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Speciation and Fate of Trace Metals in Estuarine Sediments Under Reduced and Oxidized Conditions, Seaplane Lagoon, Alameda Naval Air Station (USA)

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ABSTRACT

We have identified important chemical reactions that control the fate of metal-contaminated estuarine sediments if they are left undisturbed (*in situ*) or if they are dredged. We combined information on the molecular bonding of metals in solids from X-ray absorption spectroscopy (XAS) with thermodynamic and kinetic driving forces obtained from dissolved metal concentrations to deduce the dominant reactions under reduced and oxidized conditions. We evaluated the *in situ* geochemistry of metals (cadmium, chromium, iron, lead, manganese and zinc) as a function of sediment depth (to 100 cm) from a 60-year record of contamination at the Alameda Naval Air Station, California. Results from XAS and thermodynamic modeling of porewaters show that cadmium and most of the zinc form stable sulfide phases, and that lead and chromium are associated with stable carbonate, phosphate, phyllosilicate, or oxide minerals. Therefore, there is minimal risk associated with the release of these trace metals from the deeper sediments contaminated prior to the Clean Water Act (1975) as long as reducing conditions are maintained. Increased concentrations of dissolved metals with depth were indicative of the formation of metal HS⁻ complexes. The sediments also contain zinc, chromium, and manganese associated with detrital iron-rich phyllosilicates and/or oxides. These phases are recalcitrant at near-neutral pH and do not undergo reductive dissolution within the 60-year depositional history of sediments at this site.

The fate of these metals during dredging was evaluated by comparing *in situ* geochemistry with that of sediments oxidized by seawater in laboratory experiments. Cadmium and zinc pose the greatest hazard from dredging because their sulfides were highly reactive in seawater. However, their dissolved concentrations under oxic conditions were limited eventually by sorption to or co-precipitation with an iron (oxy)hydroxide. About 50% of the reacted CdS and 80% of the reacted ZnS were bonded to an oxide-substrate at the end of the 90-day oxidation experiment. Lead and chromium pose a minimal hazard from dredging because they are bonded to relatively insoluble carbonate, phosphate, phyllosilicate, or oxide

minerals that are stable in seawater. These results point out the specific chemical behavior of individual metals in estuarine sediments, and the need for direct confirmation of metal speciation in order to constrain predictive models that realistically assess the fate of metals in urban harbors and coastal sediments.

1. INTRODUCTION

A recent evaluation of sediment contamination of surface waters in the United States by the US Environmental Protection Agency identified 96 watersheds, mostly urban harbors, containing metal and/or organic chemical contents that are potentially hazardous to aquatic biota [1]. These harbors and coastal sediments are contaminated from past and present industrial and military waste disposal practices. One such example is the estuary sediments of the East Outfall Site of the Seaplane Lagoon, at the former Naval Air Station (NAS) Alameda located on an island in San Francisco Bay, USA (Figure 1). The most abundant metals in the sediments are cadmium, lead, chromium, zinc, copper, and nickel. Concentrations of these metal contaminants above background levels in San Francisco Bay result from a 57-year history of military and industrial activity at this site. From 1940 to 1975, the Seaplane Lagoon received about 300 million gallons of wastewater from industrial and storm-sewers from NAS Alameda. The Seaplane Lagoon and its surrounding area have been designated as a mixed-use commercial marina site in the City of Alameda land use plan [2]. A concern for this site and other urban estuarine environments is the contamination of the overlying water column as metals dissolve when reduced sediments react with oxygen-rich water during bioturbation, storm, dredging and other marina activities.

Recent studies of metal contamination in the San Francisco Bay identified previously contaminated sediments as a major source for some metals in the water column. Rivera-Duarte and Flegal calculated the total benthic fluxes of lead [3], silver [4], cadmium, cobalt, copper, nickel, and zinc [5] using measured porewater concentrations and a flux equation that combines Fickian diffusion and an irrigation flux from bioturbation and mixing of the top sediments. They found that the relative benthic to fluvial inputs to the San Francisco Bay were metal specific. Lead inputs from the sediments were 30 to 930 times fluvial inputs. Silver release from the sediments near waste-water treatment outflows contributed about 2.5 times the input of the fluvial system for the entire San Francisco Bay. Benthic and fluvial inputs were similar for zinc, but nickel, cadmium, and copper showed small or negative fluxes from the sediments to the overlying waters. This approach is a useful metric to compare metal contamination sources in large watersheds, but it does not explicitly account for the geochemical reactions that control the porewater concentrations.

Important chemical controls on the flux of trace metals to the water column are the oxidation and reduction of sulfur and iron in surficial estuarine sediments, as indicated by *in situ* measurement of trace metal fluxes across the sediment – water boundary in Gullmarsfjorden [6, 7]. In these studies, high fluxes of cadmium, copper, and zinc from the sediments to the overlying water in the oxygen-enhanced portion of the experiment were reversed when the overlying water went anoxic and trace metals were transferred to the sediments. However, the iron flux showed the opposite trend with a negative flux to the sediments during oxidation and positive flux to the water column as they became anoxic. The negative correlation between

these trace metals and iron and the reported lack of correlation with carbonate flux suggests that cadmium, copper, and zinc are present in the sediments as sulfides which can be easily dissolved by oxygen-rich waters. The increase in dissolved iron as the sediments become anoxic represents the reductive dissolution of iron hydroxides that formed during the oxidation experiment. *In situ* measurements of this kind provide valuable insight into trace metal geochemistry, but final interpretation of the data lack confirmation of the reactions in the solid phases in the sediment.

Much of our knowledge of solid chemical form of trace metals in reduced estuarine sediments has been derived indirectly from water analyses and from chemical extractions. Although there is ambiguity among studies, trace metal uptake in the sediments is often linked to iron sulfides such as pyrite (FeS_2) and monosulfides (amorphous FeS or mackinawite). For example, Kornicker and Morse [8] reported cadmium, manganese, and nickel sorption to pyrite in solution-based experiments. In estuarine sediments, copper and manganese have been identified as pyrite co-precipitates because they dissolved in the pyrite extraction. In contrast, cadmium, chromium, lead, and zinc are believed to be sequestered by other sulfides or oxides because a significant amount of these metals dissolved with less aggressive, non-pyrite extractions [9]. Similarly trace metal sorption or co-precipitation with amorphous FeS or mackinawite have been observed [10, 11]. An improved method to the use of chemical extractions is to determine trace metal bonding in sediments using synchrotron radiation X-ray absorption spectroscopy (XAS). This method is a unique molecular probe for complex materials because it is element specific, has relatively high sensitivity, does not require a vacuum, and is non-destructive. Thus, spectra for a number of elements can be directly measured on a bulk, untreated sediment samples with porewater present.

In this paper, we examined the chemical processes that impact the fate of metal contaminated estuarine sediments if they left are undisturbed (*in situ*) or if they are dredged. We discuss the *in situ* geochemistry of metals (cadmium, chromium, copper, lead, manganese nickel, and zinc) with depth in contaminated estuarine sediments from one site in the Seaplane Lagoon. We also discuss the geochemical processes responsible for the transfer of these metals from reduced contaminated estuarine sediments to oxygen-rich seawater by comparing in-situ geochemistry with that of the oxidized sediments. To do this, we combine bulk sediment and porewater analyses, flow-through oxidation experiments, geochemical modeling, and X-ray absorption spectroscopy. Combination of the geochemical and spectroscopic data yields a more robust picture of the reactions that control the fate of trace metal contaminants in urban harbors and coastal sediments.

2. METHODS

2.1. Sample Collection and Analysis

Between July 1997 and November 1998, a series of sediment cores were collected from the East Outfall Site, Seaplane Lagoon (Figure 1). For the geochemical and spectroscopic results given here, we focus on 0.5 m Plexiglas push cores that were collected on July 10, 1997 and on November 10, 1997 within the same general location (GH-CC-SC2, GH-CC-SC4, GH-CC-SC7, and GH-CC-SC9; referred to here as SC2, SC4, SC7, and SC9). Sediment cores were sectioned under argon and sub-samples taken at 3 cm intervals from the center portion of the core to ensure no oxidation. Sediment compositions are reported for the push cores SC2 to SC4 and for deeper gravity cores to 1 m (GH-CC-C1, GH-CC-C2 and GH-CC-C3; referred to here as C1, C2,

and C3). From core SC4, we extracted porewater for sulfur, chloride, trace and major element concentrations by centrifugation (5000 rpm for 60 min in argon-filled centrifuge tubes) and filtration (using 0.22 μm polycarbonate filters), and we measured wet sediment pH. From core SC2, we extracted porewater by Reeburgh-type pneumatic core squeezers in a nitrogen glove box for total phosphorus, sulfur and carbon concentrations. Synchrotron X-ray absorption spectroscopy (XAS) data were collected from frozen samples stored in N_2 (SC2, SC4, C1, C3) and from fresh, unfrozen sediments (SC7, SC9) within days of core recovery maintaining the oxic water column. Based on comparisons of fresh and frozen samples, freezing and thawing the sediments under controlled environments did not alter the metal chemistry.

2.2 Sediment Oxidation Experiments

Three samples of reduced Seaplane Lagoon sediment from core SC4 at 31.5 cm (SC4-11) were reacted with filtered, oxygen-rich seawater for 92 days to determine the net metal dissolution and changes in sediment metal coordination. The seawater (pH=7.9) was collected offshore from the Pacific Ocean by Long's Marine Laboratory, University of California, Santa Cruz. The experiments were performed in well-mixed, flow-through reactors at room temperature [12]. Reaction vessels and sample bottles were cleaned in a Class 100 clean room. Twenty samples were collected during the experiment and sample pH was measured immediately after the sample was collected. Samples for trace element analysis were acidified with ultra pure nitric acid to prevent precipitation. Sample bottles were double bagged and stored in a laminar flow hood until they were analyzed in a Class 100 clean room. An identical control experiment with seawater and no sediment was also run to provide procedural blanks.

2.3. Water Analyses

2.3.1. Trace Metals

Seaplane Lagoon porewaters and output solutions from the oxidation experiments were analyzed for Al, Cd, Cr, Cu, Fe, Pb, Mn, Ni, and Zn using a Hewlett-Packard HP4500 inductively coupled plasma-mass spectrometer (ICP-MS). An isotope dilution method was used to measure the porewater Cd, Cr, Cu, Pb, Ni, and Zn concentrations, by equilibrating the samples with a mixed enriched isotope spike (^{111}Cd , ^{52}Cr , ^{65}Cu , ^{206}Pb , ^{61}Ni , ^{67}Zn) at temperature for 48 hours, and then concentrating the trace metals from the equilibrated porewater by precipitating $\text{Mg}(\text{OH})_2$ from seawater at pH 10, which scavenges a number of trace metals. The precipitate was then carefully washed with pH 10 ultra pure ammonium hydroxide solution to remove sea salts, and then dissolved in 2% ultra pure nitric acid for trace metal analyses [13]. Because Cd and Ni were not concentrated on the $\text{Mg}(\text{OH})_2$ precipitate, the supernatant and washes were combined and concentrated using a Cetac Corporation DSX-100 system. Cd and Ni were run under normal plasma conditions, Cr and Cu were run under cool plasma conditions to reduce interference from ArC and ArMg, and Pb and Zn were run under hot plasma conditions to enhance sensitivity at high masses. For all isotope dilution determinations, the error in the measured ratios was less than 10% and generally in the range of 1–4%, and precision was 10–15% for Cr, Ni, Cd and Pb; and 15–20% for Cu and Zn.

For the porewater Al, Mn, and Fe analyses, aliquots of the saline porewater were diluted to 1 psu with ultra pure 2% nitric acid and spiked with Sc and Y as internal standards and run under normal plasma conditions. Calibration curves were made in a seawater reference standard (NASS-4) diluted to 1 psu to correct for matrix effects. Detection limits determined

from the reproducibility of procedural blanks were 1 ng g⁻¹ for Al, 0.1 ng g⁻¹ for Mn, and 100 ng g⁻¹ for Fe, and precision was generally less than 5–10%.

Filtered output samples from the oxidation experiments were concentrated 5 to 10 times using a Cetac Corporation DSX-100 system, spiked with Sc, Y, In, Tb, and Bi internal standards to correct for matrix effects and instrument drift, and run under hot plasma conditions. Calibration curves were made in a series of standards in 2% ultra pure nitric acid. Reported errors include both measurement and calibration uncertainties. Detection limits were determined by processing ion-exchange resin beads through the DSX-100 chemistry under the same conditions as the output samples. No significant differences were seen in different batches of resin. Accuracy was measured against metal concentrations in two seawater reference standards, NASS-4 and CASS-3.

2.3.3. Major Elements, Sulfur, Chloride, and Carbon Analyses

Total dissolved Al, Ca, Fe, K, Mg, Mn, Na, P, S, and Si were analyzed by a Fisons Instruments (Model 3560) inductively coupled plasma-atomic emission spectrometer against multi-point calibration curves in distilled and deionized water. The reproducibility of this technique was better than 2%. Sulfur speciation and concentrations were determined by ion chromatography (Beckman 421A controller, a LDC Milton Roy Conducto Monitor III conductivity detector, and a Waters 4.6 × 150 mm IC-Pak Anion HC column) against multi-point calibration curves. Samples were injected in a helium-purged, 5-mM sodium phosphate solution. Detection limit was 5 mg L⁻¹ for each sulfur species, and precision and accuracy were better than 10%. Chloride concentrations were determined using an ion-specific probe against a multi-point NaCl calibration curve in distilled and deionized water. The detection limit was 10 ng g⁻¹, and precision and accuracy were better than 10%. Dissolved carbon analyses were made with an infrared carbon analyzer (O. I. Analytical TOC 700). Total inorganic carbon (TIC) and total organic carbon (TOC) were measured in sequence by first acidifying the sample to pH < 4, heating it to 100°C, and trapping and detecting the evolved CO₂. The dissolved organic carbon in the sample was then oxidized with sodium persulfate at 100°C and the evolved CO₂ was trapped and detected. Total carbon (TC) was measured directly by combining the TIC and TOC methods into a single step.

