2$ was elucidated with EXAFS spectroscopy. Molybdate adsorbed on FeS$_2$ contains both Mo-O and Mo-Fe shells (Fig. 8). The Mo-O shell is fit with a single Mo-O distance, $d$(Mo-O), of about 1.76 Å (Table 2), consistent with that of molybdate. Disordered coordination environments are commonly observed for strongly adsorbed (inner-sphere) molybdate species, which contain short Mo=O bonds near 1.7 Å and longer bridging Mo-O bonds at about 1.9 Å (Bare et al., 1993, Takenaka et al., 1998). Octahedral polymolybdate species, such as heptamolybdate, also contain a disordered Mo-O shell with distances ranging from 1.7 to 2.1 Å (Hu et al., 1995). The symmetry of the Mo-O shell agrees with the macroscopic observations that the adsorbed Mo complexes are relatively weak; strong complexes would lead to different bond lengths for bridging and terminal Mo-O bonds.

The structure of the adsorbed molybdate can be probed in more detail using the Mo-Fe shell. The Mo-Fe shell of 12 µmol MoO$_4^{2-}$/g FeS$_2$ is fit with a single Fe atom at ~2.85 Å (Table 2), consistent with the formation of a bidentate, mononuclear complex (Fig. 9). The Mo-Fe shell was not detected for the 3 µmol MoO$_4^{2-}$/g FeS$_2$ sample;
however, a more disordered shell and limited k-range would prohibit detection. A bidentate complex is formed for molybdate adsorption to a variety of other substrates, including iron and aluminum (hydr)oxides (Bibak and Borggard, 1994).

The spectra of MoS$_4^{2-}$ adsorbed on FeS$_2$ are more complex than that for MoO$_4^{2-}$ (Fig. 8). Three spectral features are resolved in the RSF, an Mo-O shell, a Mo-S shell, and a Mo-Fe shell. The Mo-O shell is fit at a distance of 1.75 Å, similar to other molybdate species and indicates a limited conversion of MoS$_4^{2-}$ to MoO$_4^{2-}$ during reaction. The change toward oxo-coordination is limited during the timescale of the experiment (the Mo-O coordination number is only 1) and does not impact our ability to determine the structure of adsorbed thiomolybdate species. The second shell is fit with a Mo-S pair at 2.40 Å, while the MoS$_4^{2-}$ reference material has Mo-S distances of 2.19 Å. The Mo-S bond is elongated relative to the standard, but the Mo-Fe interatomic distance remains constricted at only 2.68 to 2.70 Å. Thus, MoS$_4^{2-}$ undergoes significant structural rearrangement as a consequence of adsorption on FeS$_2$.

The presence of a Mo-Fe shell at 2.7 Å also indicates that Mo forms an inner-sphere complex on FeS$_2$, in agreement with non-reversible adsorption (Fig. 3) and only a small dependence on ionic strength. Given the long (2.40 Å) Mo-S bonds, the minimum Mo-Fe distance for a bidentate, mononuclear complex would be about 3.1 Å, even given a tilt angle (the Mo-O-Fe bond angle) of nearly 90 degrees. Monodentate complexes, or bidentate, binuclear complexes have longer Mo-Fe distances. The observed Mo-Fe distances are about 2.7 Å, too short to be either a monodentate or bidentate complex. Thus, a face-sharing (tridentate) adsorption complex must be formed though MoS$_4^{2-}$ adsorption on FeS$_2$. 

Face-sharing anion complexes are rare because they result in short interatomic distances between ions of similar and high charge. However, Mo forms a wide variety of cubanes with Fe and S (Fig. 9), in which Mo-S and Fe-S tetrahedra are face-shared (Christou et al., 1978; Garner et al., 1987). Cubanes occur in a wide variety of chemical environments, including the active site of nitrogenase (Cramer et al., 1978; Chan et al., 1993), and have a similar coordination environment to that observed in these samples—elongated Mo-S bonds (at about 2.35-2.4 Å) and short Mo-Fe bonds at about 2.7 Å (Table 2). Therefore, we identified MoS$_4^{2-}$ adsorbed on FeS$_2$ as a Mo-Fe-S cubane.

**Adsorption Model**

The combination of spectral and adsorption data allow us to create a chemical expression describing Mo adsorption. A bidentate, mononuclear complex was identified for MoO$_4^{2-}$ adsorption on FeS$_2$. One possible reaction forming such a complex is described below (Equation 2).

$$
≡Fe – OH + MoO_4^{2-} ⇔≡Fe – O_2MoO_2^- + OH^-
$$

Such a reaction is consistent with Mo adsorption on a range of other media, including iron and aluminum oxides (Bibak and Borggard, 1994; Wu et al., 1998). Additionally, it explains the reactivity of protonated surface groups and the observed pH dependence. Similar reactions are proposed for anion adsorption on other sulfide minerals (Gärd et al., 1995; Balsley et al., 1996):

$$
≡Me – OH + HCO_3^- ⇔≡Me – OHCO_2^0 + OH^-
$$

A reaction can also be postulated for the adsorption of MoS$_4^{2-}$ species on FeS$_2$. One possible reaction forming a Mo-Fe-S cubane is described in Equation 4.
While many cubane structures are found in the environment, this cubane is chosen since the Fe atoms can remain associated with the surface, resulting in a relatively simple inner-sphere complex. Sandwich-type cubanes or other structures may have similar EXAFS spectra but require appreciable rearrangement. Reaction 5 is also consistent with the observed pH dependence of MoS$_4^{2-}$ adsorption.

Equations 2 through 4 assume that the reactive surface groups are protonated hydroxyls. Hydroxyl species are also presumed to the reactive surface groups for anion adsorption on other sulfides (Gärd et al., 1995; Balsley et al., 1996). This assumption is only reasonable for sulfdie minerals in low sulfide-activity solutions owing to the conversion of hydroxyls to sulfhydryl functional groups (Stumm, 1995; Guevremont et al., 1998), Reaction 5:

$$\equiv Fe-OH + H_2S \iff \equiv Fe-SH + H_2O$$  \[5\]

The competition between aqueous sulfide and molybdenum species for the hydroxyl surface groups limits adsorption of the latter. The dramatic decrease in Mo adsorption observed in sulfide-rich solutions suggests that this model of sulfide competitive adsorption may be valid. Although these reactions are plausible and are consistent with the observed data, further studies are needed to determine the stoichiometry and complete reaction of MoO$_4^{2-}$ and MoS$_4^{2-}$ with FeS$_2$. Nevertheless, the data presented here serve as useful descriptors of Mo adsorption.
CONCLUSIONS

Molybdate and tetrathiomolybdate adsorption on FeS$_2$ conform to a Langmuir isotherm. Molybdate formed a labile bidentate, mononuclear complex on FeS$_2$ with a maximum surface concentration at pH 5. Tetrathiomolybdate adsorbed through a complex mechanism that was irreversible and resulted in a Mo-Fe-S cubane. Cubanes are often encountered in nature, although their presence on FeS$_2$ surfaces is somewhat surprising. The accompanying structural rearrangement required for cubane formation may be responsible for the irreversible adsorption.

Molybdenum enrichment in sulfidic environments has been explained by a combination of MoS$_2$ precipitation, Mo coprecipitation with iron sulfides or other phases, and adsorption on mineral surfaces. Although Mo is probably retained through each of these mechanisms in some environments, the results presented here suggest that pyrite adsorption reactions may play an important role in Mo sequestration. Furthermore, our results support the hypothesis (Helz et al., 1996; Clarke and Helz, 2000; Erickson and Helz, 2000) that the conversion of MoO$_4^{2-}$ to MoS$_4^{2-}$ drives Mo retention in anoxic sediments. The sulfidization of molybdate (Equation 6) occurs at a threshold HS$^-$ activity, about 1 mM when buffered with seawater (Brule et al., 1998; Helz et al., 1996).

\[ MoO_4^{2-} + xHS^- \leftrightarrow MoO_{4-x}S_x^{2-} + xOH^- , \quad 1 < x < 4 \]

Molybdate and iron (hydr)oxides are stable in oxic environments and react reversibly, and thus are not retained permanently in most sediments. Under conditions in which molybdate persists and FeS$_2$ is present, molybdate will react with sediments weakly. Molybdate and pyrite may coexist in environments in which the total sulfide concentration is below the pH-dependent threshold, about 1 mM in seawater (Brule et al.,
1998; Helz et al., 1996), and in transient environments in which molybdate is not converted to MoS₄²⁻ due to slow reaction (Erickson and Helz, 2000). As a consequence of the weak interaction of molybdate and pyrite, Mo will quickly desorb as conditions change, thereby eliminating appreciable Mo enrichment. Thus, Mo will not be enriched in suboxic environments. A significant body of evidence supports this hypothesis—Mo enrichment does not occur in sediments such as the Saanich Inlet found to accumulate other elements through more facile redox processes (e.g., Crusius et al., 1996; Morford and Emerson, 1999).

