



Speciation and natural attenuation of arsenic and iron in a tidally influenced shallow aquifer

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Abstract

The mobility of subsurface arsenic is controlled by sorption, precipitation, and dissolution processes that are tied directly to coupled redox reactions with more abundant, but spatially and temporally variable, iron and sulfur species. Adjacent to the site of a former pesticide manufacturing facility near San Francisco Bay (California, USA), soil and groundwater arsenic concentrations are elevated in sediments near the prior source, but decrease to background levels downgradient where shallow groundwater mixes with infiltrating tidal waters at the plume periphery, which has not migrated appreciably in over two decades of monitoring. We used synchrotron X-ray absorption spectroscopy, together with supporting characterizations and sequential chemical extractions, to directly determine the oxidation state of arsenic and iron as a function of depth in sediments from cores recovered from the unsaturated and saturated zones of a shallow aquifer (to 3.5 m below the surface). Arsenic oxidation state and local bonding in sediments, as As-sulfide, As(III)-oxide, or As(V)-oxide, were related to lithologic redox horizons and depth to groundwater. Based on arsenic and iron speciation, three subsurface zones were identified: (i) a shallow reduced zone in which sulfide phases were found in either the arsenic spectra (realgar-like or orpiment-like local structure), the iron spectra (presence of pyrite), or both, with and without As(III) or As(V) coordinated by oxygen; (ii) a middle transitional zone with mixed arsenic oxidation states (As(III)–O and As(V)–O) but no evidence for sulfide phases in either the arsenic or iron spectra; and (iii) a lower oxidized zone in the saturated freshwater aquifer in which sediments contained only oxidized As(V) and Fe(III) in labile (non-detrital) phases. The zone of transition between the presence and absence of sulfide phases corresponded to the approximate seasonal fluctuation in water level associated with shallow groundwater in the sand-dominated, lower oxic zone. Total sediment arsenic concentrations showed a minimum in the transition zone and an increase in the oxic zone, particularly in core samples nearest the former source. Equilibrium and reaction progress modeling of aqueous-sediment reactions in response to decreasing oxidation potential were used to illustrate the dynamics of arsenic uptake and release in the shallow subsurface. Arsenic attenuation was controlled by two mechanisms, precipitation as sulfide phases under sulfate-reducing conditions in the unsaturated zone, and adsorption of oxidized arsenic to iron hydroxide phases under oxidizing conditions in saturated groundwaters. This study demonstrates that both realgar-type and orpiment-type phases can form in sulfate-reducing sediments at ambient temperatures, with realgar predicted as the thermodynamically stable phase in the presence of pyrite and As(III) under more reduced conditions than orpiment. Field and modeling results indicate that the potential for release of arsenite to solution is maximized in the transition between sulfate-reduced and iron-oxidized conditions when concentrations of labile iron are low relative to arsenic, pH-controlled arsenic sorption is the primary attenuation mechanism, and mixed Fe(II,III)-oxide phases do not form and generate new sorption sites.

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1. INTRODUCTION

Biogeochemical factors that control the concentration of dissolved arsenic in groundwater aquifers have been the subject of intensive study in recent years. In the U.S., the federal drinking water standard for the maximum contaminant level (MCL) of arsenic was lowered in January, 2006 from 50 to 10 $\mu\text{g L}^{-1}$ (to the same level as the World Health Organization), requiring thousands of public water suppliers to provide additional treatment or to change water sources (USEPA, 2001). Both natural and anthropogenic sources contribute to arsenic in groundwaters. What sets arsenic apart from other inorganic contaminants is that changes in its chemical speciation, mediated by microorganisms, occur in the range of pH and Eh commonly found in the shallow subsurface environment, which in turn affects its partitioning to solid phases and its aqueous mobility.

Knowledge of subsurface conditions that result in the accumulation of dissolved arsenic in porewaters is growing but predictive capability remains limited, due partly to a lack of knowledge about arsenic, iron, and sulfur speciation in subsurface sediments and to a poor understanding of how speciation changes as a function of time and space. The general behavior of arsenic solid-aqueous partitioning as a function of local oxidation potential and pH in aquifer sediments has been described (e.g., Welch et al., 2000; Inskeep et al., 2002; Smedley and Kinniburgh, 2002; Stollenwerk, 2003; McMahon and Chapelle, 2008). In oxic groundwaters, it is widely accepted that ferric iron phases are important for sorption of dissolved arsenate (as either $\text{H}_2\text{As}^{\text{V}}\text{O}_4^-$ or $\text{HAs}^{\text{V}}\text{O}_4^{2-}$) by surface adsorption or co-precipitation with Fe(III)-(hydr)oxide (Fuller et al., 1993; Waychunas et al., 1993; Raven et al., 1998; Dixit and Hering, 2003), although other phases such as clay minerals or manganese oxides may also serve as sorbents (Hering and Kneebone, 2002; Lin and Puls, 2003; Stollenwerk, 2003; Amirbahman et al., 2006). In the transition from aerobic to anoxic porewaters, arsenate is reduced to arsenite (commonly written as either $\text{H}_3\text{As}^{\text{III}}\text{O}_3$ or $\text{As}^{\text{III}}(\text{OH})_3$), mediated in most cases by microbial activity that includes metabolic and detoxification mechanisms (Inskeep et al., 2002; Orem-land et al., 2002; Stolz et al., 2006). The first acid dissociation constant ($\text{p}K_{\text{a}1}$) of arsenite is ~ 9.2 , such that the neutral species dominates in most groundwaters. In this intermediate regime, arsenite sorption to iron oxides, manganese oxides, and other sediment minerals is a primary removal mechanism at circum-neutral pH and typical dissolved arsenic concentrations, but competition for sorption sites influences arsenite partitioning (Deschamps et al., 2003; Dixit and Hering, 2003; Amirbahman et al., 2006).

Under sulfate-reducing conditions, the concentration of arsenic in solution may be controlled by the solubility of arsenic sulfide phases, such as orpiment (As_2S_3), realgar (As_4S_4), their polymorphs, or other poorly characterized As-S phases. Previous studies have proposed that arsenic associated with sulfide in aquifer sediments is present either as a substituent in biogenic, authigenic, or detrital pyrite (FeS_2 ; typically ~ 0.5 –4 wt.% As) or arsenopyrite (FeAsS) (Rittle et al., 1995; Savage et al., 2000; Kim et al., 2002; Saunders et al., 2005; Lowers et al., 2007; Peters and

Burkert, 2008; Rhine et al., 2008), is sorbed to sulfide minerals (Bostick et al., 2004; Wilkin and Ford, 2006), or forms orpiment- or realgar-type phases (Aggett and O'Brian, 1985; Moore et al., 1988; Sadiq, 1990; La Force et al., 2000; Bostick et al., 2004; O'Day et al., 2004b). In natural settings undergoing sulfate reduction, the extent of arsenic sorption versus precipitation in sulfide phases, and temporal transformations of species and phases, are not well known. Likewise, the stoichiometries and thermodynamic stabilities of aqueous thioarsenite and thioarsenate species remain poorly known (Helz et al., 1995; Wilkin et al., 2003; Bostick et al., 2005; Stauder et al., 2005; Planer-Friedrich et al., 2007; Helz and Tossell, 2008). Precipitation of arsenic sulfide phases has been reported in laboratory studies of microorganisms isolated from arsenic-rich sediments, although most commonly in mildly thermophilic conditions. For example, Huber et al. (2000) described a thermophilic archaeon that respire arsenate and precipitates realgar in its growth range of 68–100 °C in laboratory cultures. An anaerobic, moderately thermophilic, arsenic-metabolizing bacterium was shown to reduce arsenic and to produce the mineral β -realgar (Ledbetter et al., 2007). Other studies (Newman et al., 1997a,b) reported a bacterium capable of reducing As(V) to As(III) and precipitating orpiment or amorphous As_2S_3 in laboratory culture. While microorganisms undoubtedly play a role in arsenic fate in sulfidic conditions, knowledge of biotic and abiotic mechanisms of transformation and their products is incomplete.

Few studies to date have examined the spatial distribution of arsenic speciation in subsurface sediments compared with sediment chemistry and mineralogy, and aquifer chemistry, particularly with respect to the distribution and speciation of iron and sulfur. In this study, we used synchrotron X-ray absorption spectroscopy, together with supporting characterizations, to directly determine the oxidation state of arsenic and iron in sediments from cores recovered from a subsurface arsenic plume where arsenic has migrated from the surface into a shallow aquifer (~ 1 –3 m below the surface). The study site is a former pesticide manufacturing facility adjacent to south San Francisco Bay (California, USA) (Fig. 1). Although subsurface arsenic concentrations are high in sediments near the source, concentrations decrease to background levels at the plume periphery, which has not migrated appreciably in over two decades of monitoring. Thus, we were able to compare the behavior of arsenic vertically and laterally over centimeters to meters in the easily accessed subsurface, and within a range of arsenic concentrations spanning from natural background to elevated above drinking water standard in groundwater. Thermodynamic constraints and reaction path modeling guided by sediment and porewater observations are used to lend insight into biogeochemical and mineralogical changes that control arsenic mobility in the subsurface.

2. EXPERIMENTAL METHODS

2.1. Field site history and description

The manufacturing facility formerly at the study site (Fig. 1) was used principally in the formulation of various

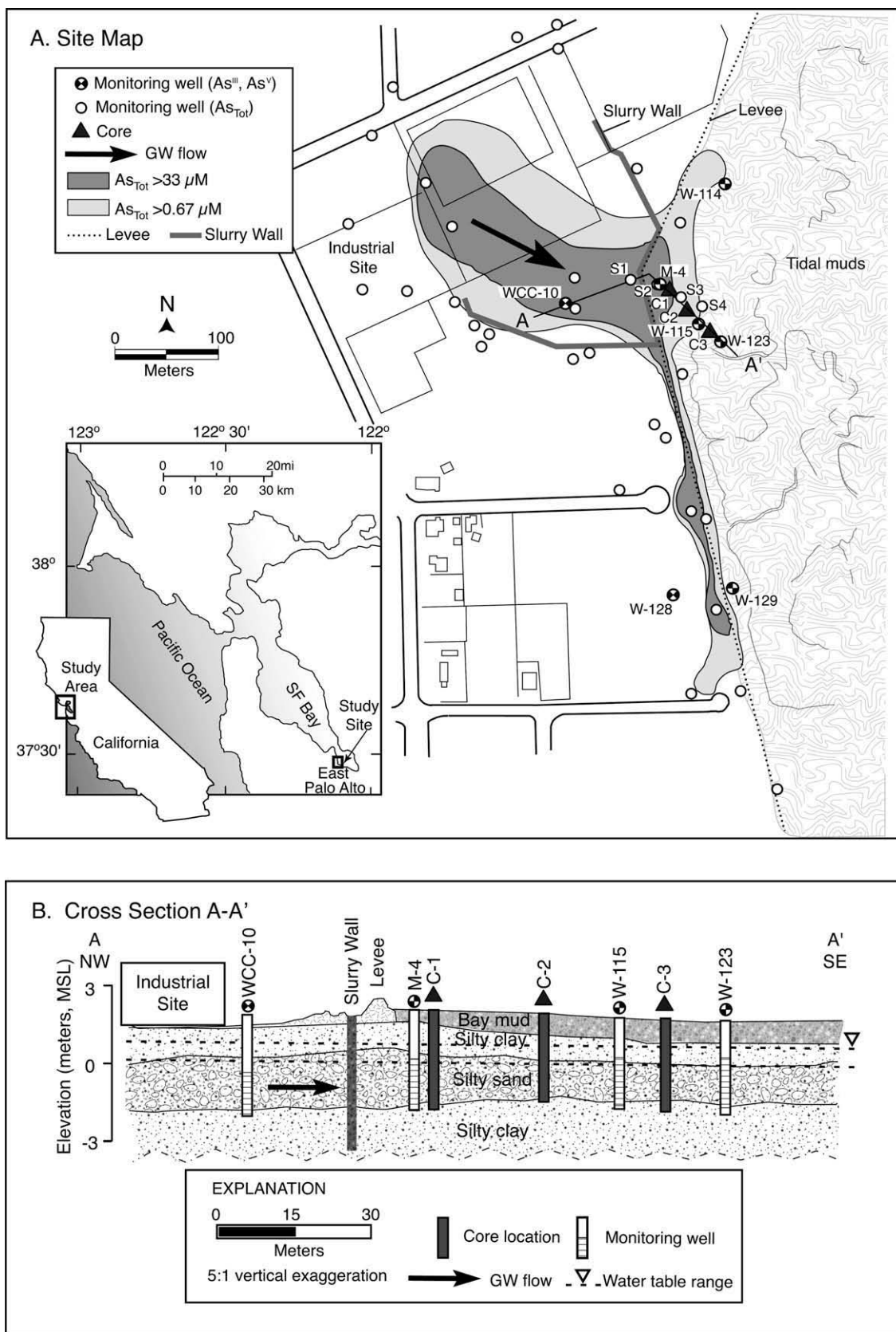


Fig. 1. (A) Location map of the study site. Contours outline the extent of the subsurface arsenic plume based on concentrations in monitoring wells (shown as dots). Water chemistry reported in Table 6 for labeled wells. Locations of sediment cores shown as triangles. (B) Schematic cross-section of the shallow subsurface through points A to A' showing locations of core samples and monitoring wells.

agricultural pesticides (railroad right-of-way liquid insecticides and arsenic-based products), which began as early as 1929. While these activities continued into the late 1960s, the bulk of the arsenic compounds were formulated prior to the end of World War II. Arsenic raw material was shipped to the facility by rail or by truck. End products were formulated primarily in an underground tank near the southern edge of the site and arsenic compounds were reportedly disposed of in a shallow sludge pond located on the site. The underground tank area, sludge pond area, and railroad track area have all been identified as source areas. Arsenic was dispersed by surface water runoff, movement of groundwater, and wind-borne dust (USEPA, 1992). An estimated 88,000 kg of arsenic was present in site soil and groundwater prior to remediation. A 5.1-hectare plume of dissolved arsenic was identified in the shallow aquifer (~1–4 m depth) underlying the site and upgradient of San Francisco Bay (USEPA, 1992). The plume boundary was defined by elevated concentrations of dissolved arsenic (greater than $50 \mu\text{g L}^{-1}$ or $0.67 \mu\text{M}$) in monitoring wells over the last 20 years (Fig. 1). The lower boundary of the plume in the shallow aquifer is hydrologically constrained by a clay aquitard located at about 10 m depth. A deeper aquifer at about 50 m has not shown elevated levels of arsenic. Groundwater concentrations as high as 340 mg L^{-1} ($\sim 4.5 \text{ mM}$) have historically been measured near the plume source, compared to background arsenic levels in shallow groundwater of local tidal marsh sediments that are less than $13 \mu\text{g L}^{-1}$ ($0.17 \mu\text{M}$). The shallow aquifer is hydrologically connected to San Francisco Bay, with groundwater flow in the area on the order of $\sim 1 \text{ m yr}^{-1}$ northwest to southeast towards the bay (USEPA, 1992).

Remedial activities began at the site in 1991. Most soils with arsenic concentrations above 5000 mg kg^{-1} were removed by excavation. Soils with residual arsenic at concentrations between 500 and 5000 mg kg^{-1} were treated with stabilizing amendments (ferrous sulfate, lime, and Portland cement) to reduce leaching and covered with an impermeable cap layer (Illera et al., 2005). The soil cap and associated storm water collection system ensure that current surface runoff from the site into the bay is not contaminated. A subsurface barrier wall (soil–bentonite and soil–cement–bentonite) extending to approximately 6 m below ground surface was installed to provide a shallow barrier between the contaminated upland groundwater sources and the wetlands (Fig. 1). Over 500 trees within the barrier wall extract groundwater as an additional control. Remediation at the site was completed in 2003 but monitoring of the shallow subsurface aquifer continues.

2.2. Sediment sample collection and analysis

All chemicals used for sample preservation, analysis and reagent preparation were reagent grade or higher. Deionized water ($18.2 \text{ M}\Omega\text{-cm}$, MilliQ+, Millipore Corp) was used for all solutions and dilutions. Three sediment cores, spaced 20–25 m apart, were collected at the site using a manual, slide-hammer piston-core with either a split-spoon or extrudeable auger, and polybutyrate sample core liners. Core 1 (to 360 cm) was collected in April 2001 and Cores

2 (to 305 cm) and 3 (to 335 cm) were collected in January 2002 (Fig. 1). Cores were immediately sealed after removal from the sampler, packed under ice, and transported within hours to the Stanford Synchrotron Radiation Lightsource (SSRL) where they were transferred to a subzero freezer. All sediment sample sectioning and handling were done in a glove bag under a N_2 atmosphere. Cores were sectioned at 10–30 cm intervals to preserve sediment stratigraphy. Sub-samples were taken at 5–10 cm intervals and homogenized using a mortar and pestle under N_2 . For XAS data collection, sediment samples were loaded into 2 mm-thick Teflon sample holders and sealed with Kapton tape. Samples were kept frozen in a N_2 atmosphere until XAS data collection (within 1–5 days). To investigate the integrity of sample preservation, selected duplicate samples were stored frozen (-20°C) and at room temperature in N_2 . Arsenic oxidation state was monitored by repeat bulk XAS measurements and was unchanged for at least 8 months in samples sealed in N_2 and stored frozen (-20°C). Changes in oxidation state during XAS data collection were not observed for sample spectra collected under cryogenic conditions (10–20 K).

Extractions were performed on core samples using published methods (Pickering, 1981; Keon et al., 2001) in the following sequence: (1) 1.0 M MgCl_2 ; (2) 1.0 M NaH_2PO_4 ; (3a) 0.2 M ammonium oxalate and oxalic acid; (3b) 1.0 M HCl . A final aqua-regia reflux ($12 \text{ M HCl} + \text{HNO}_3$) was done on a separate 500 mg sample split. Sediment aliquots ($\sim 400 \text{ mg}$) were sequentially treated with each extractant solution (solid:solution = 0.01 by mass), the suspensions were centrifuged (25 min at 8500 rpm), and the supernatant was decanted and filtered ($0.45 \mu\text{m}$ nylon membrane filters). Between extraction steps, sediments were washed with 10 mL of deionized ($18.2 \text{ M}\Omega\text{-cm}$) water, centrifuged, and the supernatant decanted. The filtrate from each extraction step was analyzed by GFAA except for the NaH_2PO_4 step, which was analyzed by ICP-OES because of matrix interference from high phosphate.