2.4. Bulk Sediment Chemistry and Mineralogy

2.4.1. Sediment digestion

The chemical depth profiles were determined for cores SC2-4 and C1-3 from sediment samples digested with acid UA2 solutions (mixture of concentrated HF and HCl from Unisolv, Inc.) in a microwave and neutralized and stabilized with UNS2A/2B solutions (mixtures of H₃BO₃, TETA and EDTA from Unisolv, Inc.). Reported Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, S, and Zn concentrations were analyzed by inductively coupled plasma-atomic emission spectrometry. Analysis

protocol adheres to EPA SW-846 Method 6010A augmented to include all elements listed above. A scandium spike was added to all samples to correct for viscosity effects resulting from the high silica content of these sediments and instrument drift. Detection limits and analytical reproducibility are reported in the data. The quartz content prevented recovery of silica concentrations because silica did not stay in solution. The external standard was the NIST Buffalo River sediment.

2.4.2. X-ray diffraction

Sediment mineralogy was determined by X-ray diffraction (XRD) on freeze dried and ground sediment samples from cores SC2-4 and C1-3. Data were collected from random orientation powder samples with a Scintag PAD V instrument using a Cu-K α source at 45 kV and 35 mA from 2 to 92 deg 2θ in 0.02-deg steps. XRD cannot detect amorphous solids or minerals that are present at <2 wt %. For a few samples, XRD spectra were collected on air-dried and ethylene-glycol-saturated sediments to separate some of the diagnostic clay peaks (e.g., smectite from chlorite). Reported mineral abundance is estimated by assigning minimum XRD detection limits to the trace mineral components (~2 wt %).

2.5. XAS Data Collection and Analysis

X-ray absorption spectroscopy (XAS), including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses, were used to characterize the speciation and bonding of metals in sediments from cores. Fluorescence spectra were collected at Stanford Synchrotron Radiation Laboratory (SSRL) on wiggler beamlines 4-1 and 4-3 using either a 13-element Ge array detector, a 4-element Ge array detector, or a Lytle detector. Either a Si(111) or Si(220) monochromator crystal was used, depending on which crystal produced the higher quality spectra for a given element, and detuned 50-70% of maximum intensity to minimize higher-order harmonic reflections. XANES spectra for chromium and manganese were collected with a Si(220) crystal to achieve higher energy resolution. Spectra were collected at ambient temperature with the sample in an helium atmosphere to prevent oxidation of sensitive elements. For a given element, energy was calibrated using a reference foil spectrum. Absorption spectra for crystalline reference compounds and fresh precipitates for each element were collected and analyzed for comparison to sediment spectra.

XANES spectra were used to identify oxidation states for chromium and manganese and to qualitatively identify sediment components. Background-subtracted XANES spectra were normalized to maximum absorption and first-derivative spectra were fit with linear combination of reference spectra using the program DATFIT (G. George, pers. comm). EXAFS spectra were quantitatively analyzed using EXAFSPAK [14] and FEFF [15] according to methods described in O'Day et al. [16] and Carroll et al. [17]. Debye-Waller factors (S^2) were fixed on values determined from fits to reference spectra of compounds of similar structure and composition to sediment components. For trace metals (Cd, Zn, Cr, Pb, and Mn), proportions of sulfide and oxide components in the sediment spectra were estimated based on the relative proportions of first-shell oxygen and sulfur backscatterers. For these spectra, detection of a unique bonding site is estimated at about 10-15 atom-% of the total element signal. For iron, sulfide and oxide components were quantitatively determined based on integrated areas of least-squares fits. Fit areas were calibrated using spectra of standard mixtures of pyrite (commercial), nontronite (The Clay Minerals Society, Standard N_{Au}-1), and illite (The Clay Minerals Society, Standard IMt-1) in a ground quartz matrix at 5 atom-% total

iron to simulate sediment concentrations. Spectra of the reference mixtures were collected in fluorescence at room temperature at SSRL on beamlines 2-3 and 4-3. Based on sensitivity tests with known concentrations, the proportion of pyrite in these sediments can be determined to better than $\pm 5\%$ of the total iron in the sample (see [18]).

2.6. Geochemical Modeling of Porewaters

The aqueous geochemistry was modeled thermodynamically for sulfide, carbonate, oxide/hydroxide, and silicate saturation and aqueous complexation versus depth with the Geochemist's Workbench geochemical code [19] and SUPCRT92 database [20] modified to include, aqueous Cd-, Cr-, Fe-, Mn-, Ni-, Pb, and Zn-sulfide species, and Zn-, Cd-, and Pb-carbonate and hydroxide phases (Table 1). Activity coefficients were calculated from the extended Debye-Hückel method, which is valid to ionic strengths of about 3 molal. For these calculations, we used field temperature, porewater trace and major element concentrations with dissolved sulfur as HS^- , and sediment pH from core SC4. Alkalinity as HCO_3^- was calculated as a function of depth for core SC4 from a linear regression of the inorganic-carbon concentration measured in core SC2 data. For the surface sediments at 1.5 cm, alkalinity is calculated from measured pH and atmospheric CO_2 , because the linear extrapolation yielded negative values. The solution was charge balanced by adjusting the chloride concentration.

3. RESULTS

3.1. Depth Profiles of the Porewater Chemistry

We report the porewater trace and major element, chloride, sulfur, and pH for core SC4 and the porewater total phosphorus, carbon, inorganic carbon, and organic carbon for core SC2 in Figure 2 and in Tables 2 and 3. There are distinct trends in the porewater composition with depth in core SC4. Calcium, magnesium, potassium, sodium, chloride, and sulfide concentrations increase with depth to 25.5 cm and remain constant at greater depths. Aluminum concentrations are quite low and constant (with the exception of one outlying data point). Silica concentrations increase by about two times from surface sediments to a depth of 4.5 cm, and remain constant at greater depths. Iron concentrations were detected only at depths above 4.5 cm. Cadmium, chromium, and lead concentrations increase with depth following similar trends observed for their sediment concentrations. Nickel concentrations show a slight decrease with depth. Copper, manganese, and zinc depth profiles are more complicated. Manganese concentrations decrease to minimum at a depth of 4.5 cm, then increase to a maximum at a depth of 16.5 cm, and then decrease at greater depths. Zinc and copper concentrations increase to maximum at a depth of 22.5 cm, decrease between 22.5 and 28.5 – 31.5 cm, and increase at greater depths. In core SC2, total dissolved inorganic carbon and total phosphorus concentrations increase with depth.

The dissolved major metal concentrations are close to the equilibrium solubility of common soil minerals (Table 4). Dissolved silica concentrations are close to saturation with respect to β -cristobalite, a quartz polymorph, but supersaturated with respect to quartz. The dissolved aluminum concentrations are close to saturation with respect to gibbsite, $(\text{Al}(\text{OH})_3)$ and not 7-Å chlorite (micaceous clay) which was identified in the X-ray diffraction analysis of the sediments. The dissolved calcium concentrations are undersaturated with respect to calcite (CaCO_3) in the surface sediments (1.5 cm), but supersaturated at greater depths. Apatite ($\text{Ca}_5\text{OH}(\text{PO}_4)_3$) is supersaturated through out the core. In the top 5 cm, dissolved

iron concentrations are supersaturated with respect to sulfide phases, and at greater depths, iron concentrations are below detection.

Dissolved trace element concentrations are not exclusively controlled by the solubility of sulfide phases when aqueous complexation by HS^- and S^{2-} is included (Table 4). Of the seven trace elements measured, only cadmium and lead concentrations appear to be limited by the solubility of CdS(s) and galena (PbS). Zinc and nickel concentrations are supersaturated with respect to sphalerite (ZnS) and millerite (NiS) by 2-4 orders of magnitude, and manganese and chromium concentrations are undersaturated with respect to alabandnite (MnS) and CrS (we do not have thermodynamic data for Cr_2S_3). The high covellite (CuS) saturation indices (log SI 7-8) may reflect the absence of known formation constants for aqueous copper HS^- and S^{2-} complexes. With the exception of chromium, the stability of trace element HS^- and S^{2-} complexes yields porewaters that are significantly undersaturated with respect to carbonates or hydroxides. Cadmium, copper, lead, nickel, and zinc are all undersaturated with respect to otavite (CdCO_3) and Cd(OH)_2 , malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), tenorite (CuO), cerussite (PbCO_3), NiCO_3 and Ni(OH)_2 , rhodochrosite (MnCO_3) and Mn(OH)_2 , and smithsonite (ZnCO_3), and $\beta\text{-Zn(OH)}_2$. Dissolved chromium concentrations are 1 to 6 orders-of-magnitude higher than eskolaite (Cr_2O_3) and magnesiochromite (MgCrO_4) saturation. Manganese is the only trace metal that may be controlled by phosphate mineral solubility, with concentrations that are slightly undersaturated with respect to $\text{MnHPO}_4(\text{s})$.

3.2 Depth Profiles of the Bulk Sediment Chemistry and Mineralogy

The depth profiles of cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, sulfur and zinc for the cores are shown in Figure 3 and tabulated in Table 5. The chemical composition of the sediments with depth is quite uniform in the six cores. In the undisturbed 0.5 m push cores, cadmium, chromium, copper, lead, mercury, and zinc concentrations increase from low values in the surface sediments to higher values at depths greater than 20 to 30 cm below the sediment–water surface. The concentrations range from 10 to 350 mg g^{-1} for cadmium, from 230 to 1150 mg g^{-1} for chromium, from 100 to 240 mg g^{-1} for copper, from 180 to 1400 mg g^{-1} for lead, from 110 to 180 mg g^{-1} for nickel, and from 240 to 630 mg g^{-1} for zinc. Cobalt concentrations are low and vary between 14 and 30 mg g^{-1} , with peak concentrations at depths of 20 to 45 cm as high as 160 mg g^{-1} . Manganese concentrations are constant with depth and are about 450 mg g^{-1} . Iron concentrations increase from about 4.5 wt % in the surface sediments to about 5.5 wt % at depths greater than 10 cm. Sulfur concentrations increase from 1 wt % in the surface sediments to about 2 wt % at depths of 30 to 40 cm. Gravity cores sampled the sediments to greater depth (1 m) than the push cores, and show that the trace metals concentrations continue to increase to about 80 cm (Table 5). At greater depths the concentrations drop to very low levels comparable to the pristine levels in San Francisco Bay [21].

No trends in sediment mineralogy were observed as a function of depth. The sediments are primarily quartz with about 10 to 15 wt % phyllosilicate minerals. There is no difference in the bulk mineralogy as a function of depth. Minerals identified in XRD patterns are 80–90% quartz, and a minimum of 2 wt % hornblende, mica, chlorite, smectite, illite, and pyrite.

3.3 Depth Profiles of Metal Bonding from XAS Analysis

Analyses of EXAFS and XANES spectra were used to determine the dominant local coordination environment of individual metals in the sediments. In bulk samples, the absorption signal is an average of all coordination environments of a

particular element. Although absorption spectra were collected on samples with porewater present, the XAS signal is dominated by sites associated with solid phases because metal concentrations are roughly three orders-of-magnitude higher in the solids than in the associated porewater. Ligands in the first coordination shell were identified as either sulfur or oxygen. Quantitative analysis of EXAFS spectra was used to estimate the relative amount of ligation by sulfur (as sulfide) or oxygen atoms, or as a mixture of both atoms. Qualitative comparisons and linear combinations of XANES spectra of reference compounds were used to determine dominant components in the sediment samples for elements for which good quality EXAFS spectra could not be obtained.

3.3.1 Sulfide-associated Metals

X-ray absorption spectra for cadmium from two sediment samples show that cadmium is bonded only by first-neighbor sulfur atoms (Figure 4a). There is no evidence in the EXAFS spectra for coordination by oxygen, which would be evident by a shift to a shorter first-shell distance characteristic of Cd-O bond lengths. There is also no evidence for backscattering from atoms beyond the first coordination shell. Sediment spectra are identical to those of two freshly precipitated cadmium sulfide samples, which are the same regardless of whether or not iron was present in the reactant solution. First coordination shell Cd-S interatomic distances determined from least-squares fits are similar to those of crystalline CdS (Table 6), consistent with coordination in a sulfide phase (for which $N_{\text{Cd-S}} = 4$). The lack of atomic backscattering beyond the sulfur coordination shell for both the natural sediments and the reference laboratory precipitates indicates that the cadmium sulfide phase is highly disordered on a local atomic scale. Although the total cadmium concentrations differ significantly between the sample at 34.5 cm (192 mg g⁻¹Cd) and at 55.0 cm (1222 mg g⁻¹Cd), the local coordination determined by EXAFS analysis is identical.

Analyses of zinc EXAFS spectra indicate that zinc is dominantly coordinated in a sulfide phase in the sediments, with a secondary fraction of zinc associated with an oxide component (Figure 4b). Interatomic distances derived from fits indicate that the sulfide component is locally identical to that of sphalerite (ZnS, for which first coordination shell $N_{\text{Zn-S}} = 4$) (Table 6). However, the much lower peak amplitudes in the Fourier transforms of the sediment samples spectra compared to those of crystalline sphalerite show that backscattering from zinc and sulfur atoms beyond the first sulfur shell is weak. This indicates formation of a poorly crystalline sulfide phase and/or small particle size. For the oxide component, zinc EXAFS spectra do not correspond to a single zinc oxide phase. Zinc occurs in oxide and silicate compounds in both octahedral and tetrahedral

coordination. First coordination shell least-squares fits gave average Zn-O distances that were variable but consistent with dominantly octahedral coordination of zinc (Table 6). Analyses of the scattering from second neighbor Zn-Me atoms (where Me is a metal cation) gave interatomic distances indicative of edge sharing of octahedra ($R_{\text{Zn-Me}} = 3.06\text{-}3.13 \text{ \AA}$), and of corner sharing of octahedra and/or tetrahedra ($R_{\text{Zn-Me}} = 3.21\text{-}3.37 \text{ \AA}$). Because the backscattering functions overlap one another in this range of interatomic distances, the spectra could not be uniquely fit by a single element for each atomic shell. The closer Zn-Me shell could be fit with a combination of iron (or similar Z transition metal), magnesium, or aluminum. The more distant Zn-Me shell could be fit with iron, aluminum, or silicon. These observations suggest zinc substitution in one or more silicate or oxide phases. Given that phyllosilicate minerals comprise about 10 – 15 wt % of the bulk sample, it is likely that some zinc is present in these minerals. Substitution of zinc into the octahedral sites of clay minerals or micas is consistent with the interatomic distances determined for the oxide component. Substitution of small amounts of zinc into other oxide phases such as magnetite cannot be determined from these data.