Under highly sulfidic zones, sulfide concentrations commonly increases above the threshold activity to convert MoO₄²⁻ into MoS₄²⁻ (Luther et al., 1986; Helz et al., 1996) which, on the basis of this research, react much more strongly with FeS₂. Once MoS₄²⁻ reacts with pyrite, it forms stable complexes that are irreversibly retained as Mo-Fe-S cubanes. Similar Mo cubanes have been identified in sulfur-rich black shales (Helz et al., 1996). Molybdenum-containing cubanes were not identified in sulfur-deficient shales; Mo was not enriched and was present as molybdate species. Our results provide a rapid mechanism of forming Mo-Fe-S cubanes observed in the sedimentary record where Mo enrichment occurs, although it is unknown if adsorbed Mo undergoes intermediate transformations over longer, geologic timescales. Nevertheless, our results show a plausible mechanism for the accumulation of MoS₄²⁻ in preference to MoO₄²⁻ within anoxic sediments and soils.

REFERENCES


Table 1. Langmuir adsorption parameters for MoO$_4^{2-}$ and MoS$_4^{2-}$ on FeS$_2$.

<table>
<thead>
<tr>
<th>pH</th>
<th>$\Gamma_{\text{max}}^a$ (µmol/g) MoO$_4^{2-}$</th>
<th>$\Gamma_{\text{max}}^b$ (µmol/m$^2$) MoO$_4^{2-}$</th>
<th>Site Density $^c$ (sites/nm$^2$) MoO$_4^{2-}$</th>
<th>$K^d$ (L/µmol) MoO$_4^{2-}$</th>
<th>$\Gamma_{\text{max}}^a$ (µmol/g) MoS$_4^{2-}$</th>
<th>$\Gamma_{\text{max}}^b$ (µmol/m$^2$) MoS$_4^{2-}$</th>
<th>Site Density $^c$ (sites/nm$^2$) MoS$_4^{2-}$</th>
<th>$K^d$ (L/µmol) MoS$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>130.0</td>
<td>147.7</td>
<td>3.12</td>
<td>3.54</td>
<td>1.88</td>
<td>2.13</td>
<td>0.12</td>
<td>0.28</td>
</tr>
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<td>7</td>
<td>136.8</td>
<td>122.5</td>
<td>3.28</td>
<td>2.94</td>
<td>1.97</td>
<td>1.76</td>
<td>0.21</td>
<td>0.061</td>
</tr>
<tr>
<td>9</td>
<td>60.9</td>
<td>12.1</td>
<td>1.46</td>
<td>0.291</td>
<td>0.88</td>
<td>0.17</td>
<td>0.014</td>
<td>0.042</td>
</tr>
</tbody>
</table>

(a): Maximum surface coverage (monolayer capacity).
(b): Calculated using a surface area of 41.7 m$^2$/g.
(c): Calculated from the maximum surface coverage.
(d): The Langmuir adsorption affinity term.
Table 2. Molybdenum local structure for selected Mo compounds and adsorbed species on FeS$_2$. The coordination number (CN) is typically accurate to within ±1, interatomic distance (R) within ± 0.03 Å; the Debye-Waller factor ($\sigma^2$) represents the variance in R.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mo-O</th>
<th>Mo-S</th>
<th>Mo-Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CN</td>
<td>R (Å)</td>
<td>$\sigma^2$ (Å$^2$)</td>
</tr>
<tr>
<td>Na$_2$MoO$_4$·2H$_2$O</td>
<td>4$^c$</td>
<td>1.78</td>
<td>0.003</td>
</tr>
<tr>
<td>(NH$_4$)$_2$MoS$_4$</td>
<td>-$^b$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mo-Fe-S cubane$^a$:</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12 µmol/g MoO$_4^{2-}$, 0.1 mM total sulfide</td>
<td>4$^c$</td>
<td>1.76</td>
<td>0.008</td>
</tr>
<tr>
<td>3 µmol/g MoO$_4^{2-}$, 5 mM total sulfide</td>
<td>4$^c$</td>
<td>1.78</td>
<td>0.007</td>
</tr>
<tr>
<td>15 µmol/g MoS$_4^{2-}$, 0.1 mM total sulfide</td>
<td>1$^c$</td>
<td>1.77</td>
<td>0.003</td>
</tr>
<tr>
<td>5 µmol/g MoS$_4^{2-}$, 2 mM total sulfide</td>
<td>1$^c$</td>
<td>1.76</td>
<td>0.003</td>
</tr>
<tr>
<td>5 µmol/g MoS$_4^{2-}$, 5 mM total sulfide</td>
<td>0.1</td>
<td>1.77</td>
<td>0.003</td>
</tr>
</tbody>
</table>

(a): Determined by Cramer et al. (1978). Other cubanes have similar structures.
(b): Not detected.
(c): Fixed during fitting.
(d): Mo-Mo shell.
Figure 1. Absorption isotherms for MoO$_4^{2-}$ (a) and MoS$_4^{2-}$ (b) on 1 g/l FeS$_2$ as a function of pH.
Figure 2. One-site (a) and two-site (b) linearized Langmuir isotherm plots of $\text{MoO}_4^{2-}$ and $\text{MoS}_4^{2-}$ adsorption on 1 g/L FeS$_2$ at pH 7.
Figure 3. The adsorption envelopes for 50 μM MoO$_4^{2-}$ (a) and MoS$_4^{2-}$ (b) on 1 g/L FeS$_2$. 

% Mo sorbed

pH increasing
pH decreasing
Figure 4. Effect of ionic strength (I) on MoO$_4^{2-}$ and MoS$_4^{2-}$ adsorption on 1 g/L FeS$_2$ at pH 7.
Figure 5. Effect of sulfide addition on MoO$_4^{2-}$ and MoS$_4^{2-}$ adsorption on 1 g/L FeS$_2$ at pH 7.
Figure 6. Raw (a) and first-derivative (b) XANES spectra of 100 μM MoO$_4^{2-}$ adsorbed to FeS$_2$ at pH 9 under varying sulfide activities. The sulfide concentration, and surface loading are given.
Figure 7. Raw (a) and first-derivative (b) XANES spectra of 100 µM MoS$_4^{2-}$ adsorbed to FeS$_2$ at pH 9 under varying sulfide activities. The sulfide concentration, and surface loading are given.
Figure 8. The k-weighted $\chi(k)$ spectra (a) and corresponding RSF’s (b) of MoO$_4^{2-}$ and MoS$_4^{2-}$ adsorbed to FeS$_2$ at pH 9. The fits (dotted lines) of each spectrum use the fit parameters in Table 2.
Figure 9. Structural models of MoO$_4^{2-}$ (a) and MoS$_4^{2-}$ (b) adsorption to FeS$_2$. Molybdate forms a bidentate, mononuclear complex with an Fe polyhedron, while MoS$_4^{2-}$ forms a Mo-Fe-S cubane structure.
Chapter 6.