2.2.1. Elemental and species analyses

For the analysis of total metals, a homogenized sediment aliquot of $\sim 500 \text{ mg}$ was weighed, quantitatively transferred into an acid-washed borosilicate glass digestion vessel, placed in a digestion block, covered, and digested by hot acid reflux in a mixture of 6 N HCl and 6 N HNO_3 for several hours at 105°C (USEPA, 2006). Samples were quantitatively filtered through $0.45\text{-}\mu\text{m}$ filters to remove traces of undigested silicates. A separate split from the homogenized sample was analyzed for water content by drying at 100°C for at least 24 h to a constant weight. Representative sediments were selected for total digestion using HF. All sediment composition data are reported on a dry-weight basis. Elemental concentrations were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES; Thermo Jarrel Ash IRIS ICP) and graphite furnace electro-thermal atomic absorption (GFAA) with Zeeman background correction (Perkin Elmer SIMMA 6000 GFAA) (see Electronic Annex for details).

For the analysis of total organic carbon (TOC) in sediments, samples were dried at 105°C for 48 h and ashed at

400 °C for 45 min. Sulfide in sediments (Core 1 only) was determined by EPA method SW-846 9031 (“reactive sulfide”) by distillation of wet, unexposed sub-samples in sulfuric acid at 100 °C. Evolved H₂S gas was swept with N₂ into a zinc acetate solution and sulfide (as HS[−]) was measured titrimetrically by precipitation of zinc sulfide (detection limit 10 ppm = 0.3 mmol kg^{−1}) (USEPA, 2006).

2.2.2. Scanning electron microscopy (SEM) and X-ray diffraction (XRD)

A Hitachi S4700 field emission scanning electron microscope (FE-SEM) with an energy dispersive X-ray spectrometer (EDAX Phoenix) was used to collect images and spot elemental analyses (detector distance = 100 nm; current = 1.0 nA; beam diameter = 100 nm) of selected samples. Dried sediment samples were mounted on aluminum alloy stub mounts with double-stick carbon tape and gold sputter coated. Bulk sediment mineralogy was determined by powder XRD using both laboratory and synchrotron X-ray sources. Samples were dried at 40 °C in air for 24–48 h, finely ground to ~5 µm grain size powders, and randomly orientated on quartz micro-slides for laboratory XRD and on aluminum mounts for synchrotron XRD (see [Electronic Annex](#) for details).

2.2.3. XAS data collection and analysis

Arsenic and iron K-edge X-ray absorption spectra were collected at SSRL on wiggler beamline 4-3 and 4-1 under dedicated conditions (3 GeV, 70–90 mA) using an unfocused beam. Arsenic K-edge and EXAFS (to $k = 12\text{--}13 \text{ \AA}^{-1}$) fluorescence spectra were collected using Si(220) monochromator crystals (vertical beam size = 1 mm). On beamline 4-3, a 13-element solid-state Ge-array fluorescence detector was used with a He cryostat sample holder (~20 K). On beamline 4-1, a Lytle detector with a liquid nitrogen cold-finger was used. Fluorescence spectra for iron were collected at room temperature on frozen, sealed samples. Beam energy was calibrated on arsenic foil (main edge inflection) at 11,867 eV and on iron foil (first edge inflection) at 7112 eV. For arsenic edge spectra, 6–20 scans were collected and averaged; for EXAFS spectra, 10–40 scans were averaged, depending on element concentration (low total arsenic concentrations in the sediments limited the ability to collect EXAFS spectra). For iron XAS, 3–8 scans were collected. Solid arsenic reference compounds were diluted with inert B(OH)₃ and collected at 15–20 K or ~70 K in transmission mode using gas-filled ion chambers. Reference sorption samples were collected in fluorescence using the same procedures as for the sediment samples. Data collection and analysis of iron reference compounds are described in detail elsewhere (O'Day et al., 2004a).

XANES spectra were analyzed using the computer packages DATFIT and Sixpack (George and Pickering, 2000; Webb, 2006). Arsenic and iron XANES spectra (either normalized or first-derivative normalized spectra) of sediment samples were fit using linear least-squares combinations of reference compound spectra. Energy was allowed to vary in fits to account for small differences in energy calibration between sediments and references. Shifts in energy of greater than 0.85 eV were rejected as spurious.

The EXAFS spectra were analyzed with the package EXAFSPAK (George and Pickering, 2000). Spectra were fit by non-linear least-squares methods in k -space and the entire k -range was used in the fit (i.e., no reverse Fourier filtering was done). Theoretical phase-shift and amplitude reference functions were calculated with the program FEFF (Rehr, 1993; Ankudinov et al., 1998). In fits to the sediment arsenic EXAFS spectra, interatomic distance (R), and either backscatterer number (N) or Debye–Waller factor (σ^2) were varied in fits (because of the strong co-variance between N and σ^2). For most unknown spectra, σ^2 was fixed on a value estimated from fits to reference compounds with similar absorber-backscatters atomic pairs. For fits to iron EXAFS spectra, atomic shells were grouped by a sulfide component, represented by the local structure of pyrite, and a non-sulfide component, represented by a composite phyllosilicate-oxide, and fit according to the methods described previously (O'Day et al., 2004a,b). Estimated errors based on empirical fits to reference compounds are: first-shell: $R \pm 0.01 \text{ \AA}$; $N \pm 10\%$; greater than first-shell: $R \pm 0.02 \text{ \AA}$; $N \pm 30\%$; $\sigma^2 \pm 30\%$ (O'Day et al., 1998, 2004a,b) (see [Electronic Annex](#) for details).

2.3. Aqueous sample collection and analysis

Groundwater from monitoring wells ([Fig. 1](#)) was sampled for measurement of dissolved total arsenic and major and trace elements; dissolved As(III) and As(V) were measured in selected wells. Measurements of pH (by electrode, calibrated daily), dissolved O₂ (YSI model 556), redox potential (by Pt electrode, calibrated and altitude-corrected in the field), specific conductivity, turbidity, and temperature were collected in the field. Upgradient of the barrier wall, upland wells (unlabeled wells in [Fig. 1](#)) were monitored in the field for pH, Eh, temperature, and conductivity (S.S. Papadopoulos & Associates, 2000; Geomatrix and S.S. Papadopoulos & Associates, 2002). For collection of groundwater samples, two techniques were used: wells were either bailed, with ten well volumes removed prior to sampling, or samples were retrieved using a micro-purge, low-flow (200 ml min^{−1}) method. Aqueous samples were filtered through 0.45-µm filters and collected in acid-washed and deionized-water-rinsed HDPE or amber borosilicate glass bottles preserved with ultra-trace acid or reagent grade chemical preservative, depending on the intended analysis. Samples were kept on ice during transit and stored at 4 °C until analyzed.

Concentrations of dissolved elements were determined by ICP-OES and GFAA as described above. Groundwater samples were analyzed for total arsenic by GFAA. Total dissolved solids and total suspended solids determined gravimetrically (USEPA, 1983). Total organic carbon was measured with an O.I. Analytical TOC 700 Analyzer (USEPA, 1983). Alkalinity was measured by acid titration by Standard Methods 2320B (APHA, 1995). Chloride concentrations were determined by titration with mercuric nitrate (USEPA, 1983). Ferrous iron content was determined colorimetrically with 1,10-phenanthroline indicator (APHA, 1995). Nitrate and nitrite were determined spectrophotometrically at 543 nm (APHA, 1995). Sulfate

was determined gravimetrically by precipitating barium sulfate from the addition of barium chloride at pH 4.5 with HCl. No sulfide was detected in aqueous samples by EPA methods 376.1 (titrimetric; detection limit 0.5 mg L^{-1}) or 376.2 (spectrophotometric; detection limit 0.017 mg L^{-1}).

Dissolved As(III) and As(V) were measured using ion-exchange liquid chromatography in the field coupled with GFAA (methylated arsenic species were not measured) (Ficklin, 1983; Edwards et al., 1998). Ion-exchange columns were packed with acetate-converted Dowex AG1-X8 resin (50–100 chloride form, 50–100 mesh chromatography, BioRad Laboratories) secured with acid-washed glass fiber. Immediately upon collection at each well, groundwater was filtered through a $0.45\text{-}\mu\text{m}$ PTFE Luer-Lock filter, with splits of the filtrate passed through the exchange column at a flow rate of 2 mL min^{-1} for separation of As(III). A second split was preserved for analysis of total arsenic; As(V) was determined by difference. Both aliquots were collected in acid-washed Nalgene bottles, preserved with ultra-trace 0.2 N HCl , and stored at 4°C until analysis. Field and laboratory blanks and spikes of As(III) and As(V) were analyzed to determine efficacy of the ion-exchange columns; recoveries ranged from 86 to 96%.

2.4. Equilibrium and reaction path models

Equilibrium aqueous speciation and mineral saturation states were calculated using the Geochemist's Workbench (GWB) v. 7 package (Bethke, 1994) with a modified version of the Lawrence Livermore National Laboratory (LLNL) thermodynamic database (thermo.com.v8.r6+) (Delany and Lundeen, 1990) augmented with data from Nordstrom and Archer (2003) for arsenic species and from Bourrie et al. (1999) for green rust phases (Table 1). Activity coefficients were calculated with the extended Debye–Huckel (B-dot) method (Helgeson et al., 1981). Equilibrium activity diagrams depicting theoretical stability relations among solid phases and aqueous species were computed with the ACT2 program in GWB. Reaction path modeling, including speciation, redox, adsorption, and mineral precipitation-dissolution reactions, was conducted using the REACT program in GWB. Surface complexation was simulated with the modified two-layer model using constants adapted from Dzombak and Morel (1990) with additional constants for arsenic sorption from Dixit and Hering (2003) and Root et al. (2007). Equilibrium constants for arsenite sorption to magnetite from Dixit and Hering (2003) were used to estimate arsenite sorption to green rust (GR) (no constants for GR were found in the literature), since both solids form under similar conditions and have similar sorption properties. Reaction progress was tracked by the amount of organic matter (represented by acetic acid) oxidized as it was titrated into the system. Precipitation of thermodynamically stable iron minerals (hematite, goethite, and magnetite) was suppressed in order to examine interactions with the more reactive, metastable solid phases ferrihydrite ($\text{Fe}(\text{OH})_3(\text{s})$) and GR-II (sulfate form). Stoichiometries and equilibrium constants for surface complexation reactions and initial model conditions are given in Table 1.

3. RESULTS

3.1. Lithology, mineralogy, and chemistry of sediment cores

Three sediment cores were studied from the tidal marsh adjacent to the area of high subsurface arsenic contamination. The sampling location was on the downgradient side of the subsurface barrier wall installed along the existing levee (Fig. 1). The upper sediments (0 to $\sim 100\text{--}170 \text{ cm}$) are mostly clay with interbedded fine sand. Size fractions of subsections indicated predominately fine-grained material, with over 75% finer than $63 \mu\text{m}$. Groundwater level at $140\text{--}180 \text{ cm}$ below the surface coincided with the transition from mostly clay to a fine-to-medium sand layer. Sediments changed in color from dark gray-to-black from the surface to the sand layer, and then to tan-to-yellow-orange in the sand layer. This sand layer is confined at the bottom by another low porosity clay horizon. Groundwater flows from northwest to southeast (Fig. 1). Hydraulic tests at the site were used to estimate an average transmissivity in the sand aquifer upgradient of the barrier wall of about $46 \text{ m}^2 \text{ d}^{-1}$, corresponding to a hydraulic conductivity of about 0.018 cm s^{-1} , and hydraulic conductivities of less than $10^{-6} \text{ cm s}^{-1}$ for the barrier wall (S.S. Papadopoulos & Associates, 2000; Geomatrix and S.S. Papadopoulos & Associates, 2002). Little variation in lithologies were observed laterally over the $\sim 50 \text{ m}$ between Core 1 and Core 3.

Arsenic, iron, and total organic carbon (TOC) concentrations as a function of depth in sediment cores are shown in Fig. 2 (complete element analyses are reported in the Electronic Annex). The cores, with some exceptions, showed a general trend of depletion in metal concentration with depth. Contaminant arsenic accumulated below the surface between ~ 15 to 140 cm in Core 1 and to 100 cm in Cores 2 and 3 at concentrations from 1.1 to 3.7 mmol kg^{-1} (Fig. 2), which is about twenty times higher than background concentrations of arsenic in estuary mud in south San Francisco Bay (from 0.05 to $0.16 \text{ mmol kg}^{-1}$) (Hornberger et al., 1999). Arsenic concentrations generally decreased below the upper sediment zone, but increased again below 185 cm in Core 1 ($1.5\text{--}5.6 \text{ mmol kg}^{-1}$) and between 235 and 300 cm in Core 2 ($0.66\text{--}1.5 \text{ mmol kg}^{-1}$). No arsenic accumulation above background was observed below the water table in Core 3 (Fig. 2). Total iron was slightly higher in the upper $100\text{--}140 \text{ cm}$ zone ($\sim 5\text{--}7 \text{ wt.}\%$; $900\text{--}1200 \text{ mmol kg}^{-1}$) and varied between 2 and $5 \text{ wt.}\%$ ($350\text{--}900 \text{ mmol kg}^{-1}$) with increasing depth. Organic carbon (as $\text{wt.}\%$ TOC) was also elevated in the upper $100\text{--}140 \text{ cm}$ of sediment (below the surface root zone), varying between $7\text{--}12\%$ and decreasing below $\sim 160 \text{ cm}$ to $\sim 1\text{--}6\%$. Bulk analyses of Core 1 detected sulfide in two sample intervals from $30\text{--}46 \text{ cm}$ and $61\text{--}76 \text{ cm}$ (2.5 and 8.4 mmol kg^{-1} , respectively), but not in any other sample (detection limit 0.3 mmol kg^{-1}). Although extractable sulfate was measured on sediments from Core 1 (see Electronic Annex), these measurements appeared to reflect sulfate in porewater and the variable porosity of the sediments, and thus sulfate was not measured on the other two cores.

Characterization of core sediments by XRD indicated similar mineralogy as a function of depth, consisting mostly

Table 1

Thermodynamic data geochemical modeling and initial constraints for reaction progress model.

	log K^{int}	Source ^a	
<i>Aqueous arsenic species</i>			
$\text{H}_2\text{AsO}_3^- + 0.5\text{O}_2(\text{aq}) = \text{H}_2\text{AsO}_4^-$	30.5	1	
$\text{AsO}_4^{3-} + 2\text{H}^+ = \text{H}_2\text{AsO}_4^-$	18.8	1	
$\text{H}_3\text{AsO}_4(\text{aq}) = \text{H}_2\text{AsO}_4^- + \text{H}^+$	−2.30	1	
$\text{HAsO}_4^{2-} + \text{H}^+ = \text{H}_2\text{AsO}_4^-$	6.99	1	
$\text{H}_3\text{AsO}_3(\text{aq}) = \text{H}_2\text{AsO}_3^- + \text{H}^+$	−9.17	1	
$\text{HAsO}_3^{2-} + \text{H}^+ = \text{H}_2\text{AsO}_3^-$	14.1	1	
$\text{AsO}_3^{3-} + 2\text{H}^+ = \text{H}_2\text{AsO}_3^-$	29.1	1	
<i>Arsenic solids</i>			
$\text{As}(\text{s}) + 1.5\text{H}_2\text{O} + 0.75\text{O}_2(\text{aq}) = \text{H}^+ + \text{H}_2\text{AsO}_3^-$	42.80	1	
$\text{Arsenolite} (\text{As}_2\text{O}_3) + 3\text{H}_2\text{O} = 2\text{H}_2\text{AsO}_3^- + 2\text{H}^+$	−19.72	1	
$\text{Claudetite} (\text{As}_2\text{O}_3) + 3\text{H}_2\text{O} = 2\text{H}_2\text{AsO}_3^- + 2\text{H}^+$	−19.75	1	
$\text{As}_2\text{O}_5(\text{s}) + 3\text{H}_2\text{O} = 2\text{H}^+ + 2\text{H}_2\text{AsO}_4$	−3.65	1	
$\text{Realgar} (\text{AsS}) + 2.5\text{H}_2\text{O} + 0.25\text{O}_2(\text{aq}) = \text{H}_2\text{AsO}_3^- + 2\text{H}^+ + \text{HS}^-$	−7.80	1	
$\text{Orpiment} (\text{As}_2\text{S}_3) + 6\text{H}_2\text{O} = 2\text{H}_2\text{AsO}_3^- + 3\text{HS}^- + 5\text{H}^+$	−64.6	1	
$\text{As}_2\text{S}_3(\text{am}) + 6\text{H}_2\text{O} = 2\text{H}_2\text{AsO}_3^- + 3\text{HS}^- + 5\text{H}^+$	−63.2	1	
<i>Iron solids</i>			
$\text{Ferrihydrite} (\text{Fe}(\text{OH})_3) + 3\text{H}^+ = \text{Fe}^{3+} + 3\text{H}_2\text{O}$	5.66	2	
$\text{GRI}(\text{CO}_3) (\text{Fe}_6(\text{OH})_{12}\text{CO}_3) + 13\text{H}^+ = 2\text{Fe}^{3+} + 4\text{Fe}^{2+} + \text{HCO}_3^- + 12\text{H}_2\text{O}$	29.11	3	
$\text{GR II}(\text{SO}_4) (\text{Fe}_6(\text{OH})_{12}\text{SO}_4) + 12\text{H}^+ = 2\text{Fe}^{3+} + 4\text{Fe}^{2+} + \text{SO}_4^{2-} + 12\text{H}_2\text{O}$	30.55	3	
$\text{Pyrite} (\text{FeS}_2) + \text{H}_2\text{O} = \text{Fe}^{2+} + 0.25\text{SO}_4^{2-} + 1.75\text{HS}^- + 0.25\text{H}^+$	24.65	2	
<i>Surface protonation constants^b</i>			
$>\text{FeOH} + \text{H}^+ = >\text{FeOH}_2^+$	7.29	4	
$>\text{FeOH} = >\text{FeO}^- + \text{H}^+$	−8.93	4	
$>\text{MOH} + \text{H}^+ = >\text{MOH}_2^+$	4.60	5	
$>\text{MOH} = >\text{MO}^- + \text{H}^+$	−8.20	5	
<i>Arsenate surface complexation constants^c</i>			
$2>\text{FeOH} + \text{H}_3\text{AsO}_4 = (>\text{FeO})_2\text{H}_3\text{AsO}_3 + \text{H}_2\text{O}$	11.84	6	
$2>\text{FeOH} + \text{H}_3\text{AsO}_4 = (>\text{FeO})_2\text{H}_2\text{AsO}_3^- + \text{H}^+ + \text{H}_2\text{O}$	5.28	6	
$2>\text{FeOH} + \text{H}_3\text{AsO}_4 = (>\text{FeO})_2\text{HASO}_3^{2-} + 2\text{H}^+ + \text{H}_2\text{O}$	−0.362	6	
<i>Arsenite surface complexation constants^c</i>			
$2>\text{MOH} + \text{H}_3\text{AsO}_3 = (>\text{MO})_2\text{AsO}^- + \text{H}^+ + 2\text{H}_2\text{O}$	0.92	5	
<i>Reaction path model parameters (initial conditions)</i>			
pH = 7.2	$[\text{SO}_4^{2-}] = 18 \text{ mM}$	$[\text{As}(\text{V})] = 0.45 \text{ mM}$	
$[\text{O}_2(\text{aq})] = 0.2 \text{ mM}$	$[\text{Na}^+] = 469 \text{ mM}$	$[\text{Fe}]_{\text{tot}} = 100 \text{ mM as Fe}(\text{OH})_3(\text{s})$	
$p(\text{CO}_2) = 10^{-3.5}$	$[\text{Cl}^-] = 499 \text{ M}$		
Mineral	Surface area ($\text{m}^2 \text{ g}^{-1}$)	Site density (sites nm^{-2})	Source
$\text{Fe}(\text{OH})_3(\text{s})$	600	2.6	4, 5
$\text{GR II}(\text{SO}_4)$	47	1.4	5, 7

^a References: 1 – (Nordstrom and Archer, 2003); 2 – (Delany and Lundeen, 1990); 3 – (Bourrie et al., 1999); 4 – (Dzombak and Morel, 1990); 5 – (Dixit and Hering, 2003); 6 – (Root et al., 2007); 7 – (Williams and Scherer, 2001).