The relative atomic proportions of zinc sulfide and oxide components in the sediments were estimated from fits to Fourier-filtered first coordination shell EXAFS spectra. Zinc was assumed to be tetrahedrally coordinated by sulfur in the sulfide component and octahedrally coordinated by oxygen in the oxide component. In fits to the total EXAFS spectra, interatomic distances and coordination numbers (N) for zinc and sulfur shells were fixed on crystallographic values for sphalerite (Table 6), with N scaled to the proportion of sulfide component determined in the first coordination shell fit. Using this approach, there is little change in the relative proportions of sulfide and oxide components as a function of depth in core SC-4. The oxide component comprises 22-25% of the zinc atomic component even though total zinc concentration increases from 287 mg g⁻¹ at 2.5 cm to 515 mg g⁻¹ at 34.5 cm. In a different core (C-3), a sample from 55 cm depth shows a higher relative proportion of sulfide component, about 90%, although the total zinc concentration (486 mg g⁻¹) is similar to that of core SC-4 at 34.5 cm (515 mg g⁻¹).

3.3.2 Oxide-associated Metals

Both chromium and lead are associated with oxide phases in the sediments and there is no evidence for association with sulfide minerals. Analyses of XANES (Figure 4c) and EXAFS (Figure 4d) spectra for chromium show no evidence for the presence of sulfur backscatterers and indicate Cr(III) only. The presence of Cr(VI) would be readily apparent by a distinctive pre-edge feature in the XANES spectrum and by much shorter Cr-O distances than obtained in first coordination shell fits to the EXAFS spectra (Table 6). Comparison of normalized and first-derivative XANES spectra for shallow and deep sediments from two cores (SC-4 and SC-9) are very similar, with slight differences in spectral shape above the energy of maximum absorption revealed in first-derivative spectra (Figure 4c). XANES spectra of two samples from intermediate depths (SC-7-18 and SC-2-7) are very similar to the chromium spectra of shallow cores.

Likewise, EXAFS spectra for three sediment samples are generally very similar regardless of total chromium concentration which increases with depth in core SC4 from 245 mg g⁻¹ at 1.5 cm to 766 mg g⁻¹ at 34.5 cm. All spectra have identical first-shell coordination and slight differences in backscattering amplitudes for more distant atomic shells (Figure 4d and Table 6). Interatomic distances obtained from EXAFS fits do not correspond to a single identifiable chromium oxide

phase. First coordination shell Cr-O distances are typical of octahedral coordination of Cr(III) by oxygen in oxide and silicate compounds. Distances obtained from fitting of higher shells are consistent with edge-sharing of metal octahedra and corner-sharing of metal octahedra and/or tetrahedra. Differences in the amplitude of backscattering from atoms at 2.97-3.02 Å appear to be related to cancellation effects among atoms such as iron (or similar Z elements), magnesium, and aluminum at slightly different Cr-Me interatomic distances. Backscattering from atoms at 3.42-3.44 Å is more consistent and best fit with iron. These structural results are consistent with chromium substitution in phyllosilicates, association with spinel phases such as chromite or magnetite, and/or inner-sphere adsorption on oxides or silicates. As discussed below, chromium in the sediments originates from both contaminant and detrital sources, with the contaminant fraction dominant in deeper sediments. The spectral results, however, do not indicate major changes in chromium bonding with depth.

Comparison of XANES spectra for lead in the sediments and in reference compounds indicates that lead is bonded by oxygen. Coordination of lead by sulfur would result in a shift of maximum absorption at the Pb L_{III} edge to significantly lower energy (Figure 4e). The energy of maximum absorption is consistent with lead coordination in either oxide, phosphate, or carbonate phases. There are no changes in the XANES spectra of samples from core SC4 even though the total lead concentration increases significantly from 214 mg g⁻¹ at 1.5 cm to 1269 mg g⁻¹ at 34.5 cm. Previous analysis of first-neighbor atomic scattering in one lead EXAFS spectrum (SC9-12, 30 cm depth) indicated the presence of oxygen atoms only [22]. Quantitative analyses of two lead EXAFS spectra from core SC4 were precluded by poor data quality, but there was no evidence for backscattering from sulfur atoms. Lead exhibits high static disorder in its local oxygen coordination in a number of lead oxide, (oxy)hydroxide, phosphate, and carbonate compounds, and thus, first coordination shell distances are not diagnostic of a particular phase [16, 23, 24]. Evidence from the XANES and EXAFS spectra are consistent with lead coordination in either carbonate, phosphate, or (oxy)hydroxide phases, or as an oxygen-ligated sorbed complex.

3.3.3 Manganese and Iron

Manganese concentrations in the sediments vary between 350-550 mg g⁻¹ and do not generally increase with depth, as do the contaminant metals. Comparison of the manganese XANES spectra as a function of depth in core SC4 indicates no significant changes among samples between 1.5 and 31.5 cm (Figure 5a). Examination of first-derivative XANES spectra shows only slight variations in the energy positions of major inflection points among the sediment samples. The sediment XANES spectra could not be entirely fit with a single reference compound or by linear combinations of two or three manganese reference compounds, including combinations of carbonate, phosphate, sulfate, sulfide, and oxide minerals. This suggests that manganese is substituting in other minerals or forming solid solutions rather than forming pure manganese compounds. Absorption edge features from ~6548-6555 eV are similar to a natural specimen of ferrisicklerite (Li[Fe³⁺,Mn²⁺]PO₄), a mixed iron-manganese phosphate mineral, indicating a phosphate component that comprises roughly one-third to one-half of the manganese in the sediment samples. Two samples from a different core, SC9 collected in April 1998, show some spectral features below ~6548 eV that can be attributed to manganese associated with sulfide, which is variable among samples and

comprises from 0 to ~20% of manganese in the sediments*. Absorption features above 6555 eV could not be well fit with pure manganese reference compounds. The sediment samples have a second absorption maximum at 6557-6558 eV, which is near to observed maxima for Mn(III) and Mn(II,III) oxide compounds [25, 26]. Manganese(IV) oxide compounds generally have absorption maxima at higher energy (6560 eV or above) (Figure 5a). These comparisons suggest that a large fraction of manganese is bonded predominately in an oxide component as Mn(III) or as a mixture of Mn(II,III). This is consistent with substitution of manganese into detrital phyllosilicate or oxide minerals in concentrations on the order of 100-300 mg g⁻¹ (about half of the total manganese sediment concentrations).

Iron in the sediments is a major element, occurring in concentrations of about 4 – 6 wt % (Figure 3 and Table 5). Analyses of EXAFS spectra from core SC4 indicate both sulfide and oxide iron components (Figure 5b). The sulfide component is clearly identified as pyrite based on interatomic distances derived from fits of Fe-S and Fe-Fe shells (Table 6). In the sediment samples, backscattering amplitudes are lower for Fe-S and Fe-Fe shells beyond the first sulfur coordination shell than in the crystalline pyrite reference compound (Figure 5b). This suggests poor crystallinity and/or small particle size [27]. Iron monosulfide (amorphous FeS or crystalline mackinawite), which has a different atomic structure than pyrite [28], could not be fit in the spectra. If FeS is present, it must comprise less than about 5 atom-% of total iron to be undetected in the EXAFS spectra [22]. Analyses of XANES spectra indicates that below ~1-2 cm depth the primary iron oxide component in the sediment is a phyllosilicate which is most similar in structure to iron substituted into mica (e.g., illite, muscovite, or biotite) [29]. Other minor iron-oxide components that might be present include chlorite and magnetite. Based on qualitative information from XANES spectra, the oxide component in the EXAFS spectra was fit with four shells (Table 6), Fe-O at 2.00 Å, Fe-Fe at 3.08-3.10 Å, Fe-Si at 3.26 Å, and Fe-Fe at 3.39-3.42 Å, to account for all primary Fe-X distances in phyllosilicates and Fe(III) oxides (if present). Based on EXAFS fits to core SC4 spectra, the relative proportion of iron in pyrite compared to oxide phases increases only slightly with depth (~3%) from 1.5 to 34.5 cm with no change in interatomic distances. Over this interval, total iron concentration increases from 4.4 to 5.3 wt %.

3.4 Reaction Rates from Oxidation Experiments

Trace metal dissolution during the sediment oxidation experiments are shown in Figure 6 as the net rate and the percent metal dissolved versus time. The rates of reaction for each element were calculated according to:

$$\text{Rate}(\text{day}^{-1}) = D[i]_{\text{aq}} \times \text{FR} \times (\text{wt-sediment} \times [i]_{\text{sediment}})^{-1} \quad (1)$$

where $D[i]_{\text{aq}}(10^{-6} \text{ g g}^{-1})$ is the difference in concentration between the output and input (seawater blank) solutions, $\text{FR}(\text{g day}^{-1})$ is the flow rate, and $(\text{wt-sediment}(\text{g}) \times [i]_{\text{sediment}})(10^{-6} \text{ g g}^{-1})$ is the total concentration of each element in the sediment. We use the respective seawater blank analyses as our input solutions to directly correct for any trace metal contamination from the laboratory environment as a function of time (the experiments were not conducted in a Class 100 clean room). Normalization to total concentration allows reactivity among the metals to be compared directly. We also show the total metal dissolved as

*Based on the analysis of one EXAFS spectrum, the Mn-sulfide component was previously overestimated in O'Day et al. [22]. Re-analyses of XANES spectra suggest at most about 20% Mn-sulfide in the sediments.

the percent metal dissolved normalized to the concentration of the initial metal in the sediment versus time. The averaged rates, percent metal dissolved, and associated uncertainties are calculated from the triplicate experiments (Table 7).

The net release of trace elements from the sediments is complex and metal specific. The cadmium, zinc, manganese, and copper release rates exhibit a rapid increase in dissolution rate during the initial oxidation (1 to 20 days), followed by continual decrease in release rates with time. After about 50 days of reaction, cadmium, zinc, manganese, and copper dissolution slows to about 30%, 10%, 5%, and 4% of their respective initial sediment concentrations. After 90 days of reaction, the cadmium, zinc, manganese, and copper concentrations in the output solutions are near their respective concentrations in the top core section (1.5 cm, Table 2). The observed non-steady state dissolution behavior is indicative of concurrent dissolution of a reduced solid phase and precipitation of a stable secondary phase that limits the transfer of the trace metals to oxygen-rich seawater.

The net release rates of nickel, lead, and chromium are 10 to 100 times lower than the release rates of cadmium, zinc, manganese, and copper. Additionally the rates are more or less constant as a function of time, and show steady-state reaction kinetics. Nickel release rates are constant within the scatter of the data with the exception of one outlying data point at about 80 days. Lead release rates increase slightly during the first 10 days, are constant for the next 50 to 60 days, and decrease slightly after 80 days. Chromium release is characterized by minimal dissolution during the first 25 days followed by slightly greater dissolution rates that are constant for the duration of the experiment. These metals dissolve slowly with time; about 3% of the initial nickel, 1% of the initial lead and 0.1% of the initial chromium dissolve after the reduced sediments have reacted with seawater for 90 days.

For aluminum, calcium, potassium, iron, magnesium, and silica we observed minimal reactivity. There were no changes in the calcium, potassium and magnesium input and output concentrations. The dissolved iron, aluminum, and silica concentrations in the output solutions are below the analytical detection limits. This is expected because quartz, phyllosilicates, and iron oxides have very low dissolution rates in near-neutral seawater.

3.5 XAS Analysis of Metals in Oxidized Sediments

At the end of the 90-day oxidation experiment (SC4-11, 31.5 cm), sediments were re-examined with XAS to evaluate changes in oxidation state and local coordination compared to unreacted core sediments from similar depth. Cadmium, which was entirely coordinated by sulfur in unreacted sediments, is partially coordinated by oxygen in the reacted sample (Figure 7a). Analyses of the EXAFS spectrum showed about 47% atomic coordination by oxygen and 53% coordination by sulfur. The interatomic Cd-S distances are identical to those of cadmium in unreacted sediments, indicating that the original CdS phase has not completely dissolved (Table 6). The Cd-O distance in the oxide component derived from EXAFS analysis (2.31 Å) is typical of cadmium oxide phases and oxygen-coordinated sorption complexes [16, 30, 31]. However, the lack of backscattering atoms beyond the first coordination shell suggests that the Cd-O component is not a well crystallized solid.

The X-ray absorption spectrum for zinc of the reacted sample likewise shows conversion of the original sulfide phase to an oxide phase (Figure 7b). In unreacted sample SC4-12, 78% of zinc was coordinated by sulfur with local structure indicative of poorly crystalline sphalerite (ZnS). In reacted sample SC4-11, 25% of zinc remains coordinated in ZnS (distances are

identical to unreacted samples) and 75% of zinc is coordinated by oxygen. As discussed previously, the original zinc oxide component may be a composite of zinc substituted into detrital silicate and oxide phases. These phases are probably recalcitrant during reaction with seawater and would not dissolve significantly. The absorption spectrum of the reacted sample is therefore a composite of residual ZnS, the original oxide component(s), and a new zinc oxide component. Least-squares fits of the EXAFS spectrum of the reacted sample indicate a first shell of oxygen atoms at an average distance of 2.03 Å and metal backscatterers at 3.13 Å, similar to unreacted samples (Table 6). There is also evidence for metal backscatterers at a longer distance (3.39 Å) which is indicative of corner sharing of metal octahedra or tetrahedra in (oxy)hydroxides and phyllosilicates. Owing to the complicated signal, backscattering in the oxide component could not be fit with unique elements beyond the coordinating shell of oxygen atoms. The interatomic distances obtained from fits, however, are consistent with zinc association with iron (oxy)hydroxide or phyllosilicate phases in addition to the original zinc oxide components (Figure 7b).