Seasonal Fluctuations in Zinc Speciation Within a Contaminated Wetland

ABSTRACT

The cycling of common sorbents such as metal (hydr)oxides, carbonates, and sulfides in redox-active environments influences the partitioning of associated trace elements such as zinc. Consequently, fluctuations in redox status may in part determine the availability and mobility of Zn and other trace elements. This research examines the changes in Zn speciation in a contaminated wetland soil that undergoes seasonal flooding. X-ray absorption spectroscopy (XAS) was employed to identify and quantify Zn species from soil cores collected over a one-year cycle as a function of water-depth, location, and soil-depth. Zinc associated with (hydr)oxide phases in dry, oxidized soils, and with sulfides and carbonates in flooded systems. An increase in water level was accompanied by a reversible change in Zn fractionation towards ZnS and ZnCO$_3$. However, a small, recalcitrant fraction of Zn associated with (hydr)oxides remained even when the soils were exposed to highly reducing conditions. Water-depth and redox potential were the most important factors in determining Zn speciation, although spatial variation was also important. These data indicate that zinc sorption is a dynamic process influenced by environmental changes.
INTRODUCTION

Zinc is a ubiquitous contaminant that imposes a hazard to a host of plants and animals—many aquatic organisms are particularly sensitive to this element. Although it is not a redox active species within soil or aquatic environments, oxidation and reduction reactions may nevertheless affect zinc partitioning. Retention of zinc, as well as other redox-stable cations such as cadmium, can be modified by changes in substrate chemistry. Zinc sorbs strongly to iron (Benjamin and Leckie, 1981; Stahl and James, 1991a) and manganese (hydr)oxides (Loganathan and Burau, 1973; Zasoski and Burau, 1988; Stahl and James, 1991b) in aerated systems, and to sulfide (Kornicker and Morse, 1991; Huerta-Diaz and Tessier, 1998) and carbonate (Morse, 1986; Zachara et al., 1988, 1991) phases in anoxic environments. Thus, changes in redox status may shift Zn partitioning. For example, reductive dissolution of iron and manganese (hydr)oxides under suboxic conditions releases Zn into the aqueous phase; persistence of sub- or anoxic conditions may then lead to a re-partitioning of Zn into sulfide or carbonate solids. However, slow transformation rates and fluctuation in conditions may alter these predicted phase transformations.

Appreciating transformation rates of zinc partitioning is needed to predict its behavior and risk within natural environments. Model laboratory studies provide descriptions of zinc adsorption on an array of environmental solids and the solubility of neat compounds. Extending these results to natural environments provides a basis for describing zinc partitioning. However, zinc dynamics cannot be predicted with such information because changes in substrate have yet to be accounted for in the model systems. Thus, zinc speciation and partitioning within natural, dynamic environments
needs to further be examined. Unfortunately, the complexity of natural systems is not easily dealt with when determining Zn speciation. Selective extractions have been used to empirically define mineral-associated fractions (e.g., Tessier and Campbell, 1979; Shuman, 1985). While selective extractions provide a useful starting point to study Zn, or other trace element, partitioning, more direct means of analysis may provide additional, and important information.

X-ray absorption spectroscopy (XAS) is an attractive method of determining the local structure of trace metals in situ and non-destructively within soil (Fendorf et al., 1994; Henderson et al., 1995; Schulze and Bertsch 1995; Conradson, 1998). Models of Zn sorption (Hesterberg et al., 1997; O’Day et al., 1998), as well as other divalent cations (e.g., Manceau et al., 1996), have been refined with XAS; they have chronicled the importance of discrete Zn solids such as Zn hydroxides and sulfides to Zn sequestration.

In this study, XAS was used to determine changes in Zn partitioning within a seasonally saturated, mining-impacted wetland. A quantitative method was developed to determine the fractions of zinc oxide, zinc sorbed on iron (hydr)oxides, zinc sulfides, and zinc carbonates in the soil. Zinc speciation was correlated to soil redox status and the depth of the overlying water column. The response of zinc speciation to the seasonal appearance of an overlying water column was also examined to determine the extent of kinetic control on Zn speciation in the environment.

EXPERIMENTAL SECTION

Sample Collection and Handling: Wetland soil samples were collected from a contaminated riparian wetland near the Coeur d’Alene River in northern Idaho (La Force
et al., 2000a). Three principal sites were chosen for detailed study that ranged from nearly dry to submerged throughout the year. Duplicate cores were taken at each site periodically using a 3.0 cm diameter piston-coring device; additional cores were taken from other wetland locations. Cores were stored upright at 4°C and kept under nitrogen after sampling to minimize sample mixing and sample oxidation (La Force et al., 2000b). Once in the laboratory, the cores were sectioned into 0-5 cm and 5-10 cm depths in an N₂-purged glovebox and homogenized. These wet soil pastes were mounted in 3x5x40 mm acrylic sample holders, sealed with Kapton film to prevent oxidation and moisture loss, and analyzed by XAS. Soil cores were collected and prepared immediately prior to analysis and kept refrigerated to minimize transformations during storage and sample collection. Neither Fe nor Mn oxidation state transformations were detected using x-ray absorption spectroscopy during sample handling. Sample pH and Eₘ were measured for the intact cores where possible using standard electrodes immediately following extraction.

EXAFS Spectroscopy: EXAFS spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamlines 4-2 and 4-3. The storage ring operated at an energy of 3.0 GeV and at current between 50 and 100 mA. Spectra were collected about the Zn K-edge (-200 to +1000 eV) using a Si(220) double-crystal monochromator with an unfocused beam detuned approximately 50% to reject higher-order harmonic frequencies. Incident and transmitted intensities were measured with 15 cm N₂-filled ionization chambers; sample fluorescence was monitored with a multi-element Ge detector (Cramer et al., 1988) oriented 45 degrees off the sample and orthogonal to the incident radiation.
Internal energy calibration of each spectrum was achieved with a Zn foil placed between the second and third ionization chambers; its inflection edge was set to 11,659 eV.

**Data Analysis:** XAS data were analyzed using EXAFSPAK (Graham George, SSRL). The background was subtracted from averaged spectra using a polynomial fit and their absorbance was normalized to unity. A cubic spline function was fit to four points in the spectrum that followed the envelope of the decaying EXAFS, or \(\chi(k)\), spectrum, and the photon energy was converted to wavevectors using an \(E_0\) of 11,685 eV. The \(\chi(k)\) spectrum was then weighted by \(k^3\) in order to provide equal amplitude throughout the entire \(k\)-range. The \(k\)-weighted \(\chi(k)\) spectrum was Fourier-transformed without smoothing to produce a radial structure function (RSF) using a \(k\)-range of approximately 3 to 12 Å\(^{-1}\). The RSF was then sectioned to isolate the contributions of each atomic shell, and these individual shells back transformed into isolated \(\chi(k)\) functions representing each shell. The local coordination environment of Zn, including the type (Z), coordination number (CN), distance (R), and the Debye-Waller factor (\(\sigma^2\)) of neighboring atoms, was then determined by fitting the experimental spectrum using theoretical phase and amplitude functions (Rehr et al., 1991; Zabinsky et al., 1995) and an amplitude correction factor of 0.9. Known coordination numbers and interatomic distances were used for reference compounds. Final fits used raw, unsmoothed \(k^3\chi(k)\) data. The accuracy of the fits was estimated using the \(\chi^2\) statistic, for which smaller values correspond with the best fits. All fits had \(\chi^2\) values of about 2.5 with unsmoothed \(\chi(k)\) spectra and approximately 0.7 with smoothed data. By comparison with model compounds, the interatomic distances was accurate within 0.02 Å and the coordination...
number within 20% for the first shell with less accuracy for more distant shells. Elements of different atomic number ($\Delta Z > 2$) can be distinguished based on phase and amplitude functions.

Several Zn standards, including ZnS, ZnO, and ZnCO$_3$, were analyzed for comparison with natural samples and to validate the theoretical parameters used in XAS fitting. In addition, Zn-substituted CaCO$_3$ was analyzed to determine whether this solid solution could be differentiated from ZnCO$_3$. Zn-substituted calcite was synthesized according to the procedure of Reddy and Nancollas (Reddy and Nancollas, 1971), replacing 0.01 mole fraction of the calcium with Zn.