^b ($>\text{FeOH}$) represents $\text{Fe}(\text{OH})_3(\text{s})$ surface sites; ($>\text{MOH}$) represents GR or magnetite surface sites; magnetite site density from (Dixit and Hering, 2003) used for GR.

^c Mass law expression shown here for binuclear-bidentate surface complexes as an example: $K^{\text{int}} = [(\equiv \text{FeO})_2\text{H}_2\text{AsO}_2^-][\text{H}^+] / [\text{FeOH}]^2[\text{H}_3\text{AsO}_3]^{-1} \exp(-F\psi/R^{-1}T^{-1})$, where F is the Faraday constant, ψ is the surface potential, R is the gas constant, and T is the absolute temperature.

of quartz ($>50\%$) with lesser amounts of plagioclase feldspar and phyllosilicate minerals, including biotite, muscovite, clinochlore, and montmorillonite in the fine sediment fraction ($<63 \mu\text{m}$). Examination of sediments with SEM and EDS showed abundant quartz and feldspar grains ($5\text{--}50 \mu\text{m}$) and fine-grained, platy clay and detrital mica particles ($1\text{--}50 \mu\text{m}$) in all cores. A sediment sample from the upper clay/silt zone (Core 1: $61\text{--}76 \text{ cm}$) contained small, cu-

bic particles ($<1 \mu\text{m}$) with large iron and sulfur peaks in the EDS analysis (Fig. 3A), indicative of iron sulfide, probably pyrite crystals (confirmed by XAS, see below). No pyrite or other sulfide minerals were identified with XRD, probably because abundances were below the detection limit of the method ($2\text{--}5 \text{ wt.}\%$). In a transition zone sample (Core 3: $107\text{--}122 \text{ cm}$), platy minerals characteristic of fine-grained clays were abundant (Fig. 3B). In sediments from the sandy

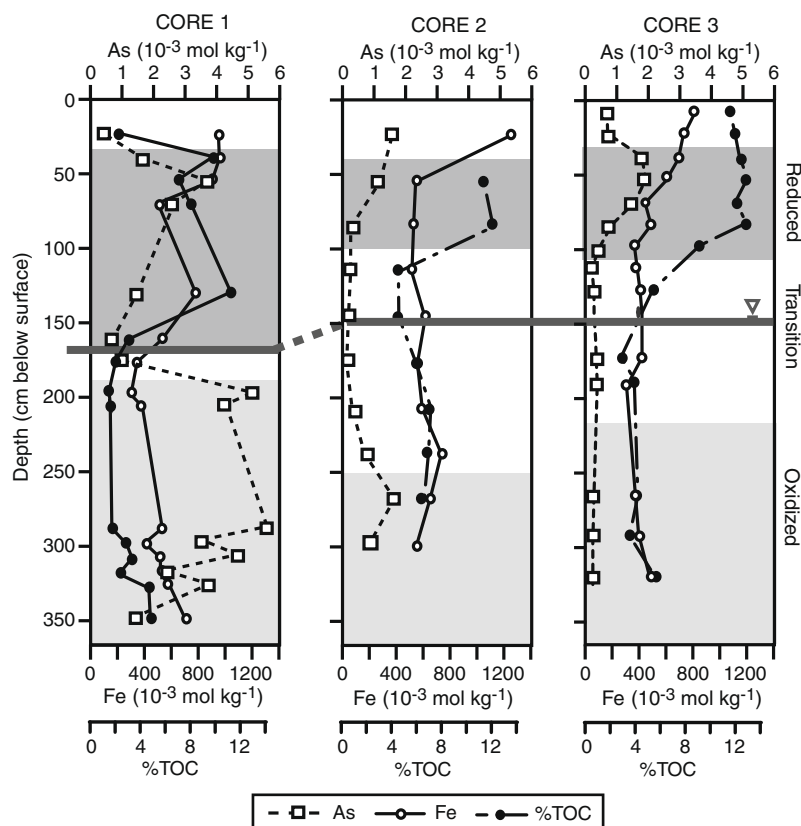


Fig. 2. Total arsenic (As), iron (Fe), and organic carbon (% TOC) in core sediments as a function of depth. Shading indicates the zones associated with reduced, transition, and oxidized conditions from spectroscopic analysis (Fig. 4), and the solid line indicates the seasonally averaged level of groundwater.

aquifer (below ~ 180 cm), SEM images and EDS analyses indicated fine-grained, iron-rich coatings (<5 μm) on larger quartz particles (example from Core 2 shown in Fig. 3C).

3.2. Arsenic and iron X-ray absorption spectroscopy of sediments

Arsenic and iron oxidation state and speciation derived from XANES and EXAFS analysis were used to identify subsurface redox zones in the three cores. The energy of maximum absorption at the arsenic K-edge is a sensitive indicator of arsenic oxidation state, with lower oxidation states shifted to lower energies of maximum absorption (Foster et al., 1998; Savage et al., 2000; Foster, 2003; O'Day et al., 2004b). Differences among the XANES spectra for iron are more subtle than those seen in arsenic XANES and thus are more apparent in first-derivative spectra, particularly in the spectral regions between 7116–7121 eV and between 7127–7130 eV (Wilke et al., 2001; O'Day et al., 2004a). Bulk iron concentrations are high relative to arsenic in sediments (by $\sim 10^3$) and allow for easier collection of EXAFS spectra. However, the bulk iron XAS signal in natural sediments is often dominated by iron substitution in non-reactive, detrital phyllosilicate minerals and more labile, reactive iron fractions are typically present in lower abundance (Carroll et al., 2002). Comparison of arsenic and iron XANES and EXAFS spectra among core

sediments showed three general subsurface zones (Fig. 4): (i) an upper reduced zone in which a sulfide fraction was identified in either the arsenic spectra, the iron spectra, or both; (ii) a middle transitional zone with mixed oxidation states for arsenic but no evidence for sulfide phases in either the arsenic or iron spectra; and (iii) a lower oxidized zone containing only oxidized As(V). The spectral evidence for each of these zones is discussed below.

3.2.1. Upper reduced zone

In Cores 1 and 2, near-surface sediments at depths of 15–30 cm contained only As(V) (Fig. 4), probably because of infiltration of oxidized surface water. Within the upper clay/silt layer to 170 cm in Core 1, to 90 cm in Core 2, and to 110 cm in Core 3, analyses of XANES and EXAFS spectra indicated that all or some of the arsenic in the sample is reduced and associated with sulfide phases. Comparison of the XANES energy of maximum absorption in the sediment spectra with sulfide reference compounds showed absorption maxima in Core 1 samples similar to that of the mineral realgar (As_4S_4) at 11,869 eV (Figs. 4 and 5A). In Cores 2 and 3, the absorption maximum at low energy was ~ 0.5 –1 eV higher than observed for Core 1 sediments, and similar to the absorption maximum for either amorphous $\text{As}_2\text{S}_3(\text{s})$ or crystalline orpiment (Figs. 4 and 5) (O'Day et al., 2004b). In addition to the sulfide absorption peak, absorption features at slightly higher energy, charac-

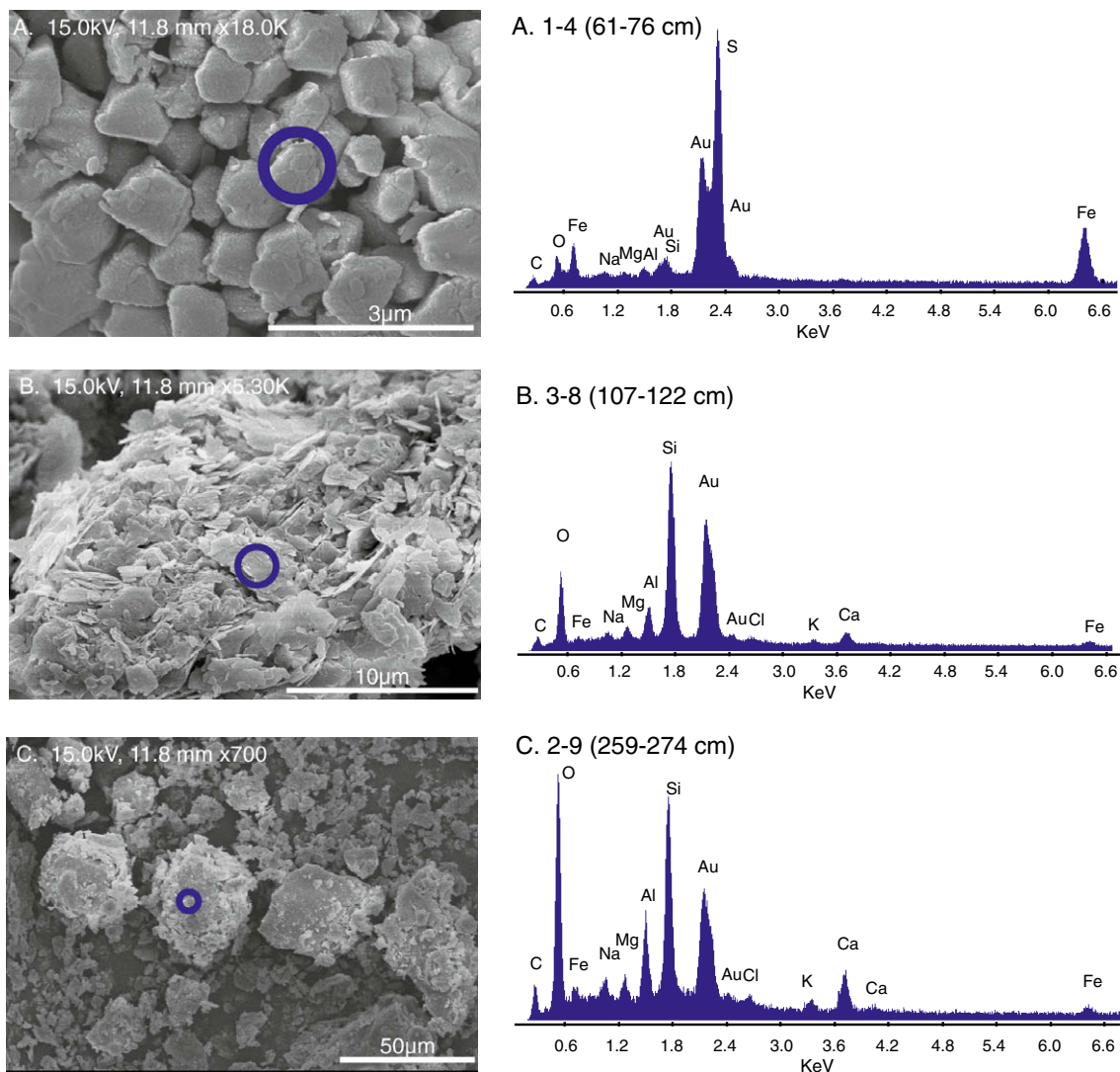


Fig. 3. Scanning electron micrographs and energy dispersive spectrometry (EDS). (A) Cubic Fe- and S-rich crystals from 61 to 76 cm in Core 1 within the upper reduced zone sediments. (B) Platy clays from 107 to 122 cm in Core 3 within the middle transition zone sediments. (C) Surface coatings on quartz from 259 to 274 cm in Core 2 within the lower oxidized zone. Gold (Au) peaks in the EDS are from sample coating.

teristic of As(III) (11,872–11,873 eV) or As(V) (11,875–11,876 eV), were present in samples in this zone from all cores, indicating mixtures of oxidized and reduced arsenic in the bulk sediment. Relative proportions of sulfide, As(III), and As(V) contributions to the XANES spectra were determined by linear combination fits using reference compounds (Table 2). The XANES fits are semi-quantitative because they have not been standardized against known mixtures of reference compounds to account for differential absorption/fluorescence response for different arsenic species (Campbell et al., 2008). All XAS data were collected at cryogenic temperature and beam-induced sample damage was not observed during data collection. We have no evidence supporting the hypothesis that mixed arsenic oxidation states were an artifact of sample handling or beam damage given the measures taken for sample preservation, lack of spectral change during data collection, and the presence of some samples containing only As-sulfide.

Thus, the spectral evidence indicates mixed As(III) and As(V) oxidation states within sulfur-reduced sediments.

Quantitative analysis of EXAFS spectra within the reduced sulfur zone corroborates the XANES observations and demonstrates distinct differences between realgar-like and orpiment-like local atomic structure. The EXAFS spectra of sample 1-4 (61–76 cm) and realgar are similar, indicating a similar local atomic environment around arsenic (Fig. 5A). Sample 3-4 also contained similar spectral features in the k -range of ~ 8 – $11 \text{ \AA}^{-1}$. Least-squares fits of sample 1-4 produced interatomic distances identical (within error) to average interatomic distances in crystalline realgar (Table 3 and Electronic Annex). The characteristic spectrum of realgar and its polymorphs results from high-amplitude backscattering from As–As dimers at a relatively short interatomic distance of $\sim 2.58 \text{ \AA}$, which is strongly present in sample 1-4. In the orpiment structure, arsenic is bonded directly to three sulfur atoms (at 2.24–2.31 $\text{\AA}$)

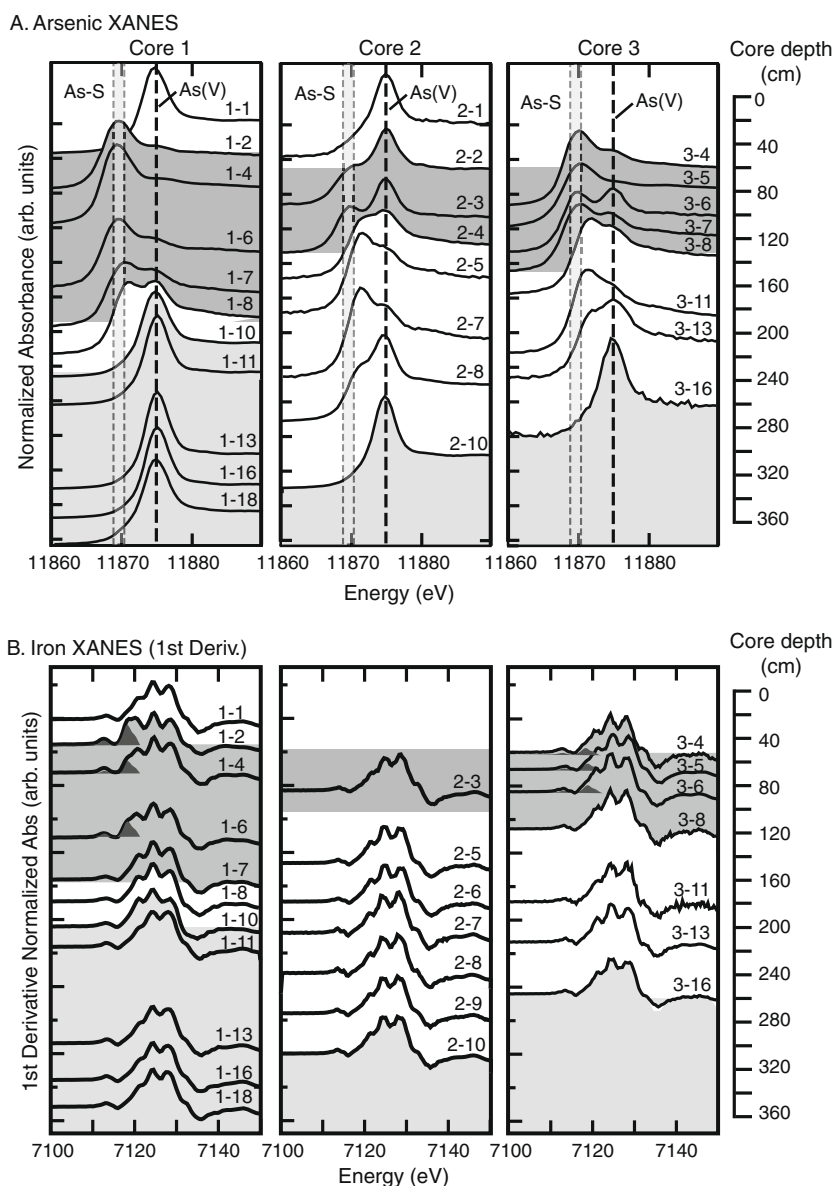


Fig. 4. Normalized XANES spectra of sediment cores as a function of depth. Shading indicates zones of reduced (dark), transition (white), and oxidized (gray) sediments in each core. (A) Arsenic K-edge spectra. Vertical lines show the energy of maximum absorption associated with arsenic sulfide minerals (As-S, shaded) and As(V) (dashed line). Results of linear combinations fits with reference compounds reported in Table 2. (B) First-derivative iron K-edge spectra. Dark shading indicates the component of the XANES that was fit with pyrite (FeS_2). Results of linear combinations fits with reference compounds reported in Table 4.

and the nearest arsenic atoms are found at $>3 \text{ \AA}$ (Mullen and Nowacki, 1972; Foster, 2003; O'Day et al., 2004b). Three other sediment samples from the reduced zone of Core 3 were of poorer spectral quality (Fig. 5A). However, the EXAFS spectra were well fit with a combination of backscattering atoms consistent with realgar-type or orpiment-type phases, and with oxygen backscattering atoms associated with As(III) or As(V) noted in the XANES spectra. Sample 3-4 contained a mixture of realgar-like, orpiment-like, and As(V)-O phases, based on comparison with interatomic distances in reference spectra (Table 3 and Electronic Annex). Sample 3-5 had $\text{S} > \text{O}$ in first-shell amplitude in Fourier transformed spectra, while sample

3-6 had $\text{S} < \text{O}$ (Fig. 5A and Table 3). Although the spectra are noisy and have a limited data range, the EXAFS of these samples were well fit assuming local near-neighbor sulfur and arsenic atoms characteristic of the orpiment structure (As_2S_3) rather than realgar. Interatomic As-O distances from the EXAFS fits for samples 3-5 and 3-6 were within the expected range for the structural arsenate (AsO_4^{3-}) group (Table 3).