In contrast to sulfide-associated metals, the XAS spectra of metals primarily associated with oxide phases show little change after reaction with seawater. There is no evidence in the chromium XAS data (XANES or EXAFS spectrum) for oxidation to Cr(VI), although a small percentage (<5 atom-%) of surface-oxidized chromium cannot be ruled out based on the bulk spectrum. The EXAFS spectrum of the reacted sample most closely resembles that of the shallow sediment sample SC4-1 (1.5 cm) and differs slightly from that of sample SC4-12 (34.5 cm) (Figure 7c). Fits indicate that these differences are related to the number of metal backscatterers beyond the first coordination shell of oxygen atoms and not to large changes in interatomic distances (Table 6). For lead and manganese, comparison of XANES spectra also indicates no significant changes in local atomic coordination after reaction (Figure 7d,e).

In the leached sediment sample, analysis of the iron EXAFS spectrum indicates a reduction of 17% in the fraction of the pyrite component compared to unreacted sediment SC4-12 (34.5 cm) based on integrated curve areas for fitted pyrite and oxide components (Figure 7f, Table 6). It is likely that iron lost from pyrite was resorbed or reprecipitated, probably as iron (oxy)hydroxides, because at most 1% of the iron was lost to solution (dissolved iron concentrations were below the detection limit of 100 ng g⁻¹). Analyses of the XANES spectrum of the leached sample indicates an small increase in the amount of Fe(III). Interatomic distances of the oxide component do not show any significant changes between reacted and unreacted sediments because distances among second-neighbor backscattering atoms in phyllosilicates and iron (oxy)hydroxides overlap (in the range of 3.03-3.15 Å). Backscattering amplitudes for second-neighbor atoms at 3.09-3.10 Å are higher in the leached sample compared to unleached samples, perhaps indicative of the precipitation of (oxy)hydroxides. At the pH of the leaching experiment (pH=7.9), we expect minimal dissolution of phyllosilicates and quartz, precluding sources of aluminum and silica. The mostly likely phase for iron reprecipitation is amorphous iron (oxy)hydroxides.

4. DISCUSSION

4.1 Trace Metal Geochemistry in Estuarine Sediments

The sediment cores represent a 60-year record of metal contamination in the Seaplane Lagoon as determined by ¹³⁷Cs, ²⁶Ra, and ²¹⁰Pb analyses of gravity cores collected at the same

location and time as our sediment cores [32]. Comparison of XANES and EXAFS spectra from suboxic sediments at 1.5 cm depth and anoxic sediments at 34.5 cm (and deeper) suggest that most of the important trace metal chemistry occurs near the sediment-water interface and/or in the suboxic zone, where metal contaminants are strongly partitioned to sulfide or oxide phases. Once buried in the anoxic zone, the metal host phases are stable for long periods of time. X-ray absorption spectra of shallow and deep sediments show that poorly crystalline cadmium and zinc sulfides form during biologically mediated sulfate reduction in the suboxic zone and remain stable in sediments with high HS^- concentrations for at least 50 to 60 years (to depths of 55 cm in deep cores). Thermodynamic calculations show porewater saturation or supersaturation with respect to both cadmium and zinc sulfide. Because of the high dissolved HS^- concentrations, metal-sulfide aqueous complexes for several trace metals are stable and produce higher aqueous concentrations of contaminants with depth.

Similarly, we infer that association of lead with carbonate or phosphate phases, manganese with phosphate, and chromium with oxides or phyllosilicates occurs within the water column, the thin oxic sediment zone, or within the suboxic zone. X-ray absorption data show that the local atomic structure around these elements is independent of depth to 34.5 cm, suggesting association with thermodynamically stable or recalcitrant phases. Although the porewaters are saturated with respect to galena (PbS), there is no evidence for lead associated with sulfides in the XAS spectra. Lead may substitute for calcium in either calcite or apatite, both of which are thermodynamically stable based on porewater concentrations, or it may be present as a sorbed complex. Likewise, XANES spectra show that manganese is partially associated with a phosphate phase, which may indicate substitution in apatite or formation of $\text{MnHPO}_4(\text{s})$ as porewaters are close to $\text{MnHPO}_4(\text{s})$ saturation ($\log \text{SI} = -1$). As one might expect, chromium is present only as Cr(III) in these highly reduced sediments. XAS data suggest that dissolved anthropogenic chromium is removed from porewater by either precipitation of chromite or by sorption of chromium to phyllosilicates in the sediments. This is consistent

with laboratory observations of Cr(III) sorption to micas and of the reduction of sorbed Cr(VI) by Fe(II) bearing micas [33]. The EXAFS data and the solution chemistry are also consistent with chromium association with oxides such as eskolaite, chromite or magnesiochromite, all of which are supersaturated. It is doubtful that chromium, lead, and manganese could be sorbed to iron (oxy)hydroxides below the oxic zone (about 1-2 cm) because XANES analysis indicates that available Fe(III) is not present below that depth [29]. Consequently, any chromium, lead, or manganese sorbed to iron (oxy)hydroxides in the water column or the oxic sediments would desorb and bond with oxides, phyllosilicates, carbonates, or phosphates below the zone of Fe(III) reduction.

Detrital phyllosilicates and oxides comprise a recalcitrant fraction of metals in these sediments. This conclusion is based on direct spectroscopic evidence, metal concentration profiles, and by comparison with metal concentrations in uncontaminated San Francisco Bay sediments [21]. The authigenic source of metals to San Francisco Bay sediments is the weathering of the ultramafic Franciscan formation, which can be seen in the iron- and zinc-oxide components. The iron-oxide component is best described as recalcitrant phyllosilicate and oxide phases, probably as iron-bearing micas such as illite, muscovite, chlorite or biotite and oxides such as magnetite, chromite, or ilmenite [18] that do not dissolve in the strongly reducing sediments at neutral pH. It is likely that the zinc-oxide fraction and part of the chromium and manganese fractions are associated with these unreactive phases. Comparison of the metal concentrations in the oxide components and in the surface sediments with metal concentrations in uncontaminated San Francisco Bay sediments further supports the detrital source for metals. Hornberger et al. [21] report background chromium concentrations of 125 to 150 mg g⁻¹, copper concentrations of 20 to 40 mg g⁻¹, lead concentrations of 5 mg g⁻¹, nickel concentrations of 75 to 100 mg g⁻¹, and zinc concentrations of 78 mg g⁻¹. These numbers compare well with zinc concentrations associated with the zinc-oxide component estimated from EXAFS (50 to 130 mg g⁻¹), and surface sediment chromium (200 mg g⁻¹), copper (100 mg g⁻¹),

¹), and nickel (100 mg g⁻¹) concentrations. We cannot resolve the anthropogenic and detrital chromium components in the EXAFS, but the data are consistent with a partial detrital component. Seaplane Lagoon nickel and manganese concentrations are fairly constant and do not show the anthropogenic signature of increasing concentration with depth that is seen for the other trace metals. Therefore, it is possible that nickel and the non-phosphate manganese fraction are associated with detrital phyllosilicates. Almost all of the lead in the sediments is anthropogenic even in the surface sediments. Lead concentrations in the Seaplane Lagoon sediments range from 200 to 1400 mg g⁻¹, and are 40 to 280 times higher than in the uncontaminated San Francisco Bay sediments.

4.2 Metal Geochemistry in Oxidized Sediments

Oxidation of reduced estuarine sediments may occur during dredging operations and during bioturbation or storm events at the interface between the surface sediments and the overlying water. In these environments, the oxidation of sulfides is an important source of dissolved cadmium, zinc, and possibly copper. However, their inherent hazard to biota is mitigated by their sorption to or co-precipitation with oxide substrates. Of these trace metals, cadmium is the most mobile because much less of it is precipitated as an oxide. In our study, about 63% of the CdS and 71% of the ZnS in the reduced sediments dissolved during the experiment, but only 50% of the reacted cadmium was taken up as an oxide, compared to 80% of the reacted zinc. These numbers are based on comparison of EXAFS analyses of the reduced and oxidized sediment, and on the net amount of metal dissolved during the experiment (Figures 6 and 7). One explanation for the low uptake of cadmium compared to zinc is much higher cadmium aqueous complexation. In seawater, about 99% of the cadmium complexes with chloride and 1% is free cadmium ion. By contrast, only 32% of the zinc complexes with chloride and 58% is free zinc ion. This comparison suggests that free metal ions have much higher affinity for hydroxide surfaces than the metal complexes. Minimal cadmium sorption may also result from competition between zinc and cadmium. This phenomena has been observed in laboratory and field studies. In laboratory experiments, cadmium sorption was suppressed by zinc and lead sorption to iron oxyhydroxide [34, 35]. A field study of mine drainage sediments showed iron – (oxy)hydroxide effectively sorb zinc [16, 36]. We assume that copper is present as a sulfide at depth and sorbs to an oxide–substrate when the sediment is oxidized, because the dissolution of copper with time is similar to the behavior of cadmium and zinc. All three elements exhibit a rapid increase in the dissolution rate followed by a decrease in the rate as they sorb to or co-precipitate with oxide–substrates.

The most likely oxide–substrate for cadmium and zinc uptake is precipitated iron–(oxy)hydroxide from the dissolution of pyrite during the oxidation experiment. Pyrite is known to dissolve in seawater. Morse [37] report 20% oxidation of pyrite in seawater in one day. In our EXAFS spectra, we detected a 17% decrease in the pyrite fraction at the end of our oxidation experiment. It is likely that the decrease in the pyrite fraction was accompanied by the precipitation of an iron

– (oxy)hydroxide because almost no dissolved iron was measured in the oxidation experiments. Another possible oxide-substrate for cadmium and zinc uptake would be phyllosilicate phases present in the sediments. It is doubtful that cadmium and zinc co-precipitates with calcium carbonate because no calcite was detected in the X-ray diffraction patterns, nor do we have evidence from solution chemistry for calcite precipitation during the oxidation experiment. It is also doubtful that cadmium and zinc sorb to manganese – (oxy)hydroxides because the concentrations of cadmium ($\sim 40 \text{ mg g}^{-1}$) and zinc ($\sim 210 \text{ mg g}^{-1}$) associated with the oxide – component approximate the total manganese ($\sim 210 \text{ mg g}^{-1}$) in non-phosphate component ($\sim 50\text{-}80\%$, which is probably associated with phyllosilicates). The non-phosphate and phosphate manganese components are stable in seawater. Although a small percentage of manganese dissolved during the first few hours of oxidation, no significant changes in the relative proportions of these phases were observed in the XANES spectra.

Oxidation of reduced contaminated sediments will not yield significant mobilization of chromium and lead because they are associated with oxides, phyllosilicates, carbonates or phosphates. Consequently, they are stable when exposed to oxygen-rich seawater and exhibit little dissolution. Additionally chromium retains its reduced oxidation state as Cr(III) when reacted with seawater. Although there is little difference in XAS spectra for the reduced and oxidized sediments, we cannot rule out the possibility that chromium and lead desorb and are taken up by the iron–(oxy)hydroxides that forms as pyrite oxidizes.

5. CONCLUSIONS

The fate of metal contaminants in urban harbor and coastal sediments depends on the form of the stable solid phase that hosts the metal as sediments are buried and reduced, which cannot necessarily be predicted from the water chemistry. In the suboxic and anoxic sediments with elevated HS^- concentrations, anthropogenic cadmium and zinc form disordered sulfides, but anthropogenic lead and chromium are associated with stable oxides. In addition to the anthropogenic metals, some chromium, manganese, and zinc and all of the nickel appear to be associated with recalcitrant detrital minerals, quite possibly in iron-rich phyllosilicates and oxides. A fraction of manganese is also present as a phosphate. Cadmium and zinc pose the greatest hazard to biota during dredging, bioturbation, or storm events because these sulfides are unstable and will dissolve in oxygen-rich seawater. Dissolved cadmium and zinc will partially sorb to available phyllosilicates or oxides, or co-precipitate with iron–(oxy)hydroxides that form as pyrite oxidizes. Uptake of cadmium and zinc by oxides significantly lowers their dissolved concentrations and reduces their overall hazard to biota. Dredging of deeper sediments poses a minimal hazard to biota for lead and chromium because they are associated with stable carbonate, phosphate, phyllosilicates or oxides. Additionally, chromium is present in its reduced form, Cr(III), in the sediments and showed no evidence for oxidation to Cr(VI) when reacted with seawater.

One significant observation from this study is that dominant reactions that remove dissolved metals from solution occur within the water column or the oxic and suboxic sediments, with minimal metal transformation within the anoxic sediments over time (and depth). As iron (oxy)hydroxides and sulfate are reduced at depths less than 5 cm, dissolved metals are taken-up by stable solids below the sediment-water interface. Once buried, the phases hosting the trace metals are stable

for a minimum of 60 years (age of the sediments). Any cadmium and zinc associated with reactive iron (oxy)hydroxides in the water column or in the oxic sediments will dissolve and re-precipitate as disordered sulfides with in suboxic sediments. In contrast, any lead bonded to stable phases such carbonate or phosphate in the oxygen-rich water column or in oxic sediments does not dissolve and re-precipitate as its thermodynamically stable sulfide phase (galena, PbS).