**Selective Sequential Extraction:** Selective sequential extractions are commonly used to provide information about the chemical speciation of associated trace metals (Tessier et al., 1979; Shuman, 1985). Accordingly, sequential extractions were used to identify Zn associations in selected samples to confirm speciation determined by XAS. These samples (12 replicates each) were extracted according to the procedure of La Force et al. (La Force et al., 2000a). Briefly, a 1 M MgCl$_2$ solution reacted with 2 g solids for 1 h was used to remove the soluble Zn species. Secondly, the carbonate phases were extracted with 1 M sodium acetate/acetic acid for 5 h. The sample was then split for determination of non-crystalline oxides and acid-volatile sulfides (AVS) fractions. Non-crystalline (hydr)oxides and AVS are extracted with 1 M HCl in one subsample, and non-crystalline (hydr)oxides were extracted with ammonium oxalate (AOD) in the other. Zn associated with AVS was then determined by difference between the HCl-extractable and AOD-extractable fractions. Sodium hypochlorite was reacted with residual solids from
the HCl extraction at 95 degrees C to remove organic matter-associated Zn. A heated hydroxyl-amine/acetic acid extraction dissolved the crystalline (hydro)oxides. Residual silicates were removed by reflux with 10M HF. Finally, pyritic sulfides were extracted using nitric acid. It should be noted that sequential extractions depend on the specific and complete extraction of a target phase, and are at best operationally defined mineralogical fractions. Despite limitations caused by inefficient or non-specific extractions, selective sequential extractions provide a useful, albeit approximate, method of quantifying Zn speciation in soils.

RESULTS AND DISCUSSION

Site Characteristics: Wetland soil samples were composed of a mixture of quartz and feldspars with some residual mine tailings minerals, including pyrite (Table 1). The total Zn content of the soils was approximately 1900 mg kg⁻¹ (determined by total digestion). Additionally, secondary Fe and Mn phase concentrations vary with site and season (20). Water levels varied substantially during the year within the wetland. During the summer, only a portion of the wetland was submerged; however, standing water up to 150 cm deep covered the wetland during winter and spring. Temperature oscillation accompanied this water level variation, with the temperature of the sediment-water interface ranging from 20°C in summer to 6°C in winter. The pH ranged from 5.6 to 6.6, generally being most acidic in dry samples and most alkaline under standing water. The redox potential (E_h) was not determined for dry samples; wet samples had an E_h of about +200 mV when soils were saturated but not ponded, and as low as −200 mV when ponded (>100 cm water column depth), although E_h was variable for any given water depth.
Model Compounds: The standard compounds of Zn used in this study contain significant variation in first-shell coordination environment that is reflected in the bond lengths and coordination numbers of the XAS data (Table 1). In ZnS, Zn is coordinated to 4 sulfur atoms at a distance of 2.33 Å, significantly longer than Zn-O bond lengths that range between 1.96 Å in ZnO and Fe$_2$ZnO$_4$ (tetrahedral Zn coordination) to 2.11 Å in ZnCO$_3$ (octahedral Zn coordination). Organically bound Zn species have a similar first coordination shell to inorganic species (e.g., Xia et al., 1997; Salt et al., 1999) and thus second-nearest neighbor information is required to discriminate between them. Zinc (hydr)oxides exhibit significant second-shell contributions due to the effective scattering of the heavy Zn atom, while organically complexed Zn exhibits only weak contributions in the second-shell. Thus, each Zn species could be identified by their unique set of interatomic distances.

Identification of Principal Zn Species in Soils: These wetland soils undergo seasonal redox transformations typical of many palustrine emergent wetlands that may alter Zn speciation. In fall, the soil in much of the wetland is dry and warm, leading to the effective oxidation of the material. Snow and rain saturates the soil in winter and spring; this saturation coupled with biological activity leads to reducing conditions. Several Zn compounds are likely present under these environmental conditions; Zn solids such as ZnO, ZnS and ZnCO$_3$ are all possible species within the wetland. The hydroxide and oxide phases are most stable under oxic conditions common in well-drained soils, while the sulfide and carbonate solids are most stable under anoxic conditions where sulfur is
reduced and gas exchange with the atmosphere is impeded. Additionally, Zn may adsorb on hydroxides, organic matter, or be incorporated into oxides or carbonates. The presence of these Zn-containing phases were evaluated by comparing the bond distances found in the soil samples with those of the model compounds.

Three distinct coordination environments in the first shell (Fig. 1) dominate the local structure of Zn in these wetland soils, Zn-O shells at 2.0 and 2.1 Å, and a Zn-S shell at 2.33 Å. Samples with a 2.0 Å Zn-O distance, $d$(Zn-O), also contained a second shell feature attributed to Zn-Zn or Zn-Fe at 3.1 Å. As water depth increased to 50 cm, the coordination number to oxygen at this short distance decreased from approximately 1.5 to 0, indicating that the fraction of this species was greatest under oxic conditions and decreased with the onset of reduction. Such bond distances are consistent with ZnO (Table 2; Abrahams and Bernstein, 1969). Adsorbed Zn species exhibit a variable structure that may also contain similar interatomic distances and thus cannot be ruled out based on this spectral data (O’Day et al., 1998). Other phases that have similar $d$(Zn-O), such as Zn$_2$SiO$_4$, Zn$_5$(OH)$_6$(CO$_3$)$_2$, and ZnFe$_2$O$_4$, can be disregarded based on their distinct second shell environments. The Zn$_2$SiO$_4$ lacks a Fe or Zn second shell entirely (29), while Zn$_5$(OH)$_6$(CO$_3$)$_2$, and ZnFe$_2$O$_4$ both have $d$(Zn-Zn/Fe) significantly longer than observed in these samples (Table 2; Ghose, 1964; Koenig and Chol, 1968)

Under flooded conditions, a Zn-S shell at 2.33 Å is noted that is indicative of ZnS (Fig. 1, Table 2). Zinc sulfide second-shells, with a $d$(Zn-Zn) of 3.8 Å, are also observed in some of the samples (Kisi and Elcombe, 1989). Both ZnS polymorphs (wurtzite and sphalerite) have similar local structures; thus, we are unable to distinguish between them using these data. Zinc sulfide is also an important Zn phase in other mine-impacted
fluvial (O’Day et al., 1998) and estuarine sediments (Lee and Kittrick, 1984). Sulfide minerals commonly form in anoxic, sulfidic environment; thus, it is not surprising that ZnS was observed. Zinc may also be complexed by other S-containing ligands such as proteins and organic sulfides (Clark-Baldwin et al., 1998). However, the organic complexes lack second-shell Zn spectral features and thus are not consistent with our analyses of the unknowns. Additionally, insufficient organic thiols are present in these soils to explain a large fraction of Zn sorption. These wetland soils contain approximately 10% organic matter (Hansel et al., 2001), which typically contains a small quantity of S. Much of this organic sulfur is also oxidized sufficiently to prevent direct coupling of Zn to S (Morra et al., 1997; Xia et al., 1998).

In flooded soil systems, the average CN of the 2.1 Å Zn-O shell was approximately 2.5, decreasing to 0 at a water depth of ~50 cm, and then increasing to 3 at water depths greater than 75 cm (Fig. 1). This bimodal distribution suggests the presence of two distinct Zn species with similar first-shell Zn-O shells. To test this premise, we examined their second coordination sphere (Fig. 2). The Zn local structure in soils under little or no standing water contained second-shells of about 1 Zn or Fe at a distance of 3.1 Å. The presence of an iron shell with low CN coupled with the short d(Zn-Fe/Zn) suggests that Zn in this system is adsorbed to an iron (hydr)oxide or within a hydroxide (Christiansen, 1969). Zn sorbed on hydrous ferric oxide, commonly encountered in oxic soils, has a similar coordination environment (Table 2; O’Day et al., 1998).

In contrast, samples with a d(Zn-O) of 2.1 Å contained a d(Zn-Fe/Zn) of 3.68-3.78 Å when under >75 cm water (Fig. 2). These bond lengths correspond with smithsonite, ZnCO₃ (Effenberger et al., 1981). Evidence of Zn-substituted calcite was
not present—the $d$(Zn-Fe/Zn) of about 3.7 Å observed is shorter and distinct from the 4.02 Å $d$(Zn-Ca) found in Zn-substituted calcite (Table 1, Reeder et al., 1999). Typically, Zn sorption on calcite results in the replacement of Ca atoms at the surface and the subsequent formation of discrete ZnCO$_3$ domains (Zachara et al., 1988, 1991; Papadopoulos and Rowell, 1989). ZnCO$_3$ also may have formed directly through precipitation with bicarbonate.