The bulk iron X-ray absorption spectra in all sediments were dominated by iron present in phyllosilicate minerals, probably a combination of detrital micas and clays. The phyllosilicate fraction was well fit with a reference illite spectrum containing $\sim 8 \text{ wt.}\%$ iron (Clay Source Minerals

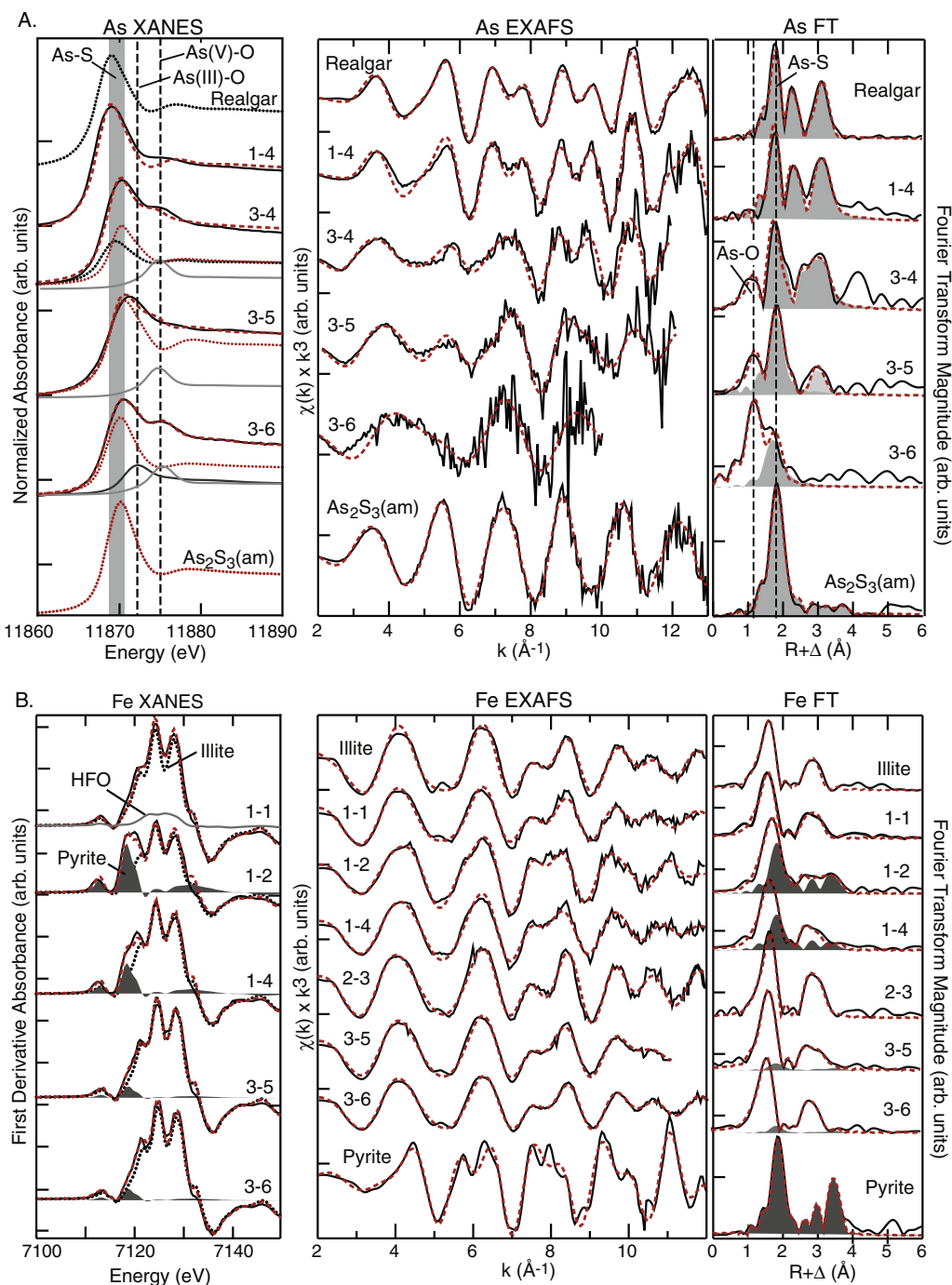


Fig. 5. X-ray absorption spectra of sediment samples from the reduced zone compared with reference compounds. Solid black lines are data; dashed lines are least-squares best fits. (A) Arsenic XANES, EXAFS, and Fourier transforms (FT). XANES shows the fit deconvolutions with reference sulfide, As(III)-O, and As(V)-O spectra (fit results in Table 2). EXAFS fit results are given in Table 3. Shading in FT shows the fraction of EXAFS amplitude associated with As-sulfide phases, if present. Reference compounds: crystalline realgar (As_4S_4); precipitated, amorphous As_2S_3 . (B) Iron XANES, EXAFS, and Fourier transforms (FT). First-derivative XANES shows fit deconvolutions with reference illite, hydrous ferric oxide (HFO), and pyrite (fit results in Table 4). EXAFS fit results are given in Table 5. Shading in XANES and FT shows the fraction of EXAFS amplitude associated with pyrite, if present. Reference compounds: natural illite (IMt-1) from Clay Mineral Society Source Clays Repository; crystalline pyrite (FeS_2) (see Electronic Annex for fits to reference compounds).

reference IMt-1) (O'Day et al., 2004a; Root et al., 2007). Linear combination fits of iron XANES spectra showed that the phyllosilicate fraction comprised about 60–100% of the bulk iron (on a per atom basis) in samples from all

three cores (Table 4). In the upper clay/silt layer, analyses of both XANES and EXAFS indicated the presence pyrite (FeS_2) in some samples in the zone in which As-sulfides were observed (Fig. 4 and Fig. 5B). The shallowest sample

Table 2
Arsenic XANES fit results.^a

Core sample	Depth (cm)	Realgar ^b (%)	Orpiment ^c (%)	Δ eV	As(III) ^d (%)	As(V) ^e (%)	Δ eV	Conf. limit	Total (%)
<i>Reduced zone</i>									
1-2	30–46	96.5	—	0.12	—	—	—	0.03	96.5
1-4	61–76	100.4	—	0.01	—	—	—	0.03	100.4
1-6	122–137	71.1	24.4	0.48	—	10.1	0.46	0.12	105.6
1-7	152–168	40.2	37.9	0.33	—	26.3	0.69	0.12	104.4
2-1	15–30	—	15.2	0.38	—	93.1	0.37	0.04	108.3
2-2	46–61	23.5	18.1	0.18	—	55.3	0.17	0.10	96.9
2-3	76–91	—	45.6	0.82	—	55.8	0.27	0.12	101.4
3-4	46–61	40.6	40.1	0.42	—	16.5	0.42	0.11	97.2
3-5	62–76	—	84.7	0.70	—	14.0	0.69	0.04	98.7
3-6	77–91	—	58.9	0.13	26.4	14.9	0.40	0.07	98.8
3-7	91–107	37.9	40.4	0.36	—	22.4	0.64	0.16	100.7
<i>Transition zone</i>									
1-8	169–183	—	—	—	64.3	29.4	0.09	0.03	93.7
2-4	107–122	—	—	—	67.5	33.2	0.44	0.04	100.7
2-5	138–152	—	—	—	85.8	17.2	0.50	0.35	103.0
2-7	198–203	—	—	—	73.5	15.1	0.45	0.02	88.6
2-8	229–244	—	—	—	45.6	54.3	0.34	0.02	99.9
3-8	107–122	—	—	—	67.2	22.0	0.67	0.03	89.2
3-11	168–183	—	—	—	77.6	16.7	0.46	0.03	94.3
3-13	198–203	—	—	—	65.5	43.4	0.21	0.05	108.9
<i>Oxidized zone</i>									
1-1	15–30 ^f	—	—	—	—	98.7	0.35	0.02	98.7
1-10	193–205	—	—	—	—	103.8	0.33	0.02	103.8
1-11	206–213	—	—	—	—	107.7	0.04	0.02	107.7
1-13	295–305	—	—	—	—	101.9	0.02	0.02	101.9
1-16	325–335	—	—	—	—	100.1	0.01	0.02	100.1
1-18	345–357	—	—	—	—	103.9	0.47	0.03	103.9
2-10	290–305	—	—	—	—	105.1	0.57	0.03	105.1
3-16	259–274	—	—	—	—	104.5	0.18	0.03	104.5

^a Results from least-squares fits with energy varied for each sulfide or oxide component (shift reported in eV). Goodness-of-fit reported as 99% confidence limit (conf. limit) equal to three times the estimated standard deviation.

^b Fit with crystalline realgar spectrum (O'Day et al., 2004b).

^c Fit with freshly precipitated orpiment prepared following Eary (1992).

^d Fit with arsenite sorbed to HFO (hydrous ferric oxide precipitated as 2-line ferrihydrite).

^e Fit with arsenate sorbed to HFO (hydrous ferric oxide precipitated as 2-line ferrihydrite).

^f Surface sediment.

from Core 1 (1-1, 15–30 cm), which contained only As(V), had mostly phyllosilicate iron with about 15% Fe(III)-oxide (fit with ferrihydrite). In samples from 30 to 140 cm, fits to XANES spectra indicated that the pyrite fraction varied from 18 to 34% of the total iron (Fig. 4 and Table 4). Fits to two EXAFS spectra in this zone (1-2 and 1-4) assuming a mixture of pyrite and illite gave good fits to the data (Fig. 5B and Table 5; these two samples also had detectable reactive sulfide). The deepest sample in the sulfide zone in Core 1 (1-7) could not be fit with iron sulfide (although arsenic sulfides were prominent), but instead contained a small component of Fe(II,III)-oxide. No iron sulfides were identified in Core 2 and the Fe XANES and EXAFS were well fit with only a phyllosilicate component. In Core 3, a small fraction of pyrite was fit in three spectra, with about 5–7% pyrite estimated from the XANES fits (Table 4 and Fig. 5B). For the samples in which iron sulfide was present, the spectra could not be fit with combinations of illite and precipitated FeS (mackinawite structure), for which the latter has a distinctly different local atomic structure than pyrite (O'Day et al., 2004a).

3.2.2. Middle transition and lower oxidized zones

With increasing depth, disappearance of spectral evidence for a fraction of arsenic or iron bonded in sulfide phases marks the transition to a zone in which arsenic is present as mixtures of As(III) and As(V) coordinated by oxygen (Fig. 4 and Fig. 6A). The proportions of different arsenic–oxygen species as a function of depth varied irregularly within this zone, as indicated by fits to XANES spectra (Fig. 4 and Table 2). Total sediment arsenic concentrations generally showed a minimum in this zone (Fig. 2) and thus collection of EXAFS spectra was often unsuccessful. One arsenic EXAFS spectrum from Core 1 (1-8) confirmed the mixed arsenic oxidation states and bonding by oxygen ligands indicated by the XANES. The spectrum, although limited in k-range, was fit well with a first-shell coordination of two oxygen distances, one associated with As(III) (at 1.77 Å) and one with As(V) (at 1.70 Å), and weak a second-neighbor shell (assumed to be iron for fitting) (Table 3).

Below the zone of mixed oxidation within the silty-sand aquifer, all arsenic was present as As(V) ligated to oxygen

Table 3
Arsenic K-edge EXAFS fit results.^a

Sample	Atom	N	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)	χ^2
<i>Reduced zone</i>						
1-4 ^b	S	2 ^c	2.24	0.0029	−8.4	1.37
	As	1 ^c	2.58	0.0031		
	As	2.5 ^c	3.49 ^c	0.0043		
	As	0.75 ^c	3.63 ^c	0.011		
	S	2.5 ^c	3.67 ^c	0.0064		
3-4	O	0.5	1.70 ^c	0.0040 ^c	−9.6	0.86
	S	1.0	2.23	0.0040 ^c		
	As	0.2	2.58 ^c	0.0048 ^c		
	S	1.7	3.17	0.014 ^c		
	As	2.0	3.21	0.0087 ^c		
	As	1.3	3.45	0.0057 ^c		
3-5	O	1.2	1.69	0.0040 ^c	−6.5 8	1.60
	S	1.6	2.25	0.0034 ^c		
	As	1.8	3.19 ^c	0.0087 ^c		
	S	1.5	3.22 ^c	0.014 ^c		
	As	0.4	3.52 ^c	0.016 ^c		
3-6	O	2.1	1.68	0.0040 ^c	−5.4	5.59
	S	1.0	2.25	0.0040 ^c		
<i>Transition zone</i>						
1-8	O	1.0	1.70 ^c	0.0040 ^c	−3.4	2.92
	O	2.2	1.77 ^c	0.0045 ^c		
	Fe	0.7	2.92	0.0031 ^c		
<i>Oxidized zone</i>						
1-16	O	4.0 ^c	1.70 ^c	0.0021	2.3	1.65
	MS ^d	1.0/	3.09/	0.0032/		
	Fe	0.7	3.29	0.0031 ^c		
2-10	O	4.0 ^c	1.70 ^c	0.0016	−2.1	4.77
	MS ^d	1.0/	3.07/	0.0024/		
	Fe	0.4	3.32	0.0031 ^c		

^a *N* is the number of backscattering atoms at distance (*R*); σ^2 , the Debye–Waller term, is the absorber-backscatterer mean-square relative displacement; ΔE_0 is the threshold energy difference; χ^2 is a reduced least-squares goodness-of-fit parameter (= *F*-factor/(# of points − # of variables)). Scale factor (S_0^2) = 1.

^b Fit reported previously (O'Day et al., 2004b).

^c Parameter fixed in least-squares fit using value from fits to reference compounds; / parameter linked in fit to the parameter directly above.

^d Spectrum fit with a multiple scattering path from As–O–O–As in arsenate tetrahedra.

atoms based on XANES absorption maxima. There was little variation in the shape of the XANES spectra among the sediment samples and compared with a reference arsenic sorption sample (Figs. 4 and 6A). Arsenic EXAFS spectra were fit with first-shell oxygen atoms at As–O distances typical of arsenate tetrahedra (Table 3), which is generally invariant (Foster, 2003). Weak second-neighbor backscattering was assumed to be iron in quantitative fits, although it is probably a mixture of iron and weaker atomic scatterers such as aluminum and silicon. The low amplitude of second-neighbor backscattering is evidence for lack of incorporation of arsenic into crystalline structures and points to adsorption as the primary mode of arsenic uptake.

Similar to the upper reduced zone, the iron X-ray absorption spectra in the transition and oxidized zones were dominated by iron associated with detrital phyllosilicates, which accounted for 65–100% of the spectral signal (Fig. 6B and Table 4). Principle components analyses and

sensitivity tests of linear combination fits showed that the XANES spectra in this zone could be fit with either one or two components in addition to the phyllosilicate component. Because of spectral overlap and lack of uniqueness, iron XANES spectra were fit conservatively with only two components, a combination of illite (IMt-1) (65–100%) and an Fe(III)-oxide component (represented by ferrihydrite), with the exception of two spectra in these zones that indicated the minor presence of an Fe(II,III)-oxide component. Rather than an Fe(III) component, these spectra were better fit with a reference synthetic green rust (2-hydroxy-sulfate form) in addition to the phyllosilicate component (Table 4 and Fig. 6B). Acceptable fits could also be produced with magnetite as the reference but results with green rust were slightly better. The iron EXAFS spectra were dominated by backscattering atoms of the phyllosilicate component such that backscattering from the second iron component overlapped those of the phyllosilicate (Table 5 and Fig. 6B).