This work was motivated by the US Navy's concern that sediments contaminated prior to the Clean Water Act (1975) would contaminate the overlying water column as metals dissolve when reduced sediments react with oxygen-rich water during bioturbation, storm, dredging and other marina activities. The results of this study can be used to help design the impact of remediation strategies.

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Table 1. Thermodynamic equilibria and constants used in the geochemical modeling of the porewater chemistry in the Seaplane Lagoon sediments. ^aExperimental values extrapolated to $I = 0$.

	$\log K$ (25°C)	Reference
$\text{Al}(\text{OH})_3(\text{gibbsite}) + 2\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O}$	7.76	[38]
$\text{AlOOH}(\text{boehmite}) + 3\text{H}^+ = 2\text{Al}^{3+} + 2\text{H}_2\text{O}$	7.56	[38]
$\text{CaCO}_3(\text{calcite}) = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-8.48	[39]
$\text{CaMg}(\text{CO}_3)_2(\text{dolomite}) = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$	-18.14	[39]
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{gypsum}) = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	-4.48	[40]
$\text{Cd}^{2+} + \text{H}_2\text{O} = \text{CdOH}^+ + \text{H}^+$	-10.08	[41]
$\text{Cd}^{2+} + 2\text{H}_2\text{O} = \text{Cd}(\text{OH})_2^0 + 2\text{H}^+$	-20.34	[41]
$\text{Cd}^{2+} + 3\text{H}_2\text{O} = \text{Cd}(\text{OH})_3^- + 3\text{H}^+$	-33.29	[41]
$\text{Cd}^{2+} + 4\text{H}_2\text{O} = \text{Cd}(\text{OH})_4^{2-} + 4\text{H}^+$	-47.33	[41]
$\text{Cd}^{2+} + \text{Cl}^- = \text{CdCl}^+$	1.97	[42]
$\text{Cd}^{2+} + 2\text{Cl}^- = \text{CdCl}_2(\text{aq})$	2.59	[42]
$\text{Cd}^{2+} + 3\text{Cl}^- = \text{CdCl}_3^-$	2.34	[42]
$\text{Cd}^{2+} + 4\text{Cl}^- = \text{CdCl}_4^{2-}$	-1.46	[42]
$\text{Cd}^{2+} + \text{CO}_3^{2-} = \text{CdCO}_3^0$	3.00	[43]
$\text{Cd}^{2+} + 2\text{CO}_3^{2-} = \text{Cd}(\text{CO}_3)_2^{2-}$	6.40	[43]
$\text{Cd}^{2+} + \text{CO}_3^{2-} + \text{H}^+ = \text{CdHCO}_3^+$	11.83	[43]
$\text{Cd}^{2+} + \text{SO}_4^{2-} = \text{CdSO}_4^0$	-0.003	[44]
$\text{CdHS}^+ = \text{HS}^- + \text{Cd}^{2+}$	-9.02	[45] ^a
$\text{Cd}(\text{HS})_2 = 2\text{HS}^- + \text{Cd}^{2+}$	-16.53	[45] ^a
$\text{Cd}(\text{OH})_2(\text{beta}) + 2\text{H}^+ = \text{Cd}^{2+} + 2\text{H}_2\text{O}$	13.64	[41]
$\text{CdS} + \text{H}^+ = \text{HS}^- + \text{Cd}^{2+}$	-15.91	[44]
$\text{CdSO}_4(\text{anglesite}) = \text{Cd}^{2+} + \text{SO}_4^{2-}$	-0.11	[44]
$\text{CdCO}_3(\text{otavite}) = \text{Cd}^{2+} + \text{CO}_3^{2-}$	-12.1	[43]
$\text{CdO}(\text{monteponite}) + 2\text{H}^+ = \text{Cd}^{2+} + \text{H}_2\text{O}$	15.1	[46]
$\text{Cr}^{3+} + \text{Cl}^- = \text{CrCl}^{2+}$	7.60	[47]
$\text{Cr}^{3+} + 2\text{Cl}^- = \text{CrCl}_2^+$	7.91	[47]
$\text{CrHS}^{2+} = \text{HS}^- + \text{Cr}^{3+}$	-9.88	[45] ^a
$\text{CrS} + 2\text{H}^+ + 0.25\text{O}_2(\text{aq}) = 0.5\text{H}_2\text{O} + \text{Cr}^{3+} + \text{HS}^-$	31.35	[47]
$\text{Cr}_2\text{O}_3(\text{eskolaite}) + 6\text{H}^+ = 3\text{H}_2\text{O} + 2\text{Cr}^{3+}$	7.64	[44]
$\text{Cu}^{2+} + \text{Cl}^- = \text{CuCl}^+$	0.40	[42]
$\text{Cu}^{2+} + 2\text{Cl}^- = \text{CuCl}_2(\text{aq})$	-0.69	[42]
$\text{Cu}^{2+} + 3\text{Cl}^- = \text{CuCl}_3^-$	-2.29	[42]
$\text{Cu}^{2+} + 4\text{Cl}^- = \text{CuCl}_4^{2-}$	-4.94	[42]

Table 1 (Continued).

	log K (25°C)	Reference
$\text{CuS(covellite)} + \text{H}^+ = \text{HS}^- + \text{Cu}^{2+}$	-22.83	[39]
$\text{CuFeS}_2(\text{chalcopyrite}) + 2\text{H}^+ = 2\text{HS}^- + \text{Fe}^{2+} + \text{Cu}^{2+}$	-32.56	[39]
$\text{Cu}_2\text{CO}_3(\text{OH})_2(\text{malachite}) + 2\text{H}^+ =$ $\text{H}_2\text{O} + \text{CO}_3^{2-} + 2\text{Cu}^{2+}$	-4.40	[39]
$\text{CuO}(\text{tenorite}) + 2\text{H}^+ = \text{Cu}^{2+} + \text{H}_2\text{O}$	7.66	[39]
$\text{FeHS}^+ = \text{HS}^- + \text{Fe}^{2+}$	-5.52	[48] ^a
$(\text{Fe})_2\text{HS}^{3+} = \text{HS}^- + 2\text{Fe}^{2+}$	-10.02	[48] ^a
$(\text{Fe})_3\text{HS}^{5+} = \text{HS}^- + 3\text{Fe}^{2+}$	-15.30	[48] ^a
$\text{Fe}^{2+} + \text{Cl}^- = \text{FeCl}^+$	-0.16	[42]
$\text{Fe}^{2+} + 2\text{Cl}^- = \text{FeCl}_2(\text{aq})$	-8.17	[42]
$\text{Fe}^{3+} + \text{Cl}^- = \text{FeCl}^{2+}$	1.47	[42]
$\text{Fe}^{3+} + 2\text{Cl}^- = \text{FeCl}_2^+$	2.13	[49]
$\text{Fe}^{3+} + 4\text{Cl}^- = \text{FeCl}_4^-$	-0.79	[49]
$\text{FeS}_2(\text{pyrite}) + \text{H}_2\text{O} = \text{Fe}^{2+} + 2\text{HS}^{2-} + 0.5\text{O}_2(\text{aq})$	-59.23	[39]
$\text{FeS}(\text{pyrrhotite}) + \text{H}^+ = \text{HS}^- + \text{Fe}^{2+}$	-3.72	[39]
$\text{FeCO}_3(\text{siderite}) = \text{Fe}^{2+} + \text{CO}_3^{2-}$	-10.52	[39]
$\text{FeOOH}(\text{goethite}) + 2\text{H}^+ =$ $\text{Fe}^{2+} + 1.5\text{H}_2\text{O} + 0.25\text{O}_2(\text{aq})$	-7.96	[40]
$\text{Na}_{.33}\text{Fe}_2\text{Al}_{.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2(\text{Na-nonttronite}) + 5.32\text{H}^+ =$ $2\text{Fe}^{2+} + 0.5\text{O}_2(\text{aq}) + 0.33\text{Na}^+ + 3.67\text{SiO}_2 + 3.66\text{H}_2\text{O}$	-28.51	[50]
$\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8(7\text{-}\text{\AA}\text{ chlorite}) + 16\text{H}^+ =$ $2\text{Al}^{3+} + 12\text{H}_2\text{O} + 3\text{SiO}_2(\text{aq}) + 5\text{Mg}^{2+}$	70.61	[39]
$\text{Mn}^{2+} + \text{Cl}^- = \text{MnCl}^+$	-0.14	[42]
$\text{Mn}^{2+} + 3\text{Cl}^- = \text{MnCl}_3^-$	-0.77	[44]
$\text{MnHS}^+ = \text{HS}^- + \text{Mn}^{2+}$	-5.00	[48] ^a
$(\text{Mn})_2\text{HS}^{3+} = \text{HS}^- + 2\text{Mn}^{2+}$	-9.55	[48] ^a
$(\text{Mn})_3\text{HS}^{5+} = \text{HS}^- + 3\text{Mn}^{2+}$	-13.63	[48] ^a
$\text{MnS}(\text{alabandite}) + \text{H}^+ = \text{HS}^- + \text{Mn}^{2+}$	-0.05	[39]
$\text{MnCO}_3(\text{rhodochrosite}) = \text{Mn}^{2+} + \text{CO}_3^{2-}$	-10.52	[39]
$\text{Ni}(\text{OH})_2 + 2\text{H}^+ = \text{Ni}^{2+} + 2\text{H}_2\text{O}$	7.64	[44]
$\text{Ni}^{2+} + \text{Cl}^- = \text{NiCl}^+$	-1.00	[42]
$\text{NiCO}_3 = \text{CO}_3^{2-} + \text{Ni}^{2+}$	-6.82	[44]
$\text{NiHS}^+ = \text{HS}^- + \text{Ni}^{2+}$	-5.29	[48] ^a
$(\text{Ni})_2\text{HS}^{3+} = \text{HS}^- + 2\text{Ni}^{2+}$	-9.82	[48] ^a
$(\text{Ni})_3\text{HS}^{5+} = \text{HS}^- + 3\text{Ni}^{2+}$	-13.65	[48] ^a
$\text{NiS}_2(\text{vaesite}) + \text{H}_2\text{O} = \text{Ni}^{2+} + 2\text{HS}^{2-} + 0.5\text{O}_2(\text{aq})$	-61.34	[39]

Table 1 (Continued).

	log K (25°C)	Reference
$\text{NiS(millerite)} + \text{H}^+ = \text{HS}^- + \text{Ni}^{2+}$	-8.03	[51]
$\text{PbS(galena)} + \text{H}^+ = \text{HS}^- + \text{Pb}^{2+}$	-14.85	[44]
$\text{Pb}^{2+} + \text{H}_2\text{O} = \text{PbOH}^+ + \text{H}^+$	-7.7	[52]
$\text{Pb}^{2+} + 2\text{H}_2\text{O} = \text{Pb(OH)}_2^- + 2\text{H}^+$	-17.09	[52]
$\text{Pb}^{2+} + 3\text{H}_2\text{O} = \text{Pb(OH)}_3^- + 3\text{H}^+$	-28.09	[52]
$\text{Pb}^{2+} + \text{Cl}^- = \text{PbCl}^+$	1.44	[42]
$\text{Pb}^{2+} + 2\text{Cl}^- = \text{PbCl}_2(\text{aq})$	2.00	[42]
$\text{Pb}^{2+} + 3\text{Cl}^- = \text{PbCl}_3^-$	1.69	[42]
$\text{Pb}^{2+} + 4\text{Cl}^- = \text{PbCl}_4^{2-}$	1.43	[42]
$\text{Pb}^{2+} + \text{CO}_3^{2-} = \text{PbCO}_3$	6.58	[53]
$\text{Pb}^{2+} + 2\text{CO}_3^{2-} = \text{Pb(CO}_3)_2^{2-}$	9.40	[53]
$\text{PbCO}_3(\text{cerussite}) = \text{Pb}^{2+} + \text{CO}_3^{2-}$	-13.54	[20]
$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2(\text{hydrocerussite}) + 2\text{H}^+ = 2\text{CO}_3^{2-} + 3\text{Pb}^{2+} + 2\text{H}_2\text{O}$	-18.81	[52]
$\text{PbSO}_4(\text{anglesite}) = \text{Pb}^{2+} + \text{SO}_4^{2-}$	-7.85	[39]
$\text{PbHS}^+ = \text{HS}^- + \text{Pb}^{2+}$	-8.62	[45] ^a
$\text{Pb(HS)}_2 = 2\text{HS}^- + \text{Pb}^{2+}$	-16.43	[45] ^a
$\text{SiO}_2(\text{quartz}) = \text{SiO}_2(\text{aq})$	-4.0	[39]
$\text{SiO}_2(\alpha\text{-cristobalite}) = \text{SiO}_2(\text{aq})$	-3.45	[39]
$\text{SiO}_2(\text{am. si.}) = \text{SiO}_2(\text{aq})$	-2.71	[39]
$\text{Zn}^{2+} + \text{H}_2\text{O} = \text{ZnOH}^+ + \text{H}^+$	-8.96	[54]
$\text{Zn}^{2+} + 2\text{H}_2\text{O} = \text{Zn(OH)}_2^0 + 2\text{H}^+$	-28.04	[44]
$\text{Zn}^{2+} + 3\text{H}_2\text{O} = \text{Zn(OH)}_3^- + 3\text{H}^+$	-28.83	[44]
$\text{Zn}^{2+} + 4\text{H}_2\text{O} = \text{Zn(OH)}_4^- + 4\text{H}^+$	-41.61	[44]
$\text{Zn}^{2+} + \text{Cl}^- = \text{ZnCl}^+$	1.99	[42]
$\text{Zn}^{2+} + 2\text{Cl}^- = \text{ZnCl}_2(\text{aq})$	2.51	[42]
$\text{Zn}^{2+} + 3\text{Cl}^- = \text{ZnCl}_3^-$	-0.02	[42]
$\text{Zn}^{2+} + \text{CO}_3^{2-} + \text{H}^+ = \text{ZnHCO}_3^+$	8.91	[54]
$\text{Zn}^{2+} + \text{CO}_3^{2-} = \text{ZnCO}_3^0$	3.9	[55]
$\text{Zn}^{2+} + \text{SO}_4^{2-} = \text{ZnSO}_4^0$	-0.026	[44]
$\text{Zn}_2\text{S}_3^{2-} + 3\text{H}^+ = 3\text{HS}^- + 2\text{Zn}^{2+}$	-1.07	[56] ^a
$\text{Zn}_4\text{S}_6^{4-} + 6\text{H}^+ = 6\text{HS}^- + 4\text{Zn}^{2+}$	-5.22	[56] ^a
$\text{ZnS(sphalerite)} + \text{H}^+ = \text{HS}^- + \text{Zn}^{2+}$	-11.44	[39]
$\text{Zn(OH)}_2(\beta) + 2\text{H}^+ = \text{Zn}^{2+} + 2\text{H}_2\text{O}$	11.93	[44]
$\text{Zn(OH)}_2(\epsilon) + 2\text{H}^+ = \text{Zn}^{2+} + 2\text{H}_2\text{O}$	11.66	[44]
$\text{Zn(OH)}_2(\gamma) + 2\text{H}^+ = \text{Zn}^{2+} + 2\text{H}_2\text{O}$	11.88	[44]
$\text{ZnSO}_4(\text{solid}) = \text{Zn}^{2+} + \text{SO}_4^{2-}$	3.55	[44]
$\text{ZnCO}_3(\text{smithsonite}) = \text{Zn}^{2+} + \text{CO}_3^{2-}$	-9.87	[20]
$\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2(\text{hydrozincite}) + 6\text{H}^+ = 5\text{Zn}^{2+} + 2\text{CO}_3^{2-} + 6\text{H}_2\text{O}$	9.65	[57]

Table 2. Porewater trace- and major-elements extracted from Seaplane Lagoon core SC4 (July 10, 1998). Calcium, iron, potassium, magnesium, manganese, sodium, and silica were measured by ICP-AES. Aluminum, cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc were measured by ICP-MS. Uncertainty for potassium was not reported.