**Quantification Method:** The XAS data suggests that 4 primary Zn species are identifiable within this wetland system: ZnO, ZnCO$_3$, Zn sorbed to a (hydr)oxide, and ZnS, although others may be present. Multiple methods have been developed to determine the fractions of various species in complex mixtures, including approaches that use coordination numbers (e.g. Boyanov et al., 1996; Nishi et al., 1998) and linear combinations of EXAFS and XANES spectra (e.g. Foster et al., 1998; Ressler et al., 2000). We determine the fractions of Zn species using the first-shell coordination numbers. This method can determine species with different crystallinity and structures. In contrast, linear combinations of EXAFS spectra are largely influenced by small differences in structure. Furthermore, the accuracy of the shell fitting approach does not require a comprehensive spectral library; shell fitting depends only on knowledge of the local structural environment.

The first-shell coordination numbers were used to calculate the fractions of each Zn species. The fraction ($\chi$) of the $i^{th}$ species was determined with the ratio of the fit coordination number ($CN_i$) to the model compound ($CN_s$):

$$\chi_i = \frac{CN_i}{CN_s} \times \frac{1}{N}$$

[1]
where $N$ is a normalization constant used to make all fractions add to unity.

$$N = \sum_{i=1}^{n} \frac{CN_{z_{n}}}{CN_{s}} = \frac{CN_{ZnO}}{4} + \frac{CN_{ZnCO3}}{6} + \frac{CN_{Zn(\text{hydr})oxide}}{4} + \frac{CN_{ZnS}}{4}$$  \[2\]

The value of $N$ was typically near one, although it varied from 0.65 to 1.3. Most variation in $N$ could be attributed to different values of $\sigma^2$ used in the EXAFS structural optimization; normalization reduced the effect of variation in the Debye-Waller factor on the fractions of Zn species determined using this method.

This fitting method does, however, involve several simplifications. The ZnCO$_3$ and Zn sorbed on (hydr)oxides fractions could not be quantified concurrently because the same Zn-O shell was used for quantifying both species. However, these species could be differentiated based on environmental conditions. Under dry or shallow water levels (oxic conditions), EXAFS data indicate that Zn is sorbed to (hydr)oxide phases. Therefore, all Zn with a 2.1 Å Zn-O bond length was assumed to be present as Zn sorbed on (hydr)oxide for water depths less than 50 cm. At water depths greater than 50 cm, all Zn coordinated to O at 2.1 Å was assumed to be ZnCO$_3$. While both phases may occur concurrently in some samples, they can be divided into two discrete groups because the bimodal occurrence of the 2.1 Å Zn-O shell indicates that the two species are largely exclusive (Fig. 1).

An additional simplification involved the combination of ZnO and Zn sorbed to (hydr)oxides into one fraction, the ZnO/sorbed fraction. Both ZnO and Zn sorbed to (hydr)oxides are found predominantly in oxic environments and their similar first-shell coordination environments often cannot be effectively resolved using XAS spectroscopy due to their similar $d(Zn-O)$ (Fig. 3). Additionally, the fit distances of the ZnO fraction may be attributed in part to hydroxides (O’Day et al., 1998). Finally, the errors
associated with shell fitting caused by the fitting of rather inaccurate coordination number should be acknowledged. Despite these limitations, shell fitting provides a favorable method for Zn speciation.

**Seasonal Variation in Zn Speciation**: Seasonal effects on Zn speciation were evaluated by repeatedly analyzing soils from each of the three sites over one year. Figure 3 contains example weighted $\chi(k)$ spectra and RSF’s for three locations within the wetland ranging from predominately dry to permanently flooded. Figure 4 shows the Zn fractions that are present in these samples as a function of collection time. In general, these spectra indicate a change in the first coordination sphere between the dry summer months and the wet winter and spring periods. The bond length of this shell typically increases as conditions shift from oxic to anoxic, indicating the gradual change in Zn fractionation towards more reduced phases such as carbonates or sulfides.

The driest location contained large shifts in Zn speciation; a small increase in water levels associated with spring flooding results in the conversion of the ZnO/sorbed fraction to the ZnS fraction (Fig. 4A). Similar fluctuations in Zn species were detected in samples from a portion of the wetland typically covered by about 30 cm water (Fig. 4B). At this site, a gradual increase in water level in winter was accompanied by a small increase in the ZnS fraction and a decrease in the ZnO/sorbed fraction. While sulfides formed the dominant Zn fraction at all sample dates, the June 24 sampling date exhibited an increase in (hydr)oxide associated Zn that correlates to a decrease in water depth during that period.
The largest changes in Zn speciation occurred in an area of the wetland covered by about 50 cm water (Fig. 4C). The ZnO/sorbed fraction decreased markedly with an increase in water depth resulting from the spring run-off. Both ZnS and ZnCO₃ were present in appreciable quantities; however, the proportion of ZnS decreased while ZnCO₃ content increased with water level during the spring. The decrease in the oxide-sorbed Zn is expected as conditions become more reduced; however, the relationship between the ZnS and ZnCO₃ fractions was not easily explained with water content.

Thus, it is apparent that Zn fractionation responds readily to changes in environmental conditions. While thermodynamic considerations describe the conditions under which ZnO/sorbed, ZnS, and ZnCO₃ occur, the kinetics of these processes are not well understood. The majority of Zn solid phases are assumed to be kinetically stable due to their low solubility (Morse, 1986; Engler and Patrick 1975; Simpson et al., 2000). For example, authigenic zinc sulfide found in oxic sediments from the Tri-State mining district undergoes incomplete oxidation (O’Day et al., 1998; Carroll et al., 1998). However, our results demonstrate that Zn speciation can respond rapidly to changes in redox status. ZnS in this system formed through secondary (authigenic) processes, while it was of primary origin in the Tri-State mining district (O’Day et al., 1998; Carroll et al., 1998).

Pure ZnO and ZnCO₃ are resistant to oxidation and reduction reactions because they do not contain species that undergo redox transformations. However, they do respond to changes in redox status. The rapid response of sorbed species to changes in environmental conditions has been documented in other flooded soils and sediments (Masscheleyn et al., 1992; Tokunaga wt al., 1996) and is often attributed to microbial
transformations (Matsunaga et al., 1993; Thamdrup et al., 1994). Microbial processes may similarly influence changes in Zn speciation within this wetland, either through direct oxidation of ZnS or the indirect dissolution of oxide (such as Fe oxides) and carbonate phases.

Pure Zn solid phases such as ZnO were found to dominate the speciation of Zn here and elsewhere (O’Day et al., 1998). However, solutions were undersaturated with respect to pure ZnO in our studies. Isomorphous substitution lowers the solubility product significantly (Farley et al., 1985; Prieto et al., 1997); Fe$^{2+}$ and Mn$^{2+}$ substitution may therefore explain the rapid conversion of Zn solids in response to environmental changes. Unfortunately, it is difficult to quantify the extent of this substitution. These explanations, though not conclusive, may explain why ZnO is observed here.

**Factors That Affect Zn Speciation:** Many factors, including water depth (redox status), spatial and temporal variation may influence Zn speciation. The water depth and the associated redox status were used to discriminate between the different Zn phases. To test the importance of water depth on Zn speciation throughout the entire wetland, the effect of these two parameters was evaluated independent of the other environmental factors, such as spatial and seasonal variation. Zinc speciation is strongly correlated with water depth (Fig. 5). In dry (oxidized) areas, nearly all Zn is sorbed on (hydr)oxides or present as a discrete ZnO phase. ZnS and ZnCO$_3$ form in response to the lowered reduction potential associated with flooding and subsequent elevated sulfide and carbonate concentrations (Stumm and Morgan, 1996). Under shallow water (10-50 cm water column depth), the $E_{h}$ was generally near +100 mV—an intermediate, suboxic
redox status. Therefore, soils under these shallow waters contained significant fractions of ZnO/sorbed and ZnS (Fig. 5). At >50 cm water column depths, the soil becomes sufficiently reduced ($E_h < -100 \text{ mV}$) and leads to the conversion of Zn to ZnS (Fig. 5). Significant quantities of ZnCO$_3$ also begin to appear in soils under deeply ponded water (>60 cm depth), leading to a decrease in the ZnS fraction. Residual ZnO/sorbed also comprises up to 15% of the total Zn, even when the redox potential decreased to –200 mV, indicating that a portion of oxidized Zn species is recalcitrant and resistant to reduction.