Table 4
Iron XANES fit results.^a

Core sample	Depth (cm)	Fit (%)	ΔeV	Conf. limit	Fit (%)	ΔeV	Conf. limit	Fit (%)	ΔeV	Conf. limit	Total (%)
Reduced zone		Phyllosilicate ^b			Iron sulfide ^c			Fe ^{II,III} -oxide ^d			
1-2	30–46	63.3	0.36	0.03	34.3	0.49	0.04	–	–	–	97.7
1-4	61–76	81.8	0.00	0.03	18.0	0.39	0.03	–	–	–	99.8
1-6	122–137	75.2	0.06	0.03	23.0	0.62	0.04	–	–	–	98.3
1-7	152–168	90.5	0.11	0.04	–	–	–	8.4	0.66	0.03	98.9
2-3	76–91	100.5	0.39	0.09	–	–	–	–	–	–	100.5
3-4	46–61	93.3	0.36	0.02	7.4	0.21	0.02	–	–	–	100.6
3-5	62–76	95.8	0.23	0.02	6.8	0.61	0.02	–	–	–	102.6
3-6	77–91	94.9	0.20	0.02	4.8	0.20	0.02	–	–	–	99.7
Transition zone		Phyllosilicate ^b			Fe ^{III} -oxide ^e			Fe ^{II,III} -oxide ^d			
1-8	169–183	92.6	0.17	0.05	–	–	–	11.1	0.73	0.04	103.7
2-5	138–152	81.5	0.19	0.06	17.1	0.20	0.060	–	–	–	98.6
2-6	153–183	86.9	0.20	0.07	10.6	0.01	0.072	–	–	–	97.5
2-7	198–203	74.5	0.12	0.07	25.0	0.53	0.090	–	–	–	99.5
2-8	229–244	68.5	0.14	0.06	30.7	0.42	0.060	–	–	–	99.2
3-11	168–183	71.2	0.09	0.08	31.4	0.35	0.084	–	–	–	102.6
3-13	198–203	102.1	0.11	0.03	–	–	–	–	–	–	102.1
Oxidized zone		Phyllosilicate ^b			Fe ^{III} -oxide ^e						
1-1	15–30	84.0	0.16	0.09	15.0	0.64	0.09	–	–	–	99.0
1-10	193–205	89.9	0.03	0.05	–	–	–	10.5	0.00	0.04	100.4
1-11	206–213	63.6	0.25	0.06	35.7	0.13	0.07	–	–	–	99.3
1-13	295–305	66.8	0.22	0.06	32.7	0.12	0.06	–	–	–	99.5
1-16	325–335	65.0	0.01	0.05	34.4	0.08	0.05	–	–	–	99.4
1-18	345–357	68.7	0.02	0.06	27.6	0.10	0.06	–	–	–	96.4
2-9	259–274	67.9	0.12	0.05	31.5	0.40	0.05	–	–	–	99.4
2-10	290–305	68.8	0.22	0.05	29.6	0.37	0.05	–	–	–	98.3
3-8	107–122	86.0	0.27	0.05	13.4	0.11	0.05	–	–	–	99.3
3-15	259–274	73.5	0.19	0.08	24.3	0.07	0.09	–	–	–	97.8

^a Results from least-squares fits with energy varied for each component (shift reported in eV). Goodness-of-fit reported as 99% confidence limit (conf. limit) equal to three times the estimated standard deviation.

^b Fit with reference illite (IMt-1), Clay Minerals Society reference mineral previously analyzed by XAS (O'Day et al., 2004a).

^c Fit with a pyrite reference spectrum O'Day et al. (2004a).

^d Fit with green rust 2-hydroxy-sulfate spectrum prepared following Drissi et al. (1995).

^e Fit with synthetic 2-line ferrihydrite spectrum prepared following Schwertmann and Cornell (1991).

3.3. Sediment sequential extractions

Arsenic and iron concentrations from sequential chemical extractions of sediments are shown in Fig. 7 (numerical results tabulated in the Electronic Annex). Both extraction step 3 (0.2 M ammonium oxalate and oxalic acid (AAO)) and step 4 (1 M HCl) partially dissolved As-sulfide in some cores, in addition to the targeted amorphous and poorly crystalline iron and aluminum oxide phases, based on the fraction of sulfide indicated by XANES in the upper reduced zone (e.g., up to 100% in Core 1), and previous work (Wilkin and Ford, 2002). Thus, the fractions of arsenic and iron extracted in these two steps were combined in Fig. 7 (AAO + HCl) since targeted phases were not well distinguished by the individual steps.

In the upper reduced zone in Core 1, extracted arsenic was mostly associated with AAO + HCl and aqua-regia steps. Only about 10–15% of total arsenic was extracted in the first two steps, typically associated with weakly and strongly bound adsorbed fractions. In one sample each from the reduced zone of Cores 2 and 3, half to all of the arsenic was extracted in the first two steps. These samples,

however, had much lower total arsenic concentrations than most of the samples in Core 1 (Fig. 7). In the middle transition zone, total arsenic concentrations were low (<0.5 mmol kg⁻¹) and almost half to all of the arsenic was extracted in the first two steps, with a significant amount removed in the MgCl₂ extraction associated with an easily exchanged fraction. In the lower oxidized zone, total arsenic concentrations were higher (1–5 mmol kg⁻¹), especially in Core 1, and arsenic was distributed between adsorbed and AAO + HCl fractions.

In contrast to arsenic, a majority of iron in many samples was bound in the fraction digested in aqua-regia, reflecting association with crystalline solids. In all sediment samples, very little iron was removed in the first two steps associated with adsorbed species (Fig. 7). In the upper reduced zone, 15–35% of total iron was extracted prior to the aqua-regia step, mostly in the AAO + HCl fractions. With increasing depth to the oxidized zone, the fraction of extractable iron in the AAO + HCl fractions increased to up to about 65% in some samples. Analyses of iron XANES indicated a fraction of iron associated with pyrite in the upper reduced zone in samples from Cores 1 and 3,

Table 5
Iron EXAFS fit results.

Sample	Non-sulfide component ^a					Pyrite component ^b					
	Atom	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	ΔE_0 (eV)	Atom	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	ΔE_0 (eV)	χ^2
<i>Reduced zone</i>											
1-1	O	6.0 ^c	2.02	0.0090	−0.3						0.49
	Fe	1.0	3.08	0.0050 ^c							
	Si	1.0	3.26 ^c	0.0065 ^c							
	Fe	1.3	3.44	0.0080 ^c							
1-2 ^d	O	1.8	2.01	0.0050 ^c	−1.0	S	1.0	2.25 ^c	0.0012 ^c	−5.8	0.44
	Fe	0.5	3.08	0.0050 ^c		S	1.0/	3.44 ^c	0.0066 ^c		
	Si	0.6	3.26 ^c	0.0065 ^c		Fe	2.0/	3.83 ^c	0.0066 ^c		
1-4 ^d	O	2.1	2.00	0.0060 ^c	−1.1	S	0.7	2.25 ^c	0.0012 ^c	−6.9	0.35
	Fe	0.7	3.08	0.0050 ^c		S	0.7/	3.44 ^c	0.0066 ^c		
	Si	0.6	3.26 ^c	0.0065 ^c		Fe	1.3/	3.83 ^c	0.010 ^c		
2-3	O	6.0 ^c	2.00	0.0064	−0.8						1.68
	Fe	2.7	3.08	0.0050 ^c							
	Si	4.1	3.26 ^c	0.0065 ^c							
	Fe	3.9	3.40	0.0080 ^c							
	Fe	3.3	3.24	0.0070 ^c							
3-5	O	5.2	2.01	0.0060 ^c	−0.3	S	0.2	2.25 ^c	0.0012 ^c	−2.7	0.20
	Fe	1.1	3.08	0.0050 ^c		S	0.2/	3.44 ^c	0.0066 ^c		
	Si	1.3	3.26 ^c	0.0065 ^c		Fe	0.4/	3.83 ^c	0.0066 ^c		
	Fe	0.9	3.43	0.0080 ^c							
3-6	O	5.8	2.01	0.0075	−0.9	S	0.2	2.25 ^c	0.0012 ^c	1.5	0.13
	Fe	1.2	3.09	0.0050 ^c		S	0.2/	3.44 ^c	0.0066 ^c		
	Si	2.0	3.26 ^c	0.0065 ^c		Fe	0.4/	3.83 ^c	0.0066 ^c		
	Fe	1.2	3.40	0.0080 ^c							
<i>Transition zone</i>						χ^2					
1-8	O	6.0 ^c	2.02	0.0093	−0.8	0.38					
	Fe	1.4	3.04	0.0050 ^c							
	Si	1.5	3.26 ^c	0.0065 ^c							
	Fe	2.1	3.41	0.0080 ^c							
	Fe	1.7	3.20	0.0070 ^c							
2-7	O	6.0 ^c	2.01	0.0074	−0.6	0.37					
	Fe	1.3	3.08	0.0050 ^c							
	Si	2.0	3.26 ^c	0.0065 ^c							
	Fe	1.4	3.37	0.0080 ^c							
2-8	O	6.0 ^c	2.00	0.0086	−0.8	0.76					
	Fe	1.4	3.04	0.0050 ^c							
	Si	3.7	3.26 ^c	0.0065 ^c							
	Fe	3.1	3.38	0.0080 ^c							
	Fe	2.8	3.20	0.0070 ^c							
3-13	O	6.0 ^c	2.01	0.0085	−1.0	0.66					
	Fe	1.4	3.06	0.0050 ^c							
	Si	3.1	3.26 ^c	0.0065 ^c							
	Fe	2.5	3.40	0.0080 ^c							
	Fe	2.1	3.22	0.0070 ^c							
<i>Oxidized zone</i>						χ^2					
1-16	O	6.0 ^c	2.00	0.0090	−0.8	0.35					
	Fe	1.0	3.06	0.0050 ^c							
	Si	1.3	3.26 ^c	0.0065 ^c							
	Fe	1.7	3.41	0.0080 ^c							
2-10	O	6.0 ^c	2.01	0.0075	−0.1	0.19					
	Fe	1.2	3.07	0.0050 ^c							
	Si	1.5	3.26 ^c	0.0065 ^c							
	Fe	1.5	3.40	0.0080 ^c							

Table 5 (continued)

^a Non-Sulfide component: Phyllosilicate-oxide composite; values for σ^2 were fixed for all shells based on empirical fits to reference compounds of similar composition and structure; R , N , and ΔE_0 (one variable for all shells) were varied, except for the Fe-Si shell, which will co-vary with Fe shells if floated independently. This shell was fixed on a typical crystallographic distances for Fe-Si in phyllosilicates (see O'Day et al., 2004a).

^b Pyrite component: Interatomic distances (R) were fixed on crystallographic values from pyrite and σ^2 was fixed on values determined from fits to reference sulfide compounds; N for each shell was varied as a linked parameter in proportions based on the known coordination in pyrite; ΔE_0 was a single variable for all shells; $S_0^2 = 1$ (O'Day et al., 2004a).

^c Parameter fixed in least-squares fit using value from fits to reference compounds; / parameter linked in fit to the parameter directly above; $S_0^2 = 0.7$ for spectra containing no Fe-sulfide (O'Day et al., 2004a).

^d Fit reported previously (O'Day et al., 2004b).

varying from about 5–34% of the XAS iron signal. It is not apparent from the extraction data if iron sulfides were dissolved in the AAO + HCl or aqua-regia steps (volatilized sulfur was not measured). It is likely that some iron sulfide was extracted in both steps, depending on its crystallinity in the sediments. In the transition and oxidized zones, no iron sulfides were present based on XANES analyses. Extraction in the AAO + HCl step probably dissolved poorly crystalline solids and small particles, such as iron oxides and clay minerals.

3.4. Aqueous chemistry

Concentrations of dissolved arsenic and other constituents in groundwater sampled from site monitoring wells are reported in Table 6. Direct information on groundwater chemistry was restricted to the screened intervals in monitoring wells, all of which were in the lower saturated zone below water table level (pore waters were not recovered successfully from sediment cores). Total dissolved arsenic concentrations decreased from a high of 42 μM in well WCC-10 beneath the former industrial site, which had the highest fraction of As(V) compared to As(III) (69%), to <0.10 μM in tidal marsh wells (Table 6 and Fig. 1). Monitoring wells within the tidal marsh had lower total arsenic and contained both dissolved As(III) (44–56%) and As(V). Well W-123, furthest downgradient in the tidal marsh, had 72% As(III). Field Eh measurements showed qualitatively a trend to more reducing conditions in the marsh subsurface compared to upland well sites (S.S. Papadopoulos & Associates, 2000; Geomatrix and S.S. Papadopoulos & Associates, 2002). Dissolved iron and manganese concentrations were also elevated in wells within the marsh area (Table 6). Total dissolved solids increased in groundwater from upland wells to the marsh from 2210 to 26,700 mg L^{-1} , indicating a change from mostly fresh groundwater to a mixture of fresh water and saline Bay water, and pH generally decreased. Trace dissolved elements in all wells (other than arsenic) did not show elevated concentrations above background levels (data not reported). Nitrate concentrations correlated with other groundwater constituents and were just above the limit of detection in most wells, with elevated nitrate in wells M-4 and W-129 (Table 6). Arsenic, iron, and manganese concentrations measured in wells in the tidal marsh area cannot be explained by mixing and dilution alone if chloride is assumed to be conservative and the chloride concentration of South San Francisco Bay water (Table 6) is used as a

qualitative guide to the extent of dilution of fresh groundwater with saline bay water.

4. DISCUSSION

4.1. Speciation of sediment arsenic and iron

4.1.1. Reduced zone

Spectroscopic characterization from arsenic and iron XAS, together with supporting electron microscopy and XRD, showed changes in arsenic and labile iron speciation on a centimeter scale that were used to define *in situ* subsurface redox zones in the tidal marsh. These results showed that arsenic sulfide phases (or possibly sorbed species, see below), with either realgar-like or orpiment-like local atomic structure, were present in the upper reduced sediment zone (below the depth of surface oxidation), with or without variable proportions of As(III) or As(V) bonded to oxygen. The source of arsenic contamination at this site was arsenate and arsenite salts for agricultural herbicide production, and no sulfide forms of arsenic were used (USEPA, 1992). Thus, arsenic reduction and precipitation of arsenic sulfide phases or species most likely occurred *in situ*.

Distinct differences in the local atomic structure around arsenic in realgar, orpiment, arsenopyrite, and arsenic-bearing pyrite permit interpretation of the primary mode(s) of arsenic speciation in sulfide phases (Savage et al., 2000; O'Day et al., 2004b; Gallegos et al., 2007; Lowers et al., 2007). The presence of As-As dimers in realgar-type phases gives rise to the strong beat pattern seen in the EXAFS, which corresponds to the large peaks in the Fourier transform between 2 and 3.5 Å (uncorrected for phase shift; Fig. 5), which are not present in orpiment-type structures and thus are diagnostic of realgar-type local structure. Realgar polymorphs (α , β , ω , and pararealgar) and related As-S compounds with near 1:1 stoichiometry have covalently bonded cage-like structures of arsenic and sulfur atoms (Porter and Sheldrick, 1972; Bonazzi et al., 1995, 1996; Bonazzi and Bindi, 2008). Because EXAFS probes local atomic structure, realgar-type polymorphs are not distinguishable from each other on the basis of their EXAFS spectra alone. However, arsenopyrite and arsenic structurally substituting for sulfur in pyrite produce distinctly different EXAFS from either orpiment or realgar (Savage et al., 2000). Substitution of As(III) for iron in pyrite has been reported recently, but its occurrence to date is limited to acidic, high sulfidation hydrothermal deposits (Deditius et al., 2008). Correlation of XANES spectra with structural determinations from

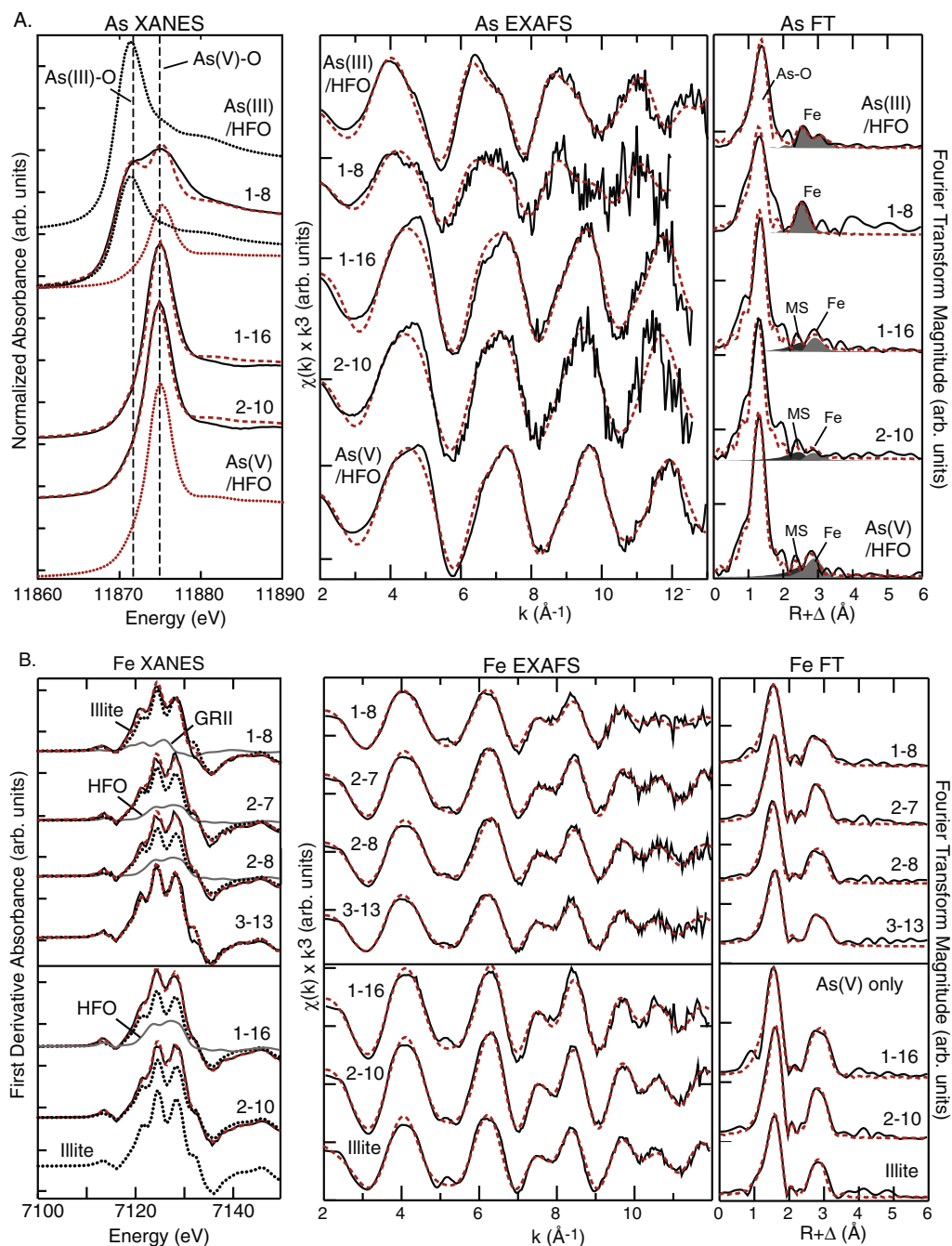


Fig. 6. X-ray absorption spectra of sediment samples from the transition and oxidized zones compared with reference compounds. Solid black lines are data; dashed lines are least-squares best fits. (A) Arsenic XANES, EXAFS, and Fourier transforms (FT). XANES shows the fit deconvolutions with reference spectra: As(III) or As(V) sorbed to hydrous ferric oxide (HFO) (fit results in Table 2). EXAFS fits results are given in Table 3. Light shading in FT shows the fraction of EXAFS amplitude associated with iron backscattering atoms; dark shading shows backscattering contributions from multiple scattering. (B) Iron XANES, EXAFS, and Fourier transforms (FT). First-derivative XANES shows fit deconvolutions with reference illite, hydrous ferric oxide (HFO), and synthetic green rust (GRII) (fit results in Table 4). EXAFS fit results are given in Table 5. Shading in XANES and FT shows the fraction of EXAFS amplitude associated with pyrite, if present. Reference compounds: natural illite (IMt-1) from Clay Mineral Society Source Clays Repository.