ICP-AES																
Sample ID	Depth (cm)	Ca (ppm)		Fe (ppm)		K (ppm)	Mg (ppm)		Mn (ppm)		Na (ppm)		Si (ppm)			
SC4-1	1.5	327	1	2.20	0.01	318	1017	2	0.366	0.002	7870	20	14.4	0.0		
SC4-2	4.5	355	1	0.20	0.00	340	1133	2	0.195	0.003	8440	20	20.9	0.0		
SC4-3	7.5	350	2	<0.2		346	1192	2	0.182	0.004	8600	30	22.4	0.1		
SC4-4	10.5	388	1	<0.2		374	1368	3	0.275	0.002	9540	20	23.0	0.1		
SC4-5	13.5	390	1	<0.2		398	1414	4	0.375	0.001	9800	40	21.3	0.1		
SC4-6	16.5	410	2	<0.2		435	1493	3	0.431	0.001	10400	200	20.9	0.0		
SC4-7	19.5	430	2	<0.2		474	1546	5	0.271	0.002	10900	100	21.3	0.1		
SC4-8	22.5	444	2	0.69		487	1620	6	0.173	0.001	11500	100	21.4	0.1		
SC4-9	25.5	438	1	<0.2		496	1604	4	<0.1	0.001	11400	100	21.6	0.1		
SC4-10	28.5	434	2	<0.2		560	1633	4	<0.1		11700	0	21.2	0.1		
SC4-11	31.5	436	3	<0.2		461	1639	3	<0.1		11800	0	21.7	0.0		
SC4-12	34.5	427	2	<0.2		509	1640	5	<0.1		11800	100	21.9	0.1		
ICP-MS																
Sample ID	Depth (cm)	Al (ppb)		Cd (ppb)		Cr (ppb)		Cu (ppb)		Fe (ppb)		Mn (ppb)		Ni (ppb)		
SC4-1	1.5	2.4	0.2	0.19	0.02	0.53	0.06	0.52	0.09	3000	60	395	4.0	2.00	0.24	
SC4-2	4.5	6.2	0.1	0.14	0.02	1.89	0.23	0.46	0.08	1400	70	165	1.7	1.38	0.17	
SC4-3	7.5	2.6	0.1	0.80	0.10	2.35	0.28	0.35	0.06	1000	70	175	3.5	1.34	0.16	
SC4-4	10.5	6.6	0.1	0.12	0.01	2.80	0.34	0.55	0.09	500	25	263	5.3	1.37	0.16	
SC4-5	13.5	2.2	0.1	0.20	0.02	2.91	0.35	0.92	0.16	<110	25	462	9.2	1.25	0.15	
SC4-6	16.5	3.8	0.3	0.08	0.01	4.19	0.50	1.00	0.17	<110		536	10.7	1.23	0.15	
SC4-7	19.5	5.3	0.2	0.12	0.01	5.40	0.65	0.76	0.13	<110		304	3.0	1.18	0.14	
SC4-8	22.5	3.5	0.2	0.25	0.03	5.74	0.69	2.67	0.45	<110		188	1.9	1.19	0.14	
SC4-9	25.5	8.2	0.3	<0.06	0.03	6.04	0.72	1.97	0.33	<110		52	0.5	<0.2		
SC4-10	28.5	38.4	0.8	0.29		0.03	7.51	0.90	1.08	0.18	<110		10	0.3	1.20	0.14
SC4-11	31.5	4.4	0.2	0.24		0.03	9.61	1.15	0.69	0.12	<110		2	0.1	1.00	0.12
SC4-12	34.5	8.3	0.2	0.63		0.08	15.38	1.85	0.94	0.16	<110		<1		0.97	0.12
ICP-MS (Continued)																
Sample ID	Depth (cm)	Pb (ppb)		Zn (ppb)												
SC4-1	1.5	0.19	0.02	4.12	0.70											
SC4-2	4.5	0.43	0.05	4.00	0.68											
SC4-3	7.5	0.30	0.04	2.82	0.48											
SC4-4	10.5	0.46	0.06	3.21	0.55											
SC4-5	13.5	0.38	0.05	5.61	0.95											
SC4-6	16.5	0.86	0.10	6.83	1.16											
SC4-7	19.5	1.06	0.13	7.36	1.25											
SC4-8	22.5	1.05	0.13	9.45	1.61											
SC4-9	25.5	0.67	0.08	6.28	1.07											
SC4-10	28.5	1.58	0.19	5.04	0.86											
SC4-11	31.5	1.65	0.20	6.88	1.17											
SC4-12	34.5	4.07	0.49	8.64	1.47											

Table 3. Porewater concentrations of total P, total carbon (TC), total inorganic carbon (TIC), and total organic carbon (TOC), total S, Cl⁻ and pH from Seaplane Lagoon cores collected on July 10, 1998 (na = not analyzed).

Core SC2					
Sample ID	Depth (cm)	P (ppm)	TC (ppm)	TIC (ppm)	TOC (ppm)
SC2-0		0.5	na	na	na
SC2-1	1.5	1.2	na	na	na
SC2-2	4.5	2.0	80	na	<14
SC2-3	7.5	1.9	95	86	<14
SC2-4	10.5	1.2	100	84	18
SC2-5	13.5	1.5	123	119	17
SC2-6	16.5	2.0	147	161	<14
SC2-7	19.5	1.7	182	na	na
SC2-8	22.5	2.2	230	250	<14
SC2-9	25.5	2.7	259	na	na
Core SC4					
Sample ID	Depth (cm)	S (ppm)	Cl ⁻ (ppt)	pH	
SC4-1	1.5	686	17.1	7.35	
SC4-2	4.5	736	17.9	7.52	
SC4-3	7.5	759	28.7	8.05	
SC4-4	10.5	859	20.2	8.09	
SC4-5	13.5	893	21.7	7.74	
SC4-6	16.5	949	21.6	7.83	
SC4-7	19.5	976	24.7	7.68	
SC4-8	22.5	996	25.2	7.75	
SC4-9	25.5	952	25.5	7.56	
SC4-10	28.5	955	26.1	7.35	
SC4-11	31.5	1036	26.0	7.76	
SC4-12	34.5	1021	27.5	7.39	

Table 4. Porewater water chemistry from Seaplane Lagoon, Alameda NAS compared with sulfide, carbonate, phosphate, silicate, oxide, and hydroxide minerals reported as the saturation index at 25°C (log *SI*). Calculations used trace and major elements; sulfide and sulfate are from core SC4 and total inorganic carbon is from core SC2.

Sulfides											
Sample ID	Depth (cm)	CdS	CrS	CuS Covellite	CuFeS ₂ Chalcopyrite	FeS ₂ Pyrite	FeS Pyrrhotite	MnS Alabandite	NiS Millerite	PbS Galena	ZnS Sphalerite
SC4-1	1.5	-0.1	-16.2	7.4	14.4	8.9	1.0	-3.0	2.4	-1.3	4.0
SC4-2	4.5	-0.1	-15.1	7.5	14.0	9.1	0.9	-3.2	2.5	-0.8	3.9
SC4-3	7.5	1.2	-15.0	7.3				-2.7	3.0	-0.4	3.56
SC4-4	10.5	0.6	-13.8	10.9				-2.5	3.0	-0.1	3.6
SC4-5	13.5	0.2	-15.1	7.9				-2.6	5.6	2.2	5.0
SC4-6	16.5	-.2	-14.9	8.1				-2.4	2.7	-0.4	3.8
SC4-7	19.5	-.1	-15.0	7.7				-2.8	2.5	-0.4	3.9
SC4-8	22.5	0.2	-14.9	8.3				-3.0	2.6	-0.4	3.9
SC4-9	25.5		-15.0	7.9				-3.7		-0.7	3.9
SC4-10	28.5	0.0	-15.2	7.3				-4.6	2.2	-0.5	4.0
SC4-11	31.5	0.6	-14.6	7.7				-4.9	2.6	-0.2	3.8
SC4-12	34.5	0.6	-14.4	7.7					2.5	0.2	3.8
Carbonates											
Sample ID	Depth (cm)	CaCO ₃ Calcite	CdCO ₃ Otavite	Cu ₂ CO ₃ (OH) ₂ Malachite	FeCO ₃ Siderite	MnCO ₃ Rhodochrosite	NiCO ₃	PbCO ₃ Cerussite	ZnCO ₃ Smithsonite		
SC4-1	1.5	-1.1	-16.2	-29.5	-4.5	-5.2	-11.1	-14.9	-9.9		
SC4-2	4.5	-0.8	-16.1	-29.0	-4.5	-5.3	-11.0	-14.4	-9.9		
SC4-3	7.5	0.9	-13.5	-27.7		-3.5	-9.2	-12.6	-8.9		
SC4-4	10.5	1.1	-14.0	-20.2		-3.1	-9.0	-12.2	-8.7		
SC4-5	13.5	0.8	-14.7	-26.9		-3.5	-6.6	-10.1	-7.6		
SC4-6	16.5	1.0	-14.9	-26.5		-3.2	-.95	-12.6	-8.8		
SC4-7	19.5	0.9	-14.8	-27.4		-3.6	-9.6	-12.6	-8.6		
SC4-8	22.5	1.1	-14.4	-26.1		-3.6	-9.4	-12.5	-8.5		
SC4-9	25.5	0.9		-27.0		-4.3		-12.8	-8.5		
SC4-10	28.5	-0.5	-15.8	-29.4		-6.4	-10.9	-13.8	-9.6		
SC4-11	31.5	1.3	-13.8	-27.1		-5.4	-9.3	-12.1	-8.4		
SC4-12	34.5	1.3	-13.7	-26.9			-9.2	-11.6	-8.3		
Silicates											
Sample ID	Depth (cm)	PbHPO ₄	Ca ₅ OH(PO ₄) ₃ Apatite	Pb ₅ PO ₄ Cl ₃ Pyromorphite	β- Zn(OH) ₂	SiO ₂ Quartz	SiO ₂ β-Cristobalite	Mg ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈ 7A-Chlorite			
SC4-1	1.5	-11.6	1.8	-55.5	-10.1	0.7	-0.3	-0.1			
SC4-2	4.5	-11.4	2.5	-53.9	-10.1	0.8	0.2	2.8			
SC4-3	7.5	-11.2	4.6	-51.8	-9.8	0.6	-0.4	5.5			
SC4-4	10.5	-10.9	5.1	-50.3	-9.6	0.7	-0.3	7.2			
SC4-5	13.5	-8.6	3.5	-39.5	-8.9	0.8	-0.2	3.8			
SC4-6	16.5	-11.2	4.3	-52.5	-10.1	0.7	-0.3	5.1			
SC4-7	19.5	-11.2	3.5	-52.6	-10.1	0.8	-0.2	4.3			
SC4-8	22.5	-11.2	4.1	-52.6	-10.1	0.8	-0.2	4.5			
SC4-9	25.5	-11.5	3.6	-52.3	-10.2	0.8	-0.2	3.8			
SC4-10	28.5	-10.7	2.8	-53.1	-10.3	0.8	-0.2	3.6			
SC4-11	31.5	-10.9	4.3	-51.5	-10.2	0.8	-0.2	4.7			
SC4-12	34.5	-10.5	4.2	-51.2	-10.1	0.8	-0.3	5.2			