Spatial heterogeneity and soil-depth may also influence Zn speciation in wetlands. To test these effects, duplicate soil cores were collected from several sites within the wetland and both the 0-5 and 5-10 cm sections were examined by XAS. Little variation was observed between the duplicate cores or the two core sections, suggesting that Zn speciation is similar within a given section of the wetland (Table 3). However, cores collected at different sites did contain different Zn species, even when their water levels were similar. Despite these differences, Zn speciation was still largely determined by the redox stability of each phase: either ZnO or adsorbed Zn on (hydr)oxides comprised the majority of Zn in oxic soil cores, while ZnS or ZnCO$_3$ dominated Zn speciation in anoxic environments (Table 3). Thus, the water depth and redox status were the most important variables in determining Zn speciation in this wetland.

**Comparison of XAS Quantitation and Selective Extraction:** Selective sequential extractions are a traditional method of determining trace metal associations in soils and sediments. Despite several caveats (e.g., Belzile et al., 1989; Davidson et al., 1994;
Stumm and Morgan, 1996; Cooper and Morse, 1998), these methods provide a means of corroborating the Zn partitioning found by XAS in these wetland samples. Additionally, they offer the opportunity to examine Zn partitioning in many phases that cannot be determined concurrently using XAS alone. Four principal Zn phases were identified with selective extractions: Zn associated with (1) non-crystalline oxides, (2) crystalline oxides, (3) carbonates, and (4) acid-volatile sulfides (Table 4). Importantly, these phases are similar to those identified using XAS, although extractions can differentiate somewhat between non-crystalline oxides and more crystalline forms. Sequential extractions also show the dynamic changes in Zn speciation throughout the seasons observed by XAS (Table 4). The fraction of Zn associated with (hydr)oxides peaked during the summer, while Zn in carbonate fractions was highest in spring and early summer when water levels were greatest. Sulfide-associated Zn also increased with water depth for the shallow, ponded site, although this trend was not observed for the flooded soil. The changes in speciation determined by sequential extractions were smaller than those determined by XAS, possibly due to incomplete or non-specific extractions (Davidson et al. 1994). Zinc associated with organic matter and silicates, both ruled out by XAS, comprised only a minor fraction of the total Zn in the system. Some Zn was exchangeable and was not determined by XAS; however, it is unclear with which phase exchangeable Zn is associated. The similarity in Zn speciation determined by XAS and extractions indicate the utility of XAS to determine Zn partitioning in these wetlands.

Four principle phases, ZnO, Zn on (hydr)oxide, ZnCO$_3$ and ZnS were found in a seasonally flooded wetland using XAS. Under aerated conditions, Zn sorbs preferentially to (hydr)oxides. Reducing conditions, promoted by the presence of standing water, favor
the formation of ZnCO$_3$ and ZnS. These phase transformations occurred readily in this environment. Thus, zinc partitioning in the environment is a dynamic, and largely reversible, process in which Zn species form in response to changing conditions. Owing to the lability of the observed Zn phases, both thermodynamic and kinetic factors need to be considered when evaluating its fate.
REFERENCES


Figures and Tables

**Table 1.** Selected characteristics of the wetland soils used in this study.

<table>
<thead>
<tr>
<th>Sampling Date</th>
<th>pH</th>
<th>Organic Matter percent</th>
<th>Fe HCl</th>
<th>HH</th>
<th>Mn HCl</th>
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<td>10.2</td>
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<td>±43</td>
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<td>±31</td>
<td>±23</td>
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</table>

† Determined using loss on ignition.
‡ Extracted using HCl, which targets both non-crystalline oxide and acid volatile sulfide phases.
§ Extracted using hydroxylamine hydrochloride, which targets crystalline oxide phases.
¥ Quartz and feldspars were analyzed by x-ray diffraction of the bulk soil, with pyrite identified by scanning electron microscopy.
Table 2. The local structures of various Zn model compounds from crystallography (XTL) and determined with x-ray absorption spectroscopy (XAS).

<table>
<thead>
<tr>
<th>Compound</th>
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<td></td>
<td></td>
<td>XT XAS</td>
<td>XT XAS ±σ² in Å²</td>
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<td>3.29 ± 3.50</td>
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<tr>
<td>ZnCO₃</td>
<td>Zn-O</td>
<td>6</td>
<td>5.87</td>
<td>2.11 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>Zn-C</td>
<td>6</td>
<td>6.12</td>
<td>2.98 ± 0.004</td>
</tr>
<tr>
<td>Zn₂SiO₄</td>
<td>Zn-O</td>
<td>4</td>
<td>5.03</td>
<td>1.96 ± 0.004</td>
</tr>
<tr>
<td></td>
<td>Zn-Si</td>
<td>4</td>
<td>10.6</td>
<td>3.1-3.3 ± 3.10 ± 0.004</td>
</tr>
<tr>
<td>Fe₂ZnO₄</td>
<td>Zn-O</td>
<td>4</td>
<td>3.55</td>
<td>1.99 ± 1.98</td>
</tr>
<tr>
<td></td>
<td>Zn-C</td>
<td>6</td>
<td>3.08</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Zn-Zn</td>
<td>2</td>
<td>6.12</td>
<td>3.18,3.55 ± 3.67,3.69 ± 4.07</td>
</tr>
<tr>
<td>Zn₂(OH)₆(CO₃)₂</td>
<td>Zn-O</td>
<td>6</td>
<td>6.46</td>
<td>2.36 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>Zn-C</td>
<td>6</td>
<td>3.21</td>
<td>-</td>
</tr>
<tr>
<td>Zn in CaCO₃</td>
<td>Zn-O</td>
<td>6</td>
<td>6.46</td>
<td>2.36 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>Zn-C</td>
<td>6</td>
<td>3.08</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Zn-Zn</td>
<td>2</td>
<td>6.12</td>
<td>3.18,3.55 ± 3.67,3.69 ± 4.07</td>
</tr>
<tr>
<td>Zn in CaCO₃ (0.01 mole fraction)</td>
<td>Zn-C</td>
<td>6</td>
<td>3.08</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Zn-Ca</td>
<td>6</td>
<td>6.57</td>
<td>4.04 ± 4.02 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>Zn-Zn</td>
<td>2</td>
<td>6.12</td>
<td>3.18,3.55 ± 3.67,3.69 ± 4.07</td>
</tr>
<tr>
<td>Zn-humate</td>
<td>Zn-O</td>
<td>6</td>
<td>6.46</td>
<td>2.36 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>Zn-C</td>
<td>-</td>
<td>2.08</td>
<td>-</td>
</tr>
<tr>
<td>Zn-thiolate in protein</td>
<td>Zn-S</td>
<td>-</td>
<td>2.30</td>
<td>-</td>
</tr>
<tr>
<td>Zn-histidine</td>
<td>Zn-O</td>
<td>-</td>
<td>1.1</td>
<td>2.08 ± 2.08</td>
</tr>
<tr>
<td></td>
<td>Zn-N</td>
<td>-</td>
<td>3.8</td>
<td>2.23 ± 2.23</td>
</tr>
<tr>
<td>Zn on HFO</td>
<td>Zn-O</td>
<td>-</td>
<td>2</td>
<td>1.92 ± 0.0042</td>
</tr>
<tr>
<td></td>
<td>Zn-Zn</td>
<td>-</td>
<td>2</td>
<td>2.04 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>Zn-Fe</td>
<td>-</td>
<td>1.2</td>
<td>3.54 ± 0.004</td>
</tr>
<tr>
<td>ZnS</td>
<td>Zn-S</td>
<td>4</td>
<td>3.83</td>
<td>2.34 ± 5.35 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>Zn-Zn</td>
<td>12</td>
<td>8.06</td>
<td>3.82 ± 3.85 ± 0.008</td>
</tr>
</tbody>
</table>

*: Not available. †: Based on calcite crystallography.
Table 3. Zn fractionation and water-depths for selected soil core sections.