EXAFS in reference compounds also establishes that shifts in maximum absorption energy shown above can be used to distinguish among realgar-type, orpiment-type, and arsenopyrite/pyrite-type arsenic species (with accurate calibration) (Savage et al., 2000; Bostick et al., 2004; O'Day et al., 2004b;

Gallegos et al., 2007; Lowers et al., 2007). The sediment sample XANES and EXAFS spectra constrain the arsenic sulfide phases to realgar-like and orpiment-like at the molecular scale, with no spectral evidence for substitution in pyrite or arsenopyrite.

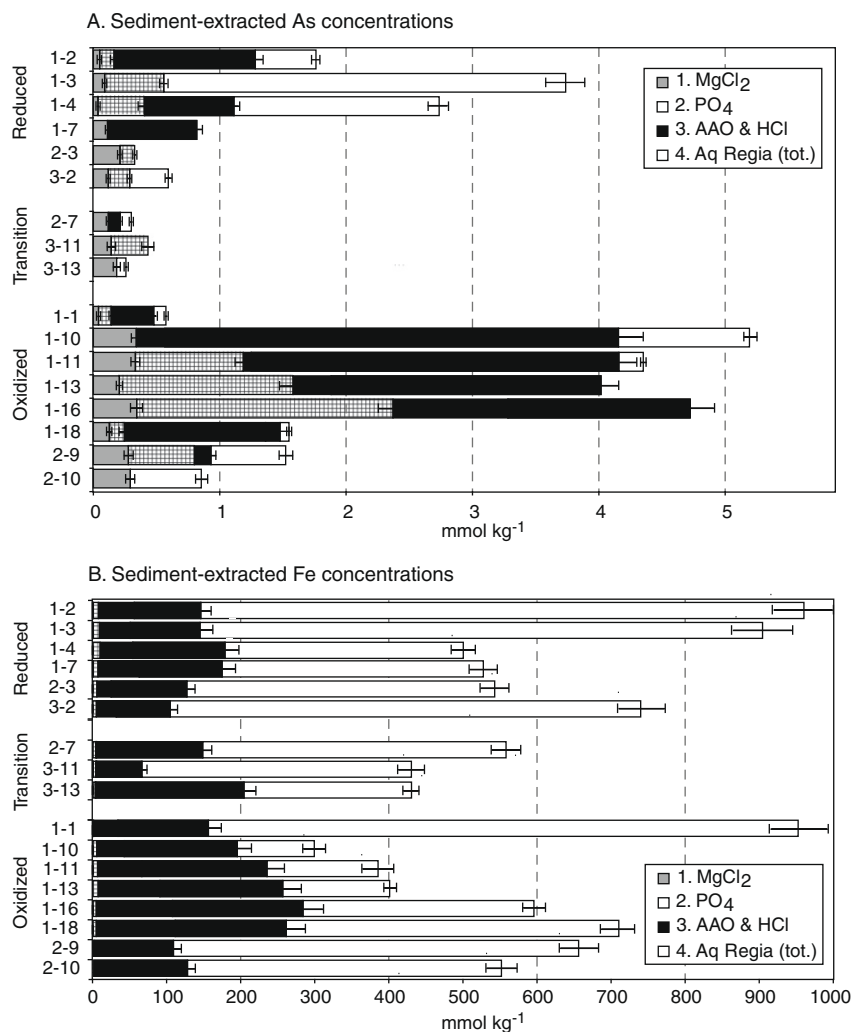


Fig. 7. Sequential chemical extractions of selected sediment core samples in the following order: (1) 1.0 M MgCl_2 ; (2) 1.0 M NaH_2PO_4 ; (3) 0.2 M ammonium oxalate and oxalic acid followed by 1.0 M HCl (extracted fractions combined); (4) aqua-regia reflux (12 M HCl + HNO_3) done on a separate sample split (total concentration). (A) Arsenic. (B) Iron.

Most of the sediments in the upper sulfide zone contained mixtures of arsenic sulfide and As(V)-O species. The presence of reduced and oxidized species in the same bulk sample is not an artifact of post-collection oxidation based on rigorous preservation and replicate measurements. Analyses of EXAFS spectra from this zone, although limited, showed structural features beyond the first coordination shell in samples with sulfide that were consistent with orpiment- or realgar-type structures, and did not indicate only thioarsenite or thioarsenate surface complexes (Bostick et al., 2005; Gallegos et al., 2007), although the presence of a minor fraction of sorbed species could be masked by crystalline phases. Arsenic was not detected with SEM/EDS, suggesting that particle size is small (perhaps micro-to-nanoscale) or particle abundance is low, or both, for arsenic-bearing phases. No sulfide phases (either arsenic or iron) were detected in bulk sediments with XRD. In the analysis of bulk sediments from Core 1, reactive sulfide was detected in only two samples that had spectroscopic evidence for both arsenic and iron sulfide.

Although detection limits by this method are not very low, bulk chemical analyses indicated that the reduced zone did not contain large amounts of sedimentary sulfide. Interestingly, some samples were dominated by arsenic sulfide species in their as X-ray spectra (up to 100%) but the corresponding Fe XANES indicated much lower fractions of iron sulfide (Table 4), indicating the importance of arsenic bonding to sulfide as a sequestration mechanism. The oxidized arsenic species in the reduced zone sediments were clearly identified in spectra as As(V)-O rather than As(III)-O , with the exception of one sample that contained both As(III)-O and As(V)-O in addition to As-sulfide. We interpret the mixture of arsenic sulfide and arsenic oxide in the bulk X-ray absorption spectra as probably spatially distinct species, although the scale is unknown and constrained spectroscopically only as greater than the molecular-scale probe of XAS ($\sim 3\text{--}5 \text{ \AA}$).

Sequential chemical extractions of sediment from the reduced zone indicated a mixture of easily desorbed and recalcitrant arsenic. Extractions from Core 1 showed that

Table 6
Groundwater chemistry in monitoring wells (see Fig. 1 for well locations).^a

Well	As _{tot} (μM)	As(III) (μM)	As(V) ^b (μM)	Ca (mM)	Fe (mM)	Mg (mM)	Mn (μM)	Na (mM)	Cl [−] (mM)	NO ₃ [−] (μM)	SO ₄ ^{2−} (mM)	Alk (as CaCO ₃) (mM)	EC (μS cm ^{−1})	pH	Eh (mV)	T (C°)
D.L. ^c	1.3 × 10 ^{−3}	1.3 × 10 ^{−3}	1.3 × 10 ^{−3}	2.5 × 10 ^{−3}	1.8 × 10 ^{−3}	4.1 × 10 ^{−3}	0.18	4.3 × 10 ^{−3}	0.06	0.15	0.02	0.02	0.1	0.01	0.1	0.1
W-114	0.422	0.235	0.187	7.76	0.217	37.24	89.19	344.07	411.8	0.16	14.05	11.2	30800	7.2	n.a.	14.7
W-115	0.410	0.184	0.226	13.22	0.362	46.08	131.1	350.59	394.9	0.32	19.57	14.8	29300	6.8, 6.9 ^d	−113, −73 ^d	14.8
W-123	0.105	0.076	0.029	9.282	0.437	38.59	54.61	365.38	425.9	0.16	16.45	12.0	29900	6.3, 7.0 ^d	n.a., −129 ^d	14.5
W-128	0.049	0.003	0.047	6.737	0.295	6.007	69.17	30.49	19.86	0.65	5.06	3.18	3090	6.5	n.a.	19.0
W-129	0.067	n.a.	n.a.	9.107	0.158	35.38	63.71	347.11	431.6	6.29	17.07	11.1	10700	6.4	n.a.	18.7
WCC-10	42.0	13.2	28.8	9.556	0.002	6.418	38.22	58.29	42.31	0.16	4.87	4.00	5290	7.1, 7.9 ^d	103, 69 ^d	19.3
M-4	3.32	1.86	1.47	6.163	0.114	24.15	7.28	230.1	249.9	4.84	13.74	7.57	21000	6.4, 7.0 ^d	−67 ^d	14.3
S-1	5.81	n.a.	n.a.	0.631	0.017	1.392	18.42	39.10	10.37	n.a.	2.00	6.66 ^e	4530	7.5	−63	18.4
S-2	26.6	n.a.	n.a.	9.282	0.211	37.30	98.82	280.3	182.5	n.a.	16.44	5.12 ^e	42900	6.8	−69	11.9
S-3	0.187	n.a.	n.a.	8.987	0.203	36.93	158.0	294.9	185.7	n.a.	16.21	4.90 ^e	43300	6.7	−58	13.0
S-4	0.093	n.a.	n.a.	8.835	0.259	38.13	156.8	305.2	187.4	n.a.	17.71	6.04 ^e	44700	6.7	−64	14.4
Bay water ^f	0.026	n.d.	n.d.	10.28 ^g	n.d.	52.66 ^h	0.07	468.9 ⁱ	498.6	0.32	9.35 ^j	n.a.	42030	7.9	n.a.	n.a.

^a n.d., not detected; n.a., not analyzed; all analyses from 2002, except where indicated.

^b As(V) was determined by difference of As_{tot} and As(III) from ion-exchange separation.

^c Instrument detection limit (D.L.).

^d Analysis from 1999.

^e Measured by titration (APHA Standard Methods 2320B); all other alkalinity values estimated from Ca + Mg concentrations.

^f Bay water from Gandesbery et al. (1999); major elements estimated from salinity measurements.

^g Olson and Chen (1982).

^h Carpenter and Manella (1973).

ⁱ Millero and Leung (1976).

^j Morris and Riley (1966).

the majority of arsenic was associated with a more recalcitrant phase or phases (samples 1-2, 1-3, 1-4, 1-7) extracted by AAO, HCl, or aqua-regia digest. XANES and EXAFS showed that this core was dominated mostly by realgar-type arsenic (with no or minor As(V)-O or orpiment-type). Cores 2 and 3, which contained more orpiment-like arsenic sulfide and As(V)-O than Core 1, had lower total arsenic concentrations and more easily extracted arsenic. This may suggest that sediments with realgar-type arsenic in Core 1, which was closer to the former contamination source and had less tidal influence than Cores 2 and 3, were more crystalline (i.e., recalcitrant) and perhaps more aged than arsenic sulfide in Cores 2 or 3. The extraction data together with spectroscopic evidence support the interpretation of arsenic sulfide predominantly as precipitated orpiment- or realgar-type phases, possibly with a variable fraction of sorbed As-sulfide species, and in association with iron sulfide solids in some samples. Realgar-type arsenic was detected in both Cores 1 and 3, and it is not expected that realgar is a product of orpiment aging. Thermodynamic calculations show that formation of either realgar- or orpiment-type phases is possible at ambient temperature depending on the activity of sulfide and arsenic, and on system pH and Eh (O'Day et al., 2004b; Gallegos et al., 2007, 2008; and analysis below). However, previous studies have noted the difficulty in abiotically precipitating crystalline or amorphous realgar at room temperature (Nordstrom and Archer, 2003; Gallegos et al., 2008), which may point to the importance of microbial mediation in the formation of arsenic sulfide phases at ambient temperatures.

Analyses of the iron EXAFS spectra indicated the formation of iron sulfide as pyrite in minor amounts in some of the sediments in the reduced zone, but not in all samples in which arsenic sulfide phases were identified. The spectral signal for iron in sediments was dominated by iron substitution in detrital phyllosilicate minerals (mostly mica-type phases). The iron sulfide fraction was identified as pyrite (comprising 0–34% of total iron from XAS), not FeS (as mackinawite or greigite) on the basis of XANES and EXAFS analysis, although minor phases would not be detected by this method (practical XAS detection limits for iron phases are about 5% Fe by atomic mass; see O'Day et al., 2004a). The spectral interpretation is consistent with SEM and EDS observations of Core 1 sediments that showed small, cubic crystals rich in iron and sulfur in some Core 1 samples. Iron sulfide phases were not detected in Core 2, and they comprised a small fraction of the iron XAS signal (<10%) in Core 3. The difference in pyrite abundances between Core 1 and Cores 2 and 3, and the presence of As(V) in Cores 2 and 3 noted above, suggest that sediments were generally more oxidized in Cores 2 and 3 than in Core 1.

4.1.2. Transition and oxidized zones

The middle transition zone, defined by absence of sulfide and the presence of both As(III) and As(V) ligated by oxygen, coincided with the approximate seasonal variation in water level in the shallow aquifer (Fig. 2). This mixed zone was more compressed vertically in Core 1 than in the other

two cores, probably because of hydrologic flow. Total sediment arsenic concentrations were lowest in this zone, with a majority of arsenic associated with easily extracted fractions. Spectroscopic and extraction results indicated mixtures of sorbed As(III)-O and As(V)-O species. Iron XANES spectra were well fit by a dominant detrital phyllosilicate component and a secondary Fe(III)-oxide component (0–35%). One spectrum in the transition zone and one spectrum near the top of the oxidized zone were better fit with a mixed Fe(II,III)-oxide phase (either green rust or magnetite) rather than Fe(III)-oxide, comprising about 10% of the total iron signal. Silt and clay sediments in the transition zone are subject to wetting and drying from seasonal raising and lowering of water level. Arsenic and iron speciation in this zone reflects cycles of arsenic reduction and oxidation, and leaching of arsenic to groundwater as indicated by the concentration minima observed in the sediments.

In the oxidized zone in which only As(V)-O was present, total arsenic concentrations increased, particularly in Core 1 (Fig. 2). Arsenic was distributed between adsorbed and HCl + AAO-extractable fractions and there was an overall increase in HCl + AAO-extractable iron compared with shallower depths (Fig. 7). The Fe(III)-oxide component from XANES fits was ~30% on average ($n = 8$; Table 4). Results from XAS and sequential extractions are consistent with a mixture of As(V) and As(V) sorbed and/or co-precipitated with Fe(III)-(hydr)oxide in this zone. Arsenic, as oxidized As(V), is probably being retained in the saturated oxic groundwater sediments by a combination of adsorption and co-precipitation with iron, with total arsenic sediment concentrations decreasing away from the former contaminant source.