Oxides/Hydroxides/Phosphates										
Sample ID	Depth (cm)	Al(OH) ₃ Gibbsite	Cd(OH) ₂	Cr ₂ O ₃ Eskolaite	CuO Tenorite	Fe(OH) ₂	FeOOH Goethite	Ni(OH) ₂	Mn(OH) ₂	MnHPO ₄
SC4-1	1.5	0.6	-20.4	-1.0	-13.8	-7.3	-4.6	-9.1	-9.4	-1.2
SC4-2	4.5	0.9	-20.4	1.8	-13.6	-7.3	-4.4	-8.9	-9.5	-1.6
SC4-3	7.5	0.0	-18.4	4.3	-13.2			-7.8	-8.4	-1.4
SC4-4	10.5	0.3	-19.0	7.0	-9.5			-7.7	-8.1	-1.2
SC4-5	13.5	0.2	-20.0	2.3	-13.1			-5.7	-8.8	-1.3
SC4-6	16.5	0.4	-20.3	3.1	-12.8			-8.5	-8.6	-1.2
SC4-7	19.5	0.7	-20.4	5.4	-13.4			-8.8	-9.1	-1.5
SC4-8	22.5	0.4	-20.0	2.8	-12.8			-8.7	-9.2	-1.6
SC4-9	25.5	1.0		1.8	-13.3				-10.1	-2.0
SC4-10	28.5	1.8	-20.5	0.8	-14.0			-9.4	-11.2	-2.7
SC4-11	31.5	0.5	-19.6	3.3	-13.4			-8.8	-11.2	-3.5
SC4-12	34.5	0.8	-19.6	3.7	-13.3			-8.8		

Sample ID	Depth (cm)	Pb ₃ (PO ₄) ₂	Ni ₃ (PO ₄) ₂	Mn ₃ (PO ₄) ₂	Cd ₃ (PO ₄) ₂	Cu ₃ (PO ₄) ₂	Zn ₃ (PO ₄) ₂ *4H ₂ O Hopeite
SC4-1	1.5	-41.4	23.1	-22.7	-53.0	-47.0	-24.6
SC4-2	4.5	-40.8	-23.5	-23.8	-53.5	-47.1	-25.4
SC4-3	7.5	-39.2	-22.0	-22.2	-49.5	-47.9	-26.5
SC4-4	10.5	-38.2	-21.8	-21.4	-51.5	-37.0	-26.1
SC4-5	13.5	-32.6	-14.6	-22.3	-53.3	-46.4	-22.6
SC4-6	16.5	-39.6	-23.2	-21.9	-54.3	-45.9	-26.3
SC4-7	19.5	-39.7	-23.7	-23.0	-54.2	-47.2	-26.0
SC4-8	22.5	-39.5	-23.5	-23.4	-53.0	-45.3	-26.0
SC4-9	25.5	-40.0		-25.1		-45.9	-25.3
SC4-10	28.5	-39.1	-23.8	-27.5	-52.9	-47.2	-24.8
SC4-11	31.5	-38.8	-23.5	-29.1	-51.7	-47.0	-26.1
SC4-12	34.5	-37.6	-23.6		-51.6	-46.8	-25.9

Sample ID	Depth (cm)	FePO ₄ *2 H ₂ O Strengite	FeCr ₂ O ₄ Chromite	MgCr ₂ O ₄ Magnesio- chromite
SC4-1	1.5	-13.2	8.3	4.8
SC4-2	4.5	-13.4	0.9	0.9
SC4-3	7.5			4.4
SC4-4	10.5			7.2
SC4-5	13.5			2.0
SC4-6	16.5			3.0
SC4-7	19.5			5.0
SC4-8	22.5			2.5
SC4-9	25.5			1.1
SC4-10	28.5			-0.3
SC4-11	31.5			3.0
SC4-12	34.5			3.4

Table 5. Bulk sediment chemistry from Seaplane Lagoon cores SC2, SC3, SC4; C1, C2 and C3 reported as the average (\pm uncertainty) of 2–4 replicate analyses multiplied by 1.47 to correct for solution viscosity.

Core SC2.

Sample ID	Depth (cm)	Al (ppm) ±	Ca (ppm) ±	Cd (ppm) ±	Co (ppm) ±	Cr (ppm) ±	Cu (ppm) ±
SC2-1	1.5	41700 4900	11000 900	11.0 2.0	22.2 2.9	230 24	98 7
SC2-2	4.5	45300 4200	9840 200	12.7 0.4	24.6 0.1	248 7	108 2
SC2-3	7.5	46300 4000	8510 330	18.8 0.2	24.7 0.8	284 14	129 3
SC2-4	10.5	49000 3400	8820 410	28.1 1.8	29.3 0.5	355 21	157 8
SC2-5	13.5	48400 3900	8730 530	32.7 2.9	31.0 2.8	385 32	164 11
SC2-6	16.5	45100 3200	8510 410	30.4 0.8	28.1 0.5	386 20	163 5
SC2-7	19.5	45500 4800	20900 600	33.1 1.9	26.9 1.7	392 20	174 6
SC2-8	22.5	44200 4000	7770 210	38.9 0.9	30.2 1.1	425 18	168 4
SC2-9	25.5	45800 4300	8040 220	53.4 1.1	50.6 2.4	494 27	163 5

Sample ID	Depth (cm)	Fe (ppm) ±	Mg (ppm)	Mn (ppm) ±	Ni (ppm) ±	Pb (ppm) ±	S (ppm)	Zn (ppm) ±
SC2-1	1.5	41300 4700	7350	382 36	108 12	183 21	9950	240 22
SC2-2	4.5	48700 1600	9180	447 8	125 2	200 21	13400	268 31
SC2-3	7.5	51800 1700	9840	456 17	136 1	240 43	15800	298 28
SC2-4	10.5	53700 2600	10300	467 24	148 9	365 27	16600	357 29
SC2-5	13.5	53400 3900	10300	459 33	147 11	415 28	16600	395 25
SC2-6	16.5	50400 1400	9890	424 16	139 2	387 46	15800	369 36
SC2-7	19.5	49000 3200	9440	402 19	138 8	414 44	14200	373 41
SC2-8	22.5	47000 1600	9400	386 12	137 3	453 36	13900	373 39
SC2-9	25.5	48000 2800	9790	384 17	146 4	568 42	13200	389 39

Table 5. Core SC3.

Sample ID	Depth (cm)	Al (ppm) ±	Ca (ppm) ±	Cd (ppm) ±	Co (ppm) ±	Cr (ppm) ±	Cu (ppm) ±
SC3-1	1.5	41600 4300	9280 216	17 1	23 0	248 8	106 4
SC3-2	4.5	42800 3800	10300 428	16 1	21 2	240 12	107 1
SC3-3	7.5	42900 4500	13200 289	13 0	27 1	242 8	107 3
SC3-6	16.5	41100 3400	10100 387	46 1	43 2	419 16	149 5
SC3-7	19.5	44500 5100	9110 555	84 5	69 5	550 51	199 14
SC3-8	22.5	45800 6600	9330 1100	81 12	33 3	481 68	162 17
SC3-9	25.5	33500 3100	10000 335	347 14	26 2	876 57	216 9
SC3-10	28.5	38200 4300	9970 45	285 8	20 0	865 33	207 4
SC3-11	31.5	37400 4000	11200 573	358 24	22 2	1150 100	236 10
SC3-12	34.5	34600 5100	14100 1110	316 33	19 2	830 74	241 18
SC3-13	37.5	35400 4900	10400 660	270 23	20 2	691 57	226 13

Sample ID	Depth (cm)	Fe (ppm) ±	Mg (ppm) ±	Mn (ppm) ±	Ni (ppm) ±	Pb (ppm) ±	S (ppm)	Zn (ppm) ±
SC3-1	1.5	43700 1400	9420 2910	384 7	112 3	210 26	10700	257 30
SC3-2	4.5	43800 1600	10100 2900	392 16	112 4	210 6	12300	251 23
SC3-3	7.5	46800 1600	10900 3300	425 11	117 1	199 15	13400	256 29
SC3-6	16.5	45100 900	11100 3400	371 10	147 1	516 47	13700	354 41
SC3-7	19.5	49400 4600	12300 3300	382 32	186 10	898 70	14100	445 40
SC3-8	22.5	56200 8400	13400 3500	436 60	163 23	676 103	16400	377 40
SC3-9	25.5	47700 2900	12400 3600	440 24	147 7	955 63	13700	386 38
SC3-10	28.5	49200 2500	12500 4000	429 12	119 6	1120 129	17800	525 70
SC3-11	31.5	52800 4400	12400 3500	399 28	150 10	1130 111	20900	631 62
SC3-12	34.5	48800 6000	11100 3600	364 34	137 16	1230 188	18900	481 72
SC3-13	37.5	49300 5300	11400 3400	385 30	125 12	784 108	18900	475 58

Table 5, Core SC4.

Sample ID	Depth (cm)	Al (ppm) ±	Ca (ppm) ±	Cd (ppm) ±	Co (ppm) ±	Cr (ppm) ±	Cu (ppm) ±
SC4-1	1.5	44300 6100	11200 1100	15 2	24 2	243 23	108 8
SC4-2	4.5	46900 6500	9800 1100	17 2	25 2	275 27	123 15
SC4-3	7.5	47100 6100	9700 1100	19 2	25 1	278 28	131 10
SC4-4	10.5	48300 6100	10200 1200	15 2	26 1	279 29	133 8
SC4-5	13.5	48900 4900	10300 900	21 2	26 2	280 21	128 11
SC4-6	16.5	48500 4800	10600 900	39 3	27 2	327 24	129 13
SC4-7	19.5	47800 4600	9200 800	38 3	28 2	351 26	148 12
SC4-8	22.5	46800 4600	9700 700	56 5	33 2	422 27	172 11
SC4-9	25.5	46900 4300	8900 600	66 5	36 2	456 26	166 11
SC4-10	28.5	48200 4900	9600 300	78 3	47 1	493 15	189 13
SC4-11	31.5	44700 7000	14800 1300	136 14	27 2	584 38	202 13
SC4-12	34.5	46200 6200	10600 700	192 18	31 2	766 45	210 14

Sample ID	Depth (cm)	Fe (ppm) ±	Mg (ppm) ±	Mn (ppm) ±	Ni (ppm) ±	Pb (ppm) ±	S (ppm)	Zn (ppm) ±
SC4-1	1.5	44000 3900	11900 3400	429 40	120 11	214 40	10100	287 52
SC4-2	4.5	49100 4700	13600 3700	443 46	130 15	242 49	12000	322 57
SC4-3	7.5	50700 4600	14000 3600	474 48	132 12	249 45	12800	318 53
SC4-4	10.5	52600 5100	14700 3600	504 54	138 17	242 42	13300	326 54
SC4-5	13.5	51100 3700	15900 3100	503 38	137 12	251 33	13200	331 40
SC4-6	16.5	51100 3600	15800 3200	543 40	139 10	338 47	14700	346 43
SC4-7	19.5	50800 3600	15900 3200	528 40	140 12	393 55	15200	374 45
SC4-8	22.5	49600 3100	15600 3200	541 35	145 10	593 79	14900	426 52
SC4-9	25.5	49700 2800	15700 3100	526 30	148 10	562 69	15300	432 47
SC4-10	28.5	53800 1800	15400 3800	518 21	173 4	831 97	16600	463 55
SC4-11	31.5	54200 4800	14900 4700	435 35	155 13	946 192	16700	496 90
SC4-12	34.5	53500 3900	15200 4300	422 30	155 11	1270 230	17100	515 84

Table 5, Core C1

Sample ID	Depth (cm)	Al (ppm) ±	Ca (ppm) ±	Cd (ppm) ±	Co (ppm) ±	Cr (ppm) ±	Cu (ppm) ±
C1-1	75.0	34700 4400	9460 350	1 0	22 2	159 9	40 4
C1-2	55.0	32000 3800	21900 600	1220 50	19 1	1730 90	232 8
C1-3	40.0	41800 5200	8680 260	72 4	27 1	470 26	165 7
C1-4	30.0	44600 5000	8950 330	29 1	34 2	424 25	177 6
C1-5	20.0	46500 4800	8810 200	30 2	28 2	346 4	150 4
C1-6	13.5	48300 4800	8930 190	20 1	27 1	300 11	137 3
C1-7	10.5	47800 4100	8860 200	15 1	25 1	271 11	118 7
C1-8	7.5	48500 6400	10000 330	14 1	25 1	262 12	116 6
C1-9	4.5	48200 4600	9400 290	11 2	27 1	259 16	116 7
C1-10	1.5	47000 6100	9210 350	15 1	26 2	264 9	123 10

Sample ID	Depth (cm)	Fe (ppm) ±	Mg (ppm) ±	Mn (ppm) ±	Ni (ppm) ±	Pb (ppm) ±	S (ppm)	Zn (ppm) ±
C1-1	75.0	46100 4100	9670 2940	952 51	129 7	57 24	3940 80	108 14
C1-2	55.0	48400 3600	12300 3500	400 18	113 5	1400 140	4770 480	574 61
C1-3	40.0	51600 4100	13200 3800	398 20	1530 10	645 69	4550 60	373 42
C1-4	30.0	54100 4300	13200 3800	427 23	153 5	475 53	4740 480	399 43
C1-5	20.0	55100 3000	13200 4200	479 6	145 5	347 55	4790 50	344 48
C1-6	13.5	57600 3500	13900 3900	508 19	145 3	241 27	5000 400	313 33
C1-7	10.5	56600 2500	13700 3800	508 17	144 3	195 24	4900 190	282 27
C1-8	7.5	55800 4100	14200 4700	505 25	140 10	185 37	4700	280 44
C1-9	4.5	54700 3000	13900 4000	478 29	133 1	188 21	4590	285 31
C1-10	1.5	52600 4500	13600 4600	430 23	131 10	206 45	4460	295 51