<table>
<thead>
<tr>
<th>Sample water depth (cm)</th>
<th>Core Section (cm)</th>
<th>%ZnO</th>
<th>% sorbed Zn on hydroxide</th>
<th>%ZnS</th>
<th>%ZnCO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0-5 cm</td>
<td>0 ± 0†</td>
<td>97 ± 2</td>
<td>3 ± 2</td>
<td>0 ± 0</td>
</tr>
<tr>
<td>0</td>
<td>5-10 cm</td>
<td>0 ± 0</td>
<td>96 ± 2</td>
<td>4 ± 2</td>
<td>0 ± 0</td>
</tr>
<tr>
<td>36</td>
<td>0-5 cm</td>
<td>0 ± 0</td>
<td>38 ± 2</td>
<td>62 ± 2</td>
<td>0 ± 0</td>
</tr>
<tr>
<td>36</td>
<td>5-10 cm</td>
<td>0 ± 0</td>
<td>36 ± 4</td>
<td>64 ± 4</td>
<td>0 ± 0</td>
</tr>
<tr>
<td>39</td>
<td>0-5 cm</td>
<td>43 ± 2</td>
<td>0 ± 0</td>
<td>57 ± 3</td>
<td>0 ± 0</td>
</tr>
<tr>
<td>39</td>
<td>5-10 cm</td>
<td>43 ± 5</td>
<td>0 ± 0</td>
<td>57 ± 5</td>
<td>0 ± 0</td>
</tr>
<tr>
<td>89</td>
<td>0-5 cm</td>
<td>0</td>
<td>0</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>89</td>
<td>5-10 cm</td>
<td>0</td>
<td>0</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>105</td>
<td>0-5 cm</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>88</td>
</tr>
<tr>
<td>105</td>
<td>5-10 cm</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>90</td>
</tr>
</tbody>
</table>

†Each value represents the average of duplicate cores ± the standard deviation. Where single values are given, only one core was analyzed.
Table 4. Zn speciation determined by selective sequential extraction for both shallow, ponded and flooded wetland sites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Date</th>
<th>Water Depth</th>
<th>MgCl₂ (Exchangeable)</th>
<th>Acetic Acid (Carbonates)</th>
<th>AOD(^\dagger) (Non-Crystalline Oxides)</th>
<th>HCl-AOD(^\dagger) (Acid-volatile sulfides)</th>
<th>NaOCl (Organic Matter)</th>
<th>HF (Silicates)</th>
<th>HNO(_3) (Pyritic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shallow Ponded</td>
<td>25 Jan</td>
<td>21</td>
<td>318 ±31(^\dagger)</td>
<td>99 ±9</td>
<td>205 ±20</td>
<td>97 ±12</td>
<td>121 ±12</td>
<td>80 ±8</td>
<td>1 ±0.1</td>
</tr>
<tr>
<td></td>
<td>5 Mar</td>
<td>33</td>
<td>3 ±0.3</td>
<td>30 ±3</td>
<td>447 ±46</td>
<td>108 ±11</td>
<td>115 ±13</td>
<td>46 ±5</td>
<td>2 ±0.2</td>
</tr>
<tr>
<td></td>
<td>13 May</td>
<td>39</td>
<td>1.3 ±0.1</td>
<td>64 ±7</td>
<td>435 ±46</td>
<td>143 ±15</td>
<td>34 ±4</td>
<td>113 ±5</td>
<td>4 ±0.4</td>
</tr>
<tr>
<td></td>
<td>8 July</td>
<td>46</td>
<td>1.8 ±0.1</td>
<td>218 ±15</td>
<td>604 ±42</td>
<td>55 ±12</td>
<td>365 ±18</td>
<td>35 ±1</td>
<td>1 ±0.4</td>
</tr>
<tr>
<td></td>
<td>15 Sept</td>
<td>0</td>
<td>475 ±37</td>
<td>200 ±16</td>
<td>100 ±782</td>
<td>63 ±5</td>
<td>242 ±19</td>
<td>65 ±2</td>
<td>2 ±0.1</td>
</tr>
<tr>
<td>Flooded</td>
<td>25 Jan</td>
<td>44</td>
<td>198 ±17</td>
<td>145 ±12</td>
<td>302 ±26</td>
<td>215 ±18</td>
<td>136 ±11</td>
<td>73 ±6</td>
<td>1.5 ±0.1</td>
</tr>
<tr>
<td></td>
<td>5 Mar</td>
<td>54</td>
<td>5 ±0.4</td>
<td>156 ±11</td>
<td>545 ±40</td>
<td>245 ±18</td>
<td>147 ±7</td>
<td>95 ±7</td>
<td>176 ±2</td>
</tr>
<tr>
<td></td>
<td>13 May</td>
<td>75</td>
<td>9 ±0.8</td>
<td>236 ±20</td>
<td>352 ±30</td>
<td>237 ±20</td>
<td>191 ±16</td>
<td>45 ±4</td>
<td>118 ±3</td>
</tr>
<tr>
<td></td>
<td>8 July</td>
<td>25</td>
<td>11 ±0.7</td>
<td>334 ±21</td>
<td>507 ±32</td>
<td>339 ±21</td>
<td>101 ±6</td>
<td>254 ±6</td>
<td>40 ±1</td>
</tr>
<tr>
<td></td>
<td>15 Sept</td>
<td>12</td>
<td>0.1 ±0.1</td>
<td>90 ±5</td>
<td>669 ±36</td>
<td>573 ±31</td>
<td>236 ±13</td>
<td>72 ±4</td>
<td>2 ±0.1</td>
</tr>
</tbody>
</table>

\(^\dagger\) Ammonium oxalate extraction. \(^\ddagger\) Hydroxylamine-hydrochloride extraction. \(^\$\) This AVS fraction is determined by difference between the HCl extraction and the AOD extraction. \(\¥\) All values are the average of 12 replicates ± the standard deviation.
Figure 1. Changes in the first-shell Zn coordination number and bond length as a function of water depth. Each point is the average coordination number of data from at least two samples of similar water depth regardless of position in the wetland or sampling date. Three principal coordination environments were found, Zn-O at distances of approximately 2.0 and 2.1 Å, and Zn-S bonds at 2.33 Å.
Figure 2. The second coordination sphere of Zn. For clarity, only data with Zn-O distances near 2.09 Å with distinguishable second-shells are included. At shallow water depths, second-shell data indicates that a (hydr)oxide phase is present, while a carbonate phase is present at higher water depths.

![Graph showing d(Zn-O) and Water Depth (cm)]
Figure 3. Weighted $\chi(k)$ spectra and RSF’s of samples collected from (A) an aerated wetland location, (B) a shallow, ponded location (average water depth of 30 cm), and (C) a flooded region of the wetland (~50 cm water).
Figure 4. Zn fractionation and water depths for three wetland locations: (A) within an aerated wetland location, (B) within a shallow, ponded region (average water depth of 30 cm), and (C) in a flooded region (~50 cm water). These fractions are determined using the spectra that appear in Figure 3 for each site. In oxidized conditions, Zn is found in the ZnO or Zn sorbed on (hydr)oxide fractions. The fraction of ZnS and ZnCO$_3$ rises with water levels in spring.
Figure 5. Zinc speciation as a function of water depth. Fractions for each depth are the average of all samples collected in the wetland with similar water depth, regardless of sampling date or sampling position. Sorption as ZnO or Zn sorbed to (hydr)oxide phases decreases as water depth increases to 50 cm, while the ZnS fraction increases rapidly to a maximum at approximately 50 cm water depths. Carbonate phases begin to appear at approximately 50 cm water depth.
Chapter 7. Conclusions

ENVIRONMENTAL SIGNIFICANCE

Sulfide minerals are commonly found in the environment. Primary mineral sulfides are present in sulfide-rich ores and their gangues, and authigenic sulfide minerals form as a consequence of biological iron and sulfur reduction in anaerobic (usually flooded) environments. The preceding studies examine the importance of sorption to the retention of chalcophiles to sulfide minerals formed in such anoxic environments. Arsenic, molybdenum, and zinc were all retained strongly by sulfide minerals both as inner-sphere complexes and surface precipitates. Thus, As, Mo, and Zn retention is controlled by sulfide minerals in reducing environments. The dynamic character of sulfidic environments will also strongly affect ion retention (they are usually undergoing either reduction or oxidation). The sulfide minerals may be oxidized under aerobic conditions, and the sorbed species were prone to both oxidation and reduction; these processes may release sorbed ions. Redox cycling often occurs in sulfidic environments, so these redox processes may strongly influence ion sorption in the environment. Consequently, both kinetic and thermodynamics must be considered when evaluating the fate of As, Mo, Zn, and, by analogy, other chalcophiles in sulfidic environments.