4.2. Spatial relationships in sediment and shallow groundwater chemistry

Vertical zonation and lateral speciation changes observed in sediments, together with groundwater chemistry from monitoring wells, provide constraints on processes controlling arsenic speciation and distribution. In the saturated zone, dissolved and sediment arsenic concentrations decreased rapidly with distance from the former source where fresh groundwater mixes with higher salinity San Francisco Bay water infiltrating the subsurface at the edge of the tidal marsh. There was also a general trend of an increasing fraction of dissolved As(III) in tidal marsh wells compared to upland wells, although the data were variable among limited measurements (Table 6). Speciation in sediments and porewaters can be interpreted from an equilibrium perspective by examining ranges of Eh, pH, and sulfur activity at arsenic and iron concentrations representative of those observed at the site (Fig. 8A). Groundwater in upland areas was relatively oxidized and fell within regions where aqueous As(V) and Fe(III) phases (shown as ferrihydrite) or Fe(II,III) phases (shown as green rust) were the predominant species, based on measured pH and Eh (Pt electrode) (Table 6 and Fig. 8A). Samples from wells in the tidal marsh were more reduced and fell within the predominant stability fields of As(III) and dissolved Fe^{2+} . None of the water samples fell within the calculated stability fields

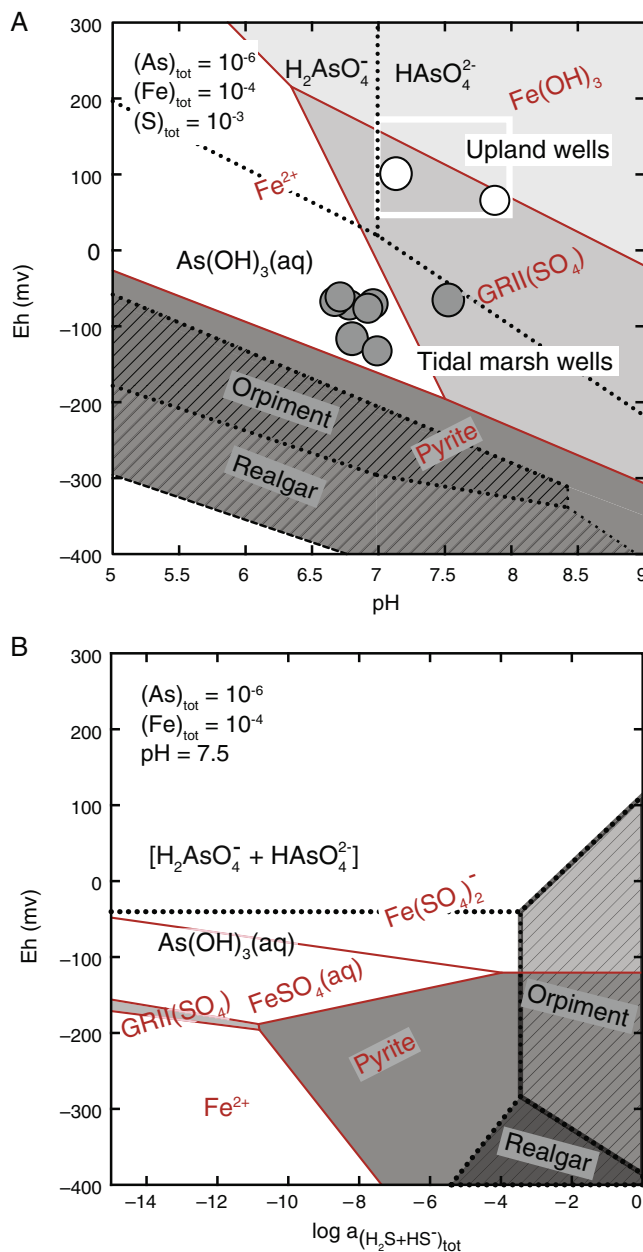


Fig. 8. Equilibrium phase relations calculated for total element activities representative of the study site. (A) Eh–pH predominance diagram showing equilibrium among dissolved (unshaded, dashed line) and solid phase (hatched, shaded) arsenic, and aqueous (unshaded, solid line) and solid phase (shaded) iron at $(\text{Fe})_{\text{total}} = 10^{-4}$, $(\text{As})_{\text{total}} = 10^{-6}$, $(\text{S})_{\text{total}} = 10^{-3}$. Field-measured Eh and pH from groundwater samples shown as circles (shaded: tidal marsh; open: upland from marsh; Table 6) were taken from wells in the saturated aquifer below the reduced sediment zone. Box shows the range of Eh and pH measured in upland wells between 1999 and 2002. (B) Phase relations among dissolved species and solid phases calculated for the same system as (A) as a function of Eh and total log sulfide ($\text{H}_2\text{S} + \text{HS}^-$) activity at pH 7.5. Hematite, goethite, and magnetite suppressed to show metastable iron phases (25 °C).

where iron or arsenic sulfide phases are predicted to be dominant, but this is not surprising since extraction of pore waters from sediments in the low porosity sulfide zone was unsuccessful. All of the analyzed groundwater was sampled from the saturated aquifer below the sulfate-reduced zone. Although the porewater analyses were limited, the presence of reduced aqueous species in the saturated zone in some wells indicates active biogeochemical reduction of arsenic and iron from sediments and partitioning to groundwater.

Evidence from spectroscopic characterization of sediments (as opposed to porewater) indicated a subsurface zone where speciation in unsaturated (above the water table) and transition zone sediments (within the range of water table fluctuation) varied on the centimeter scale from reduced (sulfide present) to oxidized (As(V)–O only present). These observations indicate a dynamic system in which the activity of reduced sulfur (as total sulfide) varies considerably in time and space, and is probably controlled

by rates of microbial sulfate reduction and biotic and abiotic sulfide oxidation. The effect of variable sulfide can be illustrated as a function of total sulfide activity ($\text{H}_2\text{S} + \text{HS}^-$) for fixed pH (= 7.5) and variable Eh (Fig. 8B) at the same total arsenic and iron concentrations used in Fig. 8A. At equilibrium under these conditions, orpiment may stably co-exist with dissolved As(III) and/or As(V), but with the latter only at high total sulfide activity and slightly more oxidized conditions. Orpiment may or may not co-exist with pyrite at equilibrium. Realgar, in contrast, can co-exist only with dissolved As(III) and not with As(V) at equilibrium, and is stable only under conditions of pyrite stability.

It is important to recognize that the sizes of the predominance fields for solid phases shown in Fig. 8 are dependent on the total concentrations of arsenic, iron, and sulfur selected for the calculation (see e.g., O'Day et al., 2004b), as well as uncertainty in thermodynamic data for metastable phases such as green rust and ferrihydrite. For systems in which precipitation and dissolution are relatively rapid, the labile fraction of the component, rather than the total sediment concentration, is probably a more representative concentration for modeling natural systems. In these calculations, total iron concentration (representing rapidly reacting iron in the system) was two orders of magnitude higher than total arsenic concentration, which is in the range of many sites contaminated with arsenic. Calculations at higher iron concentration expand the stability field of metastable green rust; at lower pH, green rust is not stable. Total sulfur in many systems may be similar to the concentration of labile iron but it cycles rapidly, such that sulfide activity is probably locally variable. Although an equilibrium analysis neglects kinetic processes that are obviously important, these calculations point out that arsenate(aq), arsenite(aq), and orpiment(s) may co-exist at equilibrium under conditions of pH and arsenic, iron, and sulfur concentrations found in natural environments. Thus, the spectroscopic observations of mixed arsenic species in the sediments at the study site are not necessarily a result of kinetic limitations, and may represent local equilibrium controlled by biotic and abiotic reactions that involve sulfur reduction and oxidation, perhaps on a μm -to-cm scale.

4.3. Reaction progress modeling

The dynamic interplay between sorption/desorption and dissolution/precipitation processes among arsenic, iron, and sulfur in systems cycling from oxidized to reduced (or vice versa) can be simulated for a general case using a reaction progress modeling approach. This type of redox cycling is found, for example, in systems experiencing seasonal changes in water level elevation, or in aquifers periodically infiltrated by oxygenated recharge waters that become progressively reduced by microbial organic matter oxidation (e.g., Dhar et al., 2008; Polizzotto et al., 2008). In the absence of direct kinetic measurements, the progressive change from a sulfur- and iron-oxidized system to the reduction of iron and sulfate and presence of sulfide can be modeled by a reaction progress variable that reduces the overall redox potential (Eh or pe) of the system. Lower-

ing of system redox potential (the reaction progress) was calculated as a function of the amount of acetic acid (representing labile organic matter) titrated into the system as a surrogate for microbial organic matter respiration. One model of the consequences of this reduction pathway is illustrated in Fig. 9. The model parameters are generalizations of conditions observed at the study site, but are intended to represent arsenic, iron, and sulfur concentrations and ratios that may be found at sites of arsenic contamination from anthropogenic or natural sources.

The initial model conditions (Table 1) were set by assuming As(V) sorbed to ferrihydrite (100 mmol) and a system arsenic concentration of 0.45 mM (1 kg solution), giving a total system Fe/As ratio of 222 (Fig. 9). Initial equilibrium was established between As-sorbed ferrihydrite and an aqueous solution with major element chemistry generalized from site groundwater in the tidal marsh area at oxygenated conditions (Table 1). Therefore, this model scenario examines redox evolution under conditions of elevated sulfate and ionic strength associated with brackish, marsh porewaters rather than low salinity, fresh groundwater. At initial model conditions, all As(V) is sorbed, with a model surface concentration of $0.07 \mu\text{mol As m}^{-2}$ (assuming a ferrihydrite surface area of $600 \text{ m}^2 \text{ g}^{-1}$). Neither pH nor Eh was constrained during reaction progress.

As the system becomes progressively reduced in this scenario, ferrihydrite is reductively dissolved, which leads to the formation of a green rust phase (GR(II), sulfate form) under these conditions. Because of the high surface area of ferrihydrite, As(V) remains sorbed as long as system pH is buffered by iron mineral equilibria and ferrihydrite is present (Fig. 9). Once ferrihydrite is exhausted, arsenate is partitioned to solution and reduced to arsenite. Green rust forms at the ratio of iron to sulfur used in this model, but the total amount that forms is limited by total sulfur (rather than iron) in the system. In systems at lower pH and/or lower total iron, GR is not thermodynamically stable (O'Day et al., 2004b). It is expected that GR will be a poorer sorbent of arsenic than ferrihydrite due to its lower surface area (Table 1). The model predicts release of about 60–90% of the total arsenic in the system to solution when GR is the stable iron phase. Furthermore, when ferrihydrite is exhausted and buffering between ferrihydrite and GR eliminated, pH increases, Eh decreases, and dissolved Fe^{2+} begins to increase. These model predictions are qualitatively consistent with observations in anaerobic groundwater aquifers with elevated dissolved arsenic and iron concentrations (Amini et al., 2008; McMahon and Chapelle, 2008; Hering et al., in press).

As conditions become more reduced and dissolved sulfate is reduced to sulfide, GR(II) (sulfate form) is replaced by pyrite and GRI (carbonate form) as the stable iron phases. Arsenic is removed from solution by formation of either realgar or orpiment. At the Fe–As–S concentrations used in this model, realgar is the stable As-sulfide phase; at different Fe–As–S proportions (e.g., higher S and/or lower Fe), orpiment is stable. At the most reduced conditions, GRI becomes unstable and only sulfide phases remain. Dissolved Fe^{2+} concentrations are controlled by pyrite solubility (assuming this is the stable iron sulfide

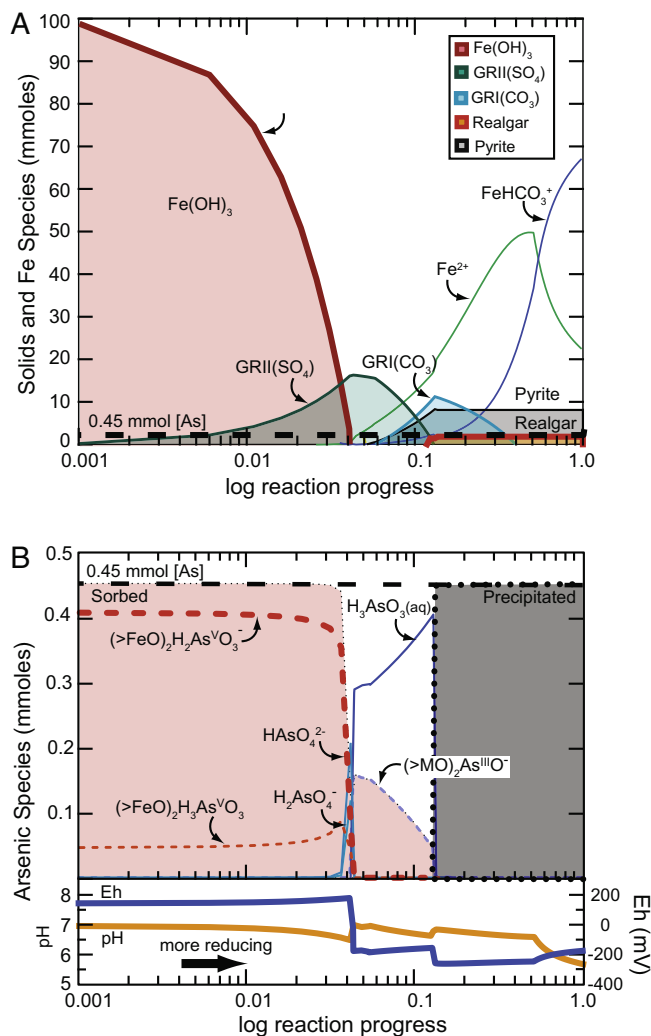


Fig. 9. Reaction progress model from oxidized to reduced conditions in the system As–Fe–S–CO₂. Reaction progress was driven by acetic acid titration as a surrogate for organic matter respiration. Initial conditions: 1 mmol Fe(OH)₃ (ferrihydrite) with [As]_{tot} = 0.45 mM (100% sorbed); pH = 7.2 (see Table 1 for complete system description). (A) Solid and dissolved iron phases (shaded) and species (unshaded). (B) Sorbed (shaded light gray), dissolved (unshaded), and solid (shaded dark gray) arsenic species and phases, and model results for pH and Eh as a function of reaction progress.

phase), whereas dissolved arsenic concentrations are controlled by the stable As-sulfide phase under selected model conditions, neglecting sorption of iron- or arsenic sulfide surface complexes (Gallegos et al., 2007), or formation of dissolved thioarsenite or thioarsenate species which may be important under conditions of high dissolved sulfide (Helz and Tossell, 2008). Most freshwater systems are expected to have lower total sulfur concentrations than the system illustrated here, such that sulfide mineral solubility will most likely control dissolved arsenic and iron concentrations under sulfate-reduced conditions, and sulfide precipitation will be limited by the amount of available sulfate and its microbially-controlled rate of reduction.

5. CONCLUSIONS

Mechanistic processes controlling arsenic speciation, sequestration, and mobilization in shallow subsurface sedi-

ments that span a range of redox conditions were examined over short vertical and horizontal spatial scales (centimeters to meters) using a combination of spectroscopic and chemical analyses and geochemical modeling. Chemical and spectroscopic characterization of vertical and lateral changes in sediment speciation and pore water chemistry showed that two different mechanisms for arsenic attenuation were active: first, sulfate reduction in the top zone, resulting in formation of arsenic and iron sulfide in sediments, provided attenuation during vertical infiltration of surface water; second, oxidation and sorption in the lower oxidized zone by the influx of oxygenated aquifer water promoted lateral attenuation. Distinct differences in the local atomic structure around arsenic in realgar-type compared to orpiment-type phases, in particular the presence of As–As dimers in realgar, are diagnostic of the presence of these phases (or their polymorphs). This study demonstrates that both realgar-type and orpiment-type phases

can form in sulfate-reducing sediments at ambient conditions, with realgar predicted as the stable phase in the presence of pyrite and As(III) under more reduced conditions than orpiment. The presence of both types of these phases at arsenic concentrations elevated above background is consistent with thermodynamic relationships (Nordstrom and Archer, 2003; Helz and Tossell, 2008), although there remain uncertainties in the rates at which realgar-type phases may form at ambient temperatures and in the thermodynamic data for arsenic sulfide species and phases.

Geochemical simulation using the reaction progress approach to provide thermodynamic constraints (solubility and sorption) during changes from oxidized to reduced conditions, with model parameters generalized from field observations, lend insight into dynamic processes and factors that may control dissolved concentrations. Arsenic mobilization may occur in the zone affected by seasonal fluctuations of groundwater level potentially during two conditions: when ground water level rises, flooding reduced sediments and promoting oxidative dissolution of sulfide; and when water level falls and oxidized sediments become progressively reduced as microbial action consumes O₂ and other electron acceptors, reducing arsenic, iron, and manganese (the latter being particularly important in low-Fe systems, e.g., Amirbahman et al., 2006; Choi et al., 2009). During an oxidative cycle, oxidation of iron and arsenic, leading to (co-)precipitation of Fe(III)-(hydr)oxides and arsenate and/or pH-controlled arsenate sorption, will be an effective attenuation mechanism as long as oxidative capacity is maintained and the ratio of arsenic to labile iron (and potentially manganese) is low. During a reduction cycle, arsenite (and labile ferrous iron) will be partitioned to porewaters until sulfate reduction produces sufficient dissolved sulfide concentrations to exceed the solubility of solid sulfide phases. At intermediate redox states, the concentration of labile iron in the system will determine whether green-rust-type phases (which may age to magnetite) form that may provide new sorption sites for arsenic. In freshwater aquifers with low dissolved sulfate and thus limited potential for sulfate reduction, pH-controlled sorption and competition with other dissolved species will control dissolved arsenic concentrations.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2009.06.025.

REFERENCES

- Aggett J. and O'Brian G. A. (1985) Detailed model for the mobility of arsenic in lacustrine sediments based on measurements in Lake Ohakuri. *Environ. Sci. Technol.* **19**, 231–238.
- Amini M., Abbaspour K. C., Berg M., Winkel L., Hug S. J., Hoehn E., Yang H. and Johnson C. A. (2008) Statistical modeling of global geogenic arsenic contamination in groundwater. *Environ. Sci. Technol.* **42**, 3669–3675.
- Amirbahman A., Kent D. B., Curtis G. P. and Davis J. A. (2006) Kinetics of sorption and abiotic oxidation of arsenic(III) by aquifer materials. *Geochim. Cosmochim. Acta* **70**, 533–547.
- Ankudinov A. L., Ravel B., Rehr J. J. and Conradson S. D. (1998) Real-space multiple-scattering calculation and interpretation of X-ray-absorption near-edge structure. *Phys. Rev. B* **58**, 7565–7576.
- APHA (1995) *Standard Methods for the Examination of Water and Wastewater*, 19th ed. APHA (American Public Health Association), AWWA (American Water Works Association), WEF (Water Environment Federation), Washington, DC.
- Bethke C. M. (1994) *The Geochemist's Workbench. A User's Guide to Rnx, Act2, TAct, React, and Gtplot*, second ed. University of Illinois.
- Bonazzi P. and Bindi L. (2008) A crystallographic review of arsenic sulfides: effects of chemical variations and changes induced by exposure to light. *Z. Kristall.* **223**, 132–147.
- Bonazzi P., Menchetti S. and Pratesi G. (1995) The crystal structure of pararealgar, As₄S₄. *Am. Mineral.* **80**, 400–403.
- Bonazzi P., Menchetti S., Pratesi G., MunizMiranda M. and Sbrana G. (1996) Light-induced variations in realgar and beta-As₄S₄: X-ray diffraction and Raman studies. *Am. Mineral.* **81**, 874–880.
- Bostick B. C., Chen C. and Fendorf S. (2004) Arsenite retention mechanisms within estuarine sediments of Pescadero, CA. *Environ. Sci. Technol.* **38**, 3299–3304.
- Bostick B. C., Fendorf S. and Brown G. E. (2005) In situ analysis of thioarsenite complexes in neutral to alkaline arsenic sulphide solutions. *Mineral. Mag.* **69**, 781–795.
- Bourrie G., Trolard F., Genin J. M. R., Jaffrezic A., Maitre V. and Abdelmoula M. (1999) Iron control by equilibria between hydroxy-green rusts and solutions in hydromorphic soils. *Geochim. Cosmochim. Acta* **63**, 3417–3427.
- Campbell K. M., Root R. A., O'Day P. A. and Hering J. G. (2008) A gel probe equilibrium sampler for measuring arsenic pore-water profiles and sorption gradients in sediments: I. Laboratory development. *Environ. Sci. Technol.* **42**, 497–503.
- Carpenter J. H. and Manella M. E. (1973) Magnesium to chlorinity ratios in sea water. *J. Geophys. Res.* **78**, 3621–3626.
- Carroll S. A., O'Day P. A., Esser B. and Randall S. (2002) Speciation and fate of trace metals in estuarine sediments under reduced and oxidized conditions, Seaplane Lagoon, Alameda Naval Air Station (USA). *Geochem. Trans.* **3**, 81–101.
- Choi S., O'Day P. A. and Hering J. G. (2009) Natural attenuation of arsenic by sediment sorption and oxidation. *Environ. Sci. Technol.* **43**, 4253–4259.
- Deditius A. P., Utsunomiya S., Renock D., Ewing R. C., Ramana C. V., Becker U. and Kesler S. E. (2008) A proposed new type of arsenian pyrite: composition, nanostructure and geological significance. *Geochim. Cosmochim. Acta* **72**, 2919–2933.
- Delany J. M. and Lundeen S. R. (1990) The LLNL Thermochemical Database. Lawrence Livermore National Laboratory Report UCRL-21658.
- Deschamps E., Ciminelli V. S. T., Weidler P. G. and Ramos A. Y. (2003) Arsenic sorption onto soils enriched in Mn and Fe minerals. *Clays Clay Miner.* **51**, 197–204.