SULFIDE SURFACE REACTIVITY

The experiments outlined in previous chapters allow us to draw conclusions about the reactivity of sulfide mineral surfaces. Typically, sorption reactions involve hydroxyl (Equation 1) and sulfhydryl (Equation 2) surface functional groups formed through hydrolysis of under-coordinated metal and sulfur atoms.
\[ \equiv M^{+} + H_{2}O \iff Me - OH + H^{+} \] [1]

\[ \equiv S^{-} + H_{2}O \iff S - H + OH^{-} \] [2]

It should be noted that these reactions assume integral charges at the surface sites, which is generally not correct particularly for sulfides. Although sulfhydryl and hydroxyl surface groups undergo similar protonation reactions (Equations 3 and 4; Rönngren et al., 1992), the stronger acidity of sulfide groups is reflected in differences in the protonation state of the surface.

\[ \equiv Me - O^{-} \iff Me - OH \iff Me - OH_{2}^{+} \] [3]

\[ \equiv Me - S^{-} \iff Me - SH \iff Me - SH_{2}^{+} \] [4]

For sulfide minerals, the zero-point-of charge (ZPC), the pH at which the negative and positive surface charges are equal, ranges from 0.7 to 3.3 (Liu and Huang, 1992; Dekkers and Schoonen, 1994; Bebie et al., 1998) while the ZPC of (hydr)oxides is typically much higher due to the weaker acidity of surface hydroxyl groups. The surface of a sulfide mineral is thus negatively charged under typical (near-neutral pH) environmental conditions, reducing its electrostatic affinity for anions.

Authigenic sulfide minerals have significantly different surfaces than freshly cleaved or fractured surfaces. Authigenic mineral surfaces form through the reaction of uncoordinated metal sites with bisulfide (Equation 5) or through the exchange of bisulfide and surface hydroxyl functional groups (Equation 6; Rönngren et al., 1994):

\[ \equiv Me^{+} + HS^{-} \iff Me - SH \] [5]

\[ \equiv Me - OH + HS^{-} \iff Me - SH + OH^{-} \] [6]
These reactions (Equations 5 and 6) cause sulfhydryl termination to predominate under most conditions, further depressing the ZPC of the reactive solids (Parks, 1990; Bebie et al., 1998). The acid-base character of the surface functional groups largely determines the reactivity of sulfide surfaces. Sulfhydryl groups are soft Lewis bases that are commonly assumed to control the reactivity of the surface toward Lewis acids (Tossell 1977; Tossell et al., 1981; Luther, 1987; Tossell and Vaughan, 1992). Iron-localized 3dₓ²-r-type orbitals may also be important reactive surface groups on UHV-cleaved pyrite (Rosso et al., 1999); however, it is unclear how these orbitals will be stabilized in solution (Equations 1 and 5). Nevertheless, the sulfur-deficient metal centers are Lewis acids that may be important reactions sites for adsorption of oxidants and possibly other adsorbates (Guevremont et al., 1998; Rosso et al., 1999).

**SORPTION MODELS FOR SULFIDE MINERALS**

Ion sorption models have focused on substitution (e.g. Gaudin et al., 1959; Pugh and Tjus, 1987; Park and Huang, 1989) and adsorption reactions analogous to (hydr)oxide surfaces (e.g., James and Parks, 1975; Kornicker and Morse, 1991; Balsley et al., 1996; 1998). These sorption models may often describe macroscopic properties, but they provide little molecular information necessary to discern the reaction mechanism.

Simple ligand exchange mechanisms presuppose reaction with surface hydroxyls or sulfhydryls (Rönngren et al., 1994; Gärd et al., 1995; Balsley et al., 1996; Bebie et al., 1998).

\[ \equiv Hg - OH + I^- \Leftrightarrow Hg - I + OH^- \]  \[8\]
In such anion exchange mechanisms, the adsorbing ion acts as a nucleophile, displacing a weaker nucleophile. Molybdate sorption to FeS$_2$ behaves in this manner, forming a bidentate sorption complex (Equation 9).

\[ \equiv Fe - OH + MoO_4^{2-} \Leftrightarrow \equiv Fe - O_2MoO_2^- + OH^- \]  

MoS$_4^{2-}$ also sorbs to FeS$_2$ through a conventional ligand exchange mechanism, forming a tridentate Fe-Mo-S cubane surface complex.

\[ 3 \equiv Fe - OH + MoS_4^{2-} \Leftrightarrow \equiv Fe_3 - S_3MoS^- + 3OH^- \]

Interestingly, the bidentate MoO$_4^{2-}$ complex (Equation 9) is labile, while the cubane structure (formed in Equation 10) is stable for long time periods, likely due to the stability of the tridentate cubane complex.

Spectroscopic evidence often indicates that ion sorption is more complex than assumed by simple exchange or complexation models, even when macroscopic studies suggest that sorption obeys these simple models. For example, arsenic(III) sorption to iron sulfide minerals involves the reduction of As(III) to As(-I) and subsequent incorporation into an FeAsS-like precipitate, coupled to the oxidation of surface Fe and/or S. This reduction is accompanied by the direct bonding of As to Fe atoms at the surface, consistent with the models of Rosso et al. (1999) and Guevremont et al. (1998) that suggest iron centers may preferentially react. Similar redox processes have been documented for the sorption of Cd (Bostick et al., 2000), Co(II) (Large et al., 1999), Au(SH)$_2^-$ and Pd (Bancroft and Hyland, 1990). For example, Ag$^+$ sorption to pyrite yields both Ag$^0$ and Ag$_2$S (Equation 11; Hiskey et al., 1987; Scaini et al., 1995).

\[ FeS_2 + 8Ag^+ + 4H_2O \Leftrightarrow Fe^{2+} + Ag_2S + 6Ag^0 + SO_4^{2-} + 8H^+ \]
Arsenite sorption to PbS and ZnS also behaves differently than predicted based on the conventional ligand exchange models—the nucleophilic character of the surface sulfhydryl groups causes them to react with As, altering its coordination sphere.

\[ 6 \equiv \text{ZnSH} + 3\text{As(OH)}_3 \iff 6 \equiv \text{ZnOH} + \text{As}_3\text{S}_3(\text{SH})_3 + 3\text{H}_2\text{O} \quad [12] \]

While these systems are unique in that they form insoluble sulfide minerals or reduced noble metals, the identification of the reaction products indicates that simple adsorption mechanisms, whether inner-sphere or outer-sphere, provide at best an incomplete picture of ion sorption.

The arsenite sorption reactions above illustrate the variable chemistry of sulfide minerals. Arsenite reacts with sulfide surfaces through both traditional exchange reactions and redox transformations, each coupled with the formation of a stable surface species. Redox transformations originate from the presence of reduced sulfur; its facile oxidation drives the reduction of sorbed species. The structure of arsenite also influences its reactivity toward sulfide minerals. The empty valence orbital of arsenite allows it to behave effectively as a cation, undergoing nucleophilic attack on each of the sulfide minerals examined. In contrast, Mo sorbs in a more conventional manner, possibly because it is fully coordinated in both $\text{MoO}_4^{2-}$ and $\text{MoS}_4^{2-}$.

Sorption mechanisms are commonly used to imply the stability of the sorbed species. For example, it is reasonable to assume that FeAsS-like surface precipitates and Fe-Mo-S cubanes are relatively stable, potentially providing a kinetic limitation to desorption. However, examination of As, Mo and Zn sorption in natural matrices shows care should be used when appraising the stability of surface complexes based on their structure alone. The bidentate molybdate complexes are reversibly sorbed. Zinc solid
phases undergo facile conversion in response to changing environmental conditions. Changes in redox status have the potential to influence sorption as well; the arsenic surface precipitates and surface complexes are susceptible to oxidation and transformation, providing a rapid means of dissolving sorbed As species. Although the long-term stability of these sorption complexes is not directly explained by their structure, these studies provide insight into the sorption mechanism of a variety of ions on sulfide and other minerals.

REFERENCES


Park S. W. and Huang C. P. (1989b) The adsorption characteristics of some heavy metal ions onto hydrous CdS(s) surface. J. Colloid Interface Sci. 128, 245-257.