- Dhar R. K., Zheng Y., Stute M., van Geen A., Cheng Z., Shanewaz M., Shamsudduha M., Hoque M. A., Rahman M. W. and Ahmed K. M. (2008) Temporal variability of groundwater chemistry in shallow and deep aquifers of Arai-hazar, Bangladesh. *J. Contam. Hydrol.* **99**, 97–111.
- Dixit S. and Hering J. G. (2003) Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. *Environ. Sci. Technol.* **37**, 4182–4189.
- Drissi S. H., Refait P., Abdelmoula M. and Genin J. M. R. (1995) The preparation and thermodynamic properties of Fe(II)–Fe(II) hydroxide-carbonate (green-rust-1) – pourbaix diagram of iron in carbonate-containing aqueous-media. *Corros. Sci.* **37**, 2025–2041.
- Dzombak D. A. and Morel F. M. M. (1990) *Surface Complexation Modeling*. Wiley, New York.
- Eary L. E. (1992) The solubility of amorphous As_2S_3 from 25 to 90-degrees-C. *Geochim. Cosmochim. Acta* **56**, 2267–2280.
- Edwards M., Patel S., McNeil L., Chen H., Eaton A. D., Antweiler R. C. and Taylor H. E. (1998) Considerations in arsenic analysis and speciation. *J. Am. Water Works Assoc.* **90**, 103.
- Ficklin W. H. (1983) Separation of arsenic(III) and arsenic(V) in ground waters by ion-exchange. *Talanta* **30**, 371–373.
- Foster A. L. (2003) Spectroscopic investigations of arsenic species in solid phases. In *Arsenic in Groundwater* (eds. A. H. Welch and K. G. Stollenwerk). Kluwer Academic Publishers, pp. 27–65.
- Foster A. L., Brown, Jr., G. E., Tingle T. N. and Parks G. A. (1998) Quantitative arsenic speciation in mine tailings using X-ray absorption spectroscopy. *Am. Mineral.* **83**, 553–568.
- Fuller C. C., Davis J. A. and Waychunas G. A. (1993) Surface chemistry of ferrihydrite: Part 2. Kinetics of arsenate adsorption and coprecipitation. *Geochim. Cosmochim. Acta* **57**, 2271–2282.
- Gallegos T. J., Hyun S. P. and Hayes K. F. (2007) Spectroscopic investigation of the uptake of arsenite from solution by synthetic mackinawite. *Environ. Sci. Technol.* **41**, 7781–7786.
- Gallegos T. J., Han Y. S. and Hayes K. F. (2008) Model predictions of realgar precipitation by reaction of As(III) with synthetic mackinawite under anoxic conditions. *Environ. Sci. Technol.* **42**, 9338–9343.
- Gandenberg T., Hetzel F., Smith R. and Riege L. (1999) *Ambient concentrations of toxic chemicals in San Francisco Bay sediments*. San Francisco Estuary Regional Monitoring Program for Trace Substances. San Francisco Estuary Institute.
- Geomatrix and S.S. Papadopoulos & Associates Inc. (2002) *Remedial Action Implementation Report, Groundwater Containment System, 1990 Bay Road Site, East Palo Alto, California*. Prepared for Aventis CropScience USA, June 2002.
- George G. N. and Pickering I. J. (2000) *EXAFSPAK: A Suite of Computer Programs for Analysis of X-ray Absorption Spectra*. Stanford Synchrotron Radiation Laboratory.
- Helgeson H. C., Kirkham D. H. and Flowers G. C. (1981) Theoretical prediction of the thermodynamic behaviour of aqueous electrolytes at high pressures and temperatures. IV. Calculation of activities coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 5 kb and 600 °C. *Am. J. Sci.* **281**, 1241–1516.
- Helz G. R. and Tossell J. A. (2008) Thermodynamic model for arsenic speciation in sulfidic waters: a novel use of ab initio computations. *Geochim. Cosmochim. Acta* **72**, 4457–4468.
- Helz G. R., Tossell J. A., Charnock J. M., Patrick R. A. D., Vaughan D. J. and Garner C. D. (1995) Oligomerization in As(III) sulfide solutions – theoretical constraints and spectroscopic evidence. *Geochim. Cosmochim. Acta* **59**, 4591–4604.
- Hering J. G. and Kneebone P. E. (2002) Biogeochemical controls on arsenic occurrence and mobility in water supplies. In *Environmental Chemistry of Arsenic* (ed., Jr. W.T. Frankenberger). Marcel Dekker, Inc., pp. 155–181.
- Hering J. G., O'Day P. A., Ford R. G., He Y. T., Bilgin A., Reisinger H. J. and Burris D. R. (in press) MNA as a remedy for arsenic mobilized by anthropogenic inputs of organic carbon. *Ground Water Monitor. Remed.*
- Hornberger M., Luoma S., van Geen A., Fuller C. C. and Anima R. (1999) Historical trends of metals in the sediments of San Francisco Bay, California. *Mar. Chem.* **64**, 39–55.
- Huber R., Sacher M., Vollmann A., Huber H. and Rose D. (2000) Respiration of arsenate and selenate by hyperthermophilic archaea. *Syst. Appl. Microbiol.* **23**, 305–314.
- Illera V., O'Day P. A., Rivera N., Root R., Rafferty M. T. and Vlassopoulos D. (2005) *Soil Remediation of an Arsenic-Contaminated Site With Ferrous Sulfate and Type V Portland Cement*. EOS Transactions, San Francisco CA, American Geophysical Union.
- Inskeep W. P., McDermott T. R. and Fendorf S. (2002) Arsenic (V)/(III) cycling in soils and natural waters: chemical and microbiological processes. In *Environmental Chemistry of Arsenic* (ed., Jr. W. T. Frankenberger). Marcel Dekker, Inc., pp. 183–215.
- Keon N. E., Swartz C. H., Brabander D. J., Harvey C. and Hemond H. F. (2001) Validation of an arsenic sequential extraction method for evaluating mobility in sediments. *Environ. Sci. Technol.* **35**, 2778–2784.
- Kim M. J., Nriagu J. and Haack S. (2002) Arsenic species and chemistry in groundwater of southeast Michigan. *Environ. Pollut.* **120**, 379–390.
- La Force M. J., Hansel C. M. and Fendorf S. (2000) Arsenic speciation, seasonal transformations, and co-distribution with iron in a mine waste-influenced palustrine emergent wetland. *Environ. Sci. Technol.* **34**, 3937–3943.
- Ledbetter R. N., Connon S. A., Neal A. L., Dohnalkova A. and Magnuson T. S. (2007) Biogenic mineral production by a novel arsenic-metabolizing thermophilic bacterium from the Alvord Basin, Oregon. *Appl. Environ. Microbiol.* **73**, 5928–5936.
- Lin Z. X. and Puls R. W. (2003) Potential indicators for the assessment of arsenic natural attenuation in the subsurface. *Adv. Environ. Res.* **7**, 825–834.
- Lowers H. A., Breit G. N., Foster A. L., Whitney J., Yount J., Uddin N. and Muneem A. (2007) Arsenic incorporation into authigenic pyrite, Bengal Basin sediment, Bangladesh. *Geochim. Cosmochim. Acta* **71**, 2699–2717.
- McMahon P. B. and Chapelle F. H. (2008) Redox processes and water quality of selected principal aquifer systems. *Ground Water* **46**, 259–271.
- Millero F. J. and Leung W. H. (1976) The thermodynamics of seawater at one atmosphere. *Am. J. Sci.* **276**, 1035–1077.
- Moore J. N., Ficklin W. H. and Johns C. (1988) Partitioning of arsenic and metals in reducing sulfidic sediments. *Environ. Sci. Technol.* **22**, 432–437.
- Morris A. W. and Riley J. P. (1966) The bromide/chlorinity and sulphate/chlorinity ratio in seawater. *Deep-Sea Res. I* **13**, 699–705.
- Mullen D. J. E. and Nowacki W. (1972) Refinement of crystal-structures of realgar, AsS and orpiment, As_2S_3 . *Z. Kristall.* **136**, 48–65.
- Newman D. K., Beveridge T. J. and Morel F. M. M. (1997a) Precipitation of arsenic trisulfide by *Desulfotomaculum auripigmentum*. *Appl. Environ. Microbiol.* **63**, 2022–2028.
- Newman D. K., Kennedy E. K., Coates J. D., Ahmann D., Ellis D. J., Lovely D. R. and Morel F. M. M. (1997b) Dissimilatory arsenate and sulfate reduction in *Desulfotomaculum auripigmentum* sp. nov. *Arch. Microbiol.* **168**, 380–388.

- Nordstrom D. K. and Archer D. G. (2003) Arsenic thermodynamic data and environmental geochemistry. In *Arsenic in Groundwater* (eds. A. H. Welch and K. G. Stollenwerk). Kluwer Academic Publishers, pp. 1–25.
- O'Day P. A., Carroll S. A. and Waychunas G. A. (1998) Rock-water interactions controlling zinc, cadmium, and lead concentrations in surface waters and sediments, U.S. Tri-State Mining District. I. Molecular identification using X-ray absorption spectroscopy. *Environ. Sci. Technol.* **32**, 943–955.
- O'Day P. A., Rivera N., Root R. and Carroll S. A. (2004a) X-ray absorption spectroscopic study of iron reference compounds for the analysis of natural sediments. *Am. Mineral.* **89**, 572–585.
- O'Day P. A., Vlassopoulos D., Root R. and Rivera N. (2004b) The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. *Proc. Natl. Acad. Sci. USA* **101**, 13703–13708.
- Olson E. J. and Chen T. A. (1982) Interference in the determination of calcium in seawater. *Limnol. Oceanogr.* **27**, 375–380.
- Oremland R. S., Newman D. K., Kail B. W. and Stolz J. F. (2002) Bacterial respiration of arsenate and its significance in the environment. In *Environmental Chemistry of Arsenic* (ed. Jr. W. T. Frankenberger). Marcel Dekker, Inc., pp. 273–295.
- Peters S. C. and Burkert L. (2008) The occurrence and geochemistry of arsenic in groundwaters of the Newark Basin of Pennsylvania. *Appl. Geochem.* **23**, 85–98.
- Pickering W. F. (1981) Selective chemical extractions of soil components and bound metal species. *Crit. Rev. Anal. Chem.* **12**, 233–266.
- Planer-Friedrich B., London J., McCleskey R. B., Nordstrom D. K. and Wallschläger D. (2007) Thioarsenates in geothermal waters of Yellowstone National Park: determination, preservation, and geochemical importance. *Environ. Sci. Technol.* **41**, 5245–5251.
- Polizzotto M. L., Kocar B. D., Benner S. G., Sampson M. and Fendorf S. (2008) Near-surface wetland sediments as a source of arsenic release to ground water in Asia. *Nature* **454**, 505–508.
- Porter E. J. and Sheldrick G. M. (1972) Crystal structure of a new crystalline modification of tetra-arsenic tetrasulfide (2,4,6,8-tetrathia-1,3,5,7-tetra-arsatricyclo[3,3,0,0,3,7]-octane). *J. Chem. Soc., Dalton* **134**, 7–1349.
- Raven K. P., Jain A. and Loeppert R. H. (1998) Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes. *Environ. Sci. Technol.* **32**, 344–349.
- Rehr J. J. (1993) Recent developments in multiple-scattering calculations of XAFS and XANES. *Jpn. J. Appl. Phys.* **32-2**, 8–12.
- Rhine E. D., Onesios K. M., Serfes M. E., Reinfelder J. R. and Young L. Y. (2008) Arsenic transformation and mobilization from minerals by the arsenite oxidizing strain WAO. *Environ. Sci. Technol.* **42**, 1423–1429.
- Rittle K. A., Drever J. I. and Colberg P. J. S. (1995) Precipitation of arsenic during bacterial sulfate reduction. *Geomicrobiol. J.* **13**, 1–11.
- Root R. A., Dixit S., Campbell K. M., Jew A. D., Hering J. G. and O'Day P. A. (2007) Arsenic sequestration by sorption processes in high-iron sediments. *Geochim. Cosmochim. Acta* **71**, 5782–5803.
- Papadopoulos S.S. and Associates Inc. (2000) *Revised Conceptual Design for Groundwater Containment System, 1990 Bay Road Site, East Palo Alto, California*. Prepared for Rhone-Poulenc, Inc., July 2000.
- Sadiq M. (1990) Arsenic chemistry in marine environments – a comparison between theoretical and field observations. *Mar. Chem.* **31**, 285–297.
- Saunders J. A., Mohammad S., Korte N. E., Lee M.-K., Fayek M., Castle D. and Barnett M. O. (2005) Groundwater geochemistry, microbiology, and mineralogy of two arsenic-bearing Holocene alluvial aquifers from the USA. In *Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation*, vol. 915 (eds. P. A. O'Day, D. Vlassopoulos, X. Meng and L. G. Benning). American Chemical Society, pp. 191–205.
- Savage K. E., Tingle T. N., O'Day P. A., Waychunas G. A. and Bird D. K. (2000) Arsenic speciation in pyrite and secondary weathering phases, Mother Lode Gold District, Tuolumne County, California. *Appl. Geochem.* **15**, 1219–1244.
- Schwertmann U. and Cornell R. M. (1991) *Iron Oxides in the Laboratory: Preparation and Characterization*. Weinheim, VCH, New York.
- Smedley P. L. and Kinniburgh D. G. (2002) A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **17**, 517–568.
- Stauder S., Raue B. and Sacher F. (2005) Thioarsenates in sulfidic waters. *Environ. Sci. Technol.* **39**, 5933–5939.
- Stollenwerk K. G. (2003) Geochemical processes controlling transport of arsenic in groundwater: a review of adsorption. In *Arsenic in Groundwater* (eds. A. H. Welch and K. G. Stollenwerk). Kluwer Academic Publishers, pp. 67–100.
- Stolz J. E., Basu P., Santini J. M. and Oremland R. S. (2006) Arsenic and selenium in microbial metabolism. *Ann. Rev. Microbiol.* **60**, 107–130.
- USEPA (1983) Methods for the chemical analysis of water and wastes. In *Environmental Monitoring and Support Laboratory*. USEPA, EPA-600/4-79-020.
- USEPA (1992) EPA Superfund Record of Decision: Rhone-Poulenc, Inc./ZOECON Corp. United States Environmental Protection Agency Region IX.
- USEPA (2001) *National Primary Drinking Water Regulations; Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring; Final Rule: 2001*. U.S. Environmental Protection Agency, **66**(14), 6976–7066.
- USEPA (2006) *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. U.S. Environmental Protection Agency, USEPA SW-846.
- Waychunas G. A., Rea B. A., Fuller C. C. and Davis J. A. (1993) Surface chemistry of ferrihydrite: Part I. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. *Geochim. Cosmochim. Acta* **57**, 2251–2269.
- Webb S. M. (2006) SixPACK: Sam's Interface for XAS Package. Available from: <<http://www-ssrl.slac.stanford.edu/~swebb/sixpack.htm>>.
- Welch A. H., Westjohn D. B., Helsel D. R. and Wanty R. B. (2000) Arsenic in the groundwater of the United States: occurrence and geochemistry. *Ground Water* **38**, 589–604.
- Wilke M., Farges F., Petit P. E., Brown G. E. and Martin F. (2001) Oxidation state and coordination of Fe in minerals: an Fe K-XANES spectroscopic study. *Am. Mineral.* **86**, 714–730.
- Wilkin R. T. and Ford R. G. (2002) Use of hydrochloric acid for determining solid-phase arsenic partitioning in sulfidic sediments. *Environ. Sci. Technol.* **36**, 4921–4927.
- Wilkin R. T. and Ford R. G. (2006) Arsenic solid-phase partitioning in reducing sediments of a contaminated wetland. *Chem. Geol.* **228**, 156–174.
- Wilkin R. T., Wallschläger D. and Ford R. G. (2003) Speciation of arsenic in sulfidic waters. *Geochim. Trans.* **4**, 1–7.
- Williams A. G. B. and Scherer M. M. (2001) Kinetics of Cr(VI) reduction by carbonate green rust. *Environ. Sci. Technol.* **35**, 3488–3494.