Table 5, Core C2

Sample ID	Depth (cm)	Al (ppm) ±	Ca (ppm) ±	Cd (ppm) ±	Co (ppm) ±	Cr (ppm) ±	Cu (ppm) ±		
C2-1	1.5	44100 6000	9280 970	15 1	27 2	265 24	126 13		
C2-2	4.5	43800 6500	9690 1320	13 2	27 3	264 32	131 14		
C2-3	7.5	43800 6200	8680 1030	18 2	28 3	281 30	137 11		
C2-4	10.5	45000 6200	9170 1060	58 7	28 2	373 37	150 13		
C2-5	13.5	46100 6500	9120 1100	16 2	27 3	278 29	132 12		
C2-6	20.0	48400 6900	9150 1120	20 3	28 3	309 33	146 13		
C2-7	30.0	45000 6100	9180 1040	40 4	44 4	455 44	167 13		
C2-8	40.0	36000 4900	9440 1020	73 10	157 17	544 51	227 19		
C2-9	55.0	33400 4300	12200 1300	274 40	20 1	774 73	197 14		
C2-10	75.0	31200 3700	12300 800	1 0	14 1	100 6	19 3		
Sample ID	Depth (cm)	Fe (ppm) ±	Mg (ppm) ±	Mn (ppm) ±	Ni (ppm) ±	Pb (ppm) ±	S (ppm)	Zn (ppm)	±
C2-1	1.5	51400 4600	14700 4000	434 41	136 12	234 49	11800	318	55
C2-2	4.5	51700 6000	14700 4000	442 56	130 18	231 49	13000	322	61
C2-3	7.5	52600 5400	14500 4000	441 49	135 15	269 64	13500	336	61
C2-4	10.5	53900 5100	15500 4100	458 47	140 15	451 89	14200	361	62
C2-5	13.5	53300 5400	15100 4000	460 52	141 16	266 52	14300	322	57
C2-6	20.0	55300 5500	16200 4300	484 53	150 17	313 67	14900	351	62
C2-7	30.0	52000 5000	15800 4200	414 41	154 15	514 96	14500	395	68
C2-8	40.0	49200 4900	14800 4000	350 35	173 20	1169 231	13500	518	92
C2-9	55.0	46200 4200	13500 3500	406 38	114 12	895 162	16300	492	82
C2-10	75.0	23300 1600	6550 1800	341 24	73 5	55 13	6570	85	14

Table 5, Core C3

Sample ID	Depth (cm)	Al (ppm)	±	Ca (ppm)	±	Cd (ppm)	±	Co (ppm)	±	Cr (ppm)	±	Cu (ppm)	±
C3-1	1.5	46300	5600	9580	580	8	1	26	1	238	14	115	6
C3-2	4.5	47900	6200	10700	800	10	1	25	1	252	16	124	9
C3-3	7.5	50600	6100	9320	630	10	1	26	2	264	16	121	14
C3-4	10.5	49200	6700	9400	830	10	1	24	3	262	20	117	12
C3-5	13.5	51300	7100	9260	670	16	2	28	3	282	15	132	10
C3-6	20.0	46900	5800	9720	620	18	2	26	2	276	15	127	7
C3-7	30.0	54100	15500	9840	1490	28	5	37	7	475	89	221	48
C3-8	40.0	40900	5300	9330	540	68	5	103	6	511	24	170	8
C3-9	55.0	39800	5400	10300	600	214	16	28	2	792	34	205	11
C3-10	75.0	31100	4100	10000	660	391	33	18	2	869	43	214	11
C3-11	95.0	41700	5100	10500	700	0.9	0.6	24	1	184	9	40	4

Sample ID	Depth (cm)	Fe (ppm)	±	Mg (ppm)	±	Mn (ppm)	±	Ni (ppm)	±	Pb (ppm)	±	S (ppm)	Zn (ppm)	±
C3-1	1.5	51700	3100	15000	4000	434	28	132	9	182	29	9460	285	42
C3-2	4.5	55000	3900	15900	4300	461	35	136	11	201	39	12300	311	50
C3-3	7.5	56900	3600	16600	4400	528	36	146	10	209	38	14300	321	49
C3-4	10.5	55900	4600	16400	4600	518	44	148	15	196	40	14100	297	51
C3-5	13.5	57600	4200	17000	5000	523	34	153	13	233	46	14500	329	54
C3-6	20.0	53000	3300	15700	4200	466	30	138	9	276	48	15000	325	50
C3-7	30.0	58200	11600	18200	4300	478	86	176	31	600	124	28000	531	123
C3-8	40.0	49400	3100	15100	3500	364	18	177	10	739	102	15800	426	56
C3-9	55.0	47500	2900	14400	3500	379	19	136	9	1371	220	16900	486	69
C3-10	75.0	49100	2700	13900	3200	503	30	119	7	1005	137	14700	428	61
C3-11	95.0	52200	2900	12600	2800	490	23	155	9	73	11	10900	125	17

Table 6. Cadmium EXAFS analysis.

Sediments					
Core	Atom	R(Å)	N	$S^2(\text{\AA}^2)$	$DE_0(\text{eV})$
SC-4-12 34.5 cm 192 ppm	Cd-S ^a	2.50*	4.0	0.0044*	-1.0*
C-1-2 55.0 cm 1222 ppm	Cd-S ^a	2.51*	4.0	0.0051*	-1.4*
SC-4-11	Cd-S ^b	2.51	1.9*	0.0050	-4.1*
31.5 cm	Cd-O ^b	2.31*	3.2*	0.0120*	
Leached					
Reference Precipitates ^c					
Cd _{1.0} S	Cd-S	2.51*	4.0	0.0056*	-1.7*
Cd _{0.25} S	Cd-S	2.51*	4.0	0.0048*	-2.6*
Reference Compound: Greenockite (CdS) ^d					
	Cd-S	2.52	1		
	Cd-S	2.53	3		
	Cd-Cd	4.12	6		
	Cd-Cd	4.13	6		

Scale factor (S_0^2) = 1.5^aParameter varied in least-squares fits.^bFirst-shell Cd-S coordination fixed at 4; R and S^2 were varied.^cFor the sulfide component, R and S^2 were fixed on the average of values determined from fits to reference precipitates; N was varied. If $N_{\text{Cd-S}} = 4$ and $N_{\text{Cd-O}} = 6$ are assumed, then the sulfide component is 47% and the oxide component is 53% of the total absorption spectrum.^dCadmium sulfide was precipitated by adapting an FeS method [10]. XAS spectra collected on wet samples immediately after precipitation.^eCrystallographic values for greenockite from [58].

Table 6. Zinc EXAFS analysis

Sulfide Component ^a						
Core	Rel.%	Atom	R(Å)	N	s ² (Å ²)	DE ₀ (eV)
SC-4-1	75	Zn-S	2.33	3.0*	0.0065	-5.2*
2.5 cm		Zn-Zn	3.83	8.9	0.0231*	
287 ppm		Zn- S	4.49	8.9	0.0267*	
SC-4-12	78	Zn-S	2.33	3.1*	0.0065	-6.3*
34.5 cm		Zn-Zn	3.83	9.3	0.0221*	
515 ppm		Zn- S	4.49	9.3	0.0297*	
C-3-9	90	Zn-S	2.33	3.6*	0.0065	-5.2*
55.0 cm		Zn-Zn	3.83	10.8	0.0259*	
486 ppm		Zn- S	4.49	10.8	0.0257*	
SC-4-11	25	Zn-S	2.33	0.9*	0.0065	-5.9*
31.5 cm		Zn-Zn	3.82	2.6	0.0225*	
Leached		Zn- S	4.49	2.6	0.0139*	
Oxide Component ^b						
Core	Rel.%	Atom	R(Å)	N	s ² (Å ²)	DE ₀ (eV)
SC-4-1	25	Zn-O	2.04*	1.7*	0.0065	-5.2*
2.5 cm		Zn-Me ^c	3.13*	1.0*	0.0080	
287 ppm		Zn-Me ^d	3.13*	0.8*	0.0100	
SC-4-12	22	Zn-O	1.99*	1.4*	0.0065	-6.3*
34.5 cm		Zn-Me ^c	3.06*	0.9*	0.0080	
515 ppm		Zn-Me ^d	3.13*	0.8*	0.0080	
		Zn-Me ^e	3.21*	1.7*	0.0080	
C-3-9	10	Zn-O	2.09*	1.4*	0.0065	-5.2*
55.0 cm		Zn-Me ^a	3.10*	0.4*	0.0080	
486 ppm	75	Zn-O	2.02*	3.2*	0.0065	-5.9*
31.5 cm		Zn-Me ^c	3.13*	1.3*	0.0080	
Leached		Zn-Me ^e	3.39*	0.6*	0.0080	
Reference Compound: Sphalerite (ZnS) ^f						
		Atom	R(Å)	N		
		Zn-S	2.33	4		
		Zn-Zn	3.83	12		
		Zn- S	4.49	12		

Scale factor (S_0^2) = 1.0

*Parameter varied in least-squares fit.

^aSulfide component: Interatomic distances (R) for Zn-S and Zn-Zn fixed on crystallographic values in sphalerite; first-shell S^2 for Zn-S was fixed on an empirical value determined from fits to sulfide reference compounds. For higher Zn-Zn and Zn-S shells, N was fixed on the value calculated from the proportion of sphalerite component determined in fits to filtered first-shell spectra and S^2 was varied.

^bOxide component: Values for S^2 were fixed for all shells based on empirical fits to reference compounds; R and N were varied.

^cBackscatterer is Fe or similar transition metal cation; edge-sharing octahedra.

^dBackscatterer is Mg or Al; edge-sharing octahedra.

^eBackscatterer is Fe or Si; corner-sharing octahedra or tetrahedra.

^fCrystallographic values for sphalerite from [28].

Table 6. Chromium EXAFS analysis.

		Oxide Component ^a			
Core		R(Å)	N	s ² (Å ²)	DE ₀ (eV)
SC-2-7	Cr-O	1.97*	6.0	0.0035*	-8.5*
19.5 cm	Cr-Me ^b	3.01*	1.9*	0.0100	
< 2 mm	Cr-Me ^c	3.00*	1.7*	0.0100	
392 ppm	Cr-Fe	3.42*	1.8*	0.0080	
SC-4-1	Cr-O	1.98*	6.0	0.0041*	-8.9*
1.5 cm	Cr-Me ^d	2.97*	1.6*	0.0080	
243	Cr-Fe	3.44*	1.9*	0.0080	
ppm					
SC-4-12	Cr-O	1.97*	6.0	0.0041*	-6.0*
34.5 cm	Cr-Me ^d	3.02*	1.1*	0.0100	
766 ppm	Cr-Fe	3.44*	2.2*	0.0080	
SC-4-11	Cr-O	1.98*	6.0	0.0037*	-8.8*
31.5 cm	Cr-Oh ^d	3.00*	1.8*	0.0100	
Leached	Cr-Fe	3.42*	1.2*	0.0080	
Reference Compounds					
Cr ₂ S ₃ ^e	Cr-S	2.42	6		
	Cr-Cr	2.79	2		
	Cr-S	4.20	6		
K ₂ Cr ₂ O ₇ ^f	Cr-O	1.52,	4		
		1.54,			
		1.73,			
		1.85			
	Cr-Cr	3.13	1		
	Cr-K	3.26	1		

Scale factor (S₀²) = 0.90^aParameter varied in least-squares fits.^aOxide component: First-shell Cr-O coordination fixed at 6; S² was varied. For higher shells, values for S² were fixed based on empirical fits to reference compounds; R and N were varied.^bBackscatterer is Mg or Al; edge-sharing octahedra.^cBackscatterer is Fe or similar transition metal cation; edge-sharing octahedra.^dFit with single shell of Fe atoms; probably a disordered shell of Al, Mg, and Fe atoms.^eCrystallographic values from [59].^fCrystallographic values from [60].

Table 6. Iron EXAFS analysis

Pyrite Component ^a						
Core	Rel.%	Atom	R(Å)	N*	s ² (Å ²)	DE ₀ (eV)
SC-4-1 2.5 cm	35.6	Fe-S	2.25	0.80	0.0011	-7.2*
		Fe-S	3.44	0.80	0.0066	
		Fe-Fe	3.82	1.60	0.0066	
SC-4-12 34.5 cm	38.5	Fe-S	2.25	0.92	0.0011	-6.7*
		Fe-S	3.44	0.92	0.0066	
		Fe-Fe	3.82	1.84	0.0066	
SC-4-11 31.5 cm Leached	21.4	Fe-S	2.25	0.66	0.0011	-8.3*
		Fe-S	3.44	0.66	0.0066	
		Fe-Fe	3.82	1.32	0.0066	
Oxide Component ^b						
Core	Rel.%	Atom	R(Å)	N*	s ² (Å ²)	DE ₀ (eV)
SC-4-1 2.5 cm	64.4	Fe-O	2.00*	2.64	0.0048	-3.4*
		Fe-Fe	3.10*	0.53	0.0050	
		Fe-Si	3.26	1.43	0.0057	
		Fe-Fe	3.39*	0.29	0.0057	
SC-4-12 34.5 cm	61.5	Fe-O	2.00*	2.79	0.0048	-3.2*
		Fe-Fe	3.09*	0.62	0.0050	
		Fe-Si	3.26	1.15	0.0057	
		Fe-Fe	3.43*	0.41	0.0057	
SC-4-11 31.5 cm Leached	78.6	Fe-O	2.00*	3.12	0.0048	-0.5*
		Fe-Fe	3.09*	0.92	0.0050	
		Fe-Si	3.26	0.82	0.0057	
		Fe-Fe	3.39*	0.41	0.0057	
Reference Compound:Pyrite (FeS ₂) ^c						
		Atom	R(Å)	N*		
		Fe-S	2.25	6		
		Fe-S	3.44	6		
		Fe-Fe	3.82	12		

*Parameter varied in least-squares fit.

^aPyrite component: Interatomic distances (R) were fixed on crystallographic values from pyrite and S² was fixed on values determined from fits to reference sulfide compounds. N for each shell was floated as a linked variable in proportions based on the known coordination in pyrite. Relative percent (Rel. %) for pyrite or oxide components is calculated from the integrated fit areas of all atomic shells comprising each component (normalized to 100%).

^bOxide component: Values for S² were fixed for all shells based on empirical fits to reference compounds of similar composition and structure; R and N 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 distance for Fe-Si in phyllosilicates.

^cCrystallographic values from [61].

Table 7. Results of leaching experiments with sediment SC4-11 (runs A, B, C, and blank) as dissolved trace-metal concentrations. (*Flow rate not recorded, nd = not detected, na = not analyzed)

Sediment SC4-11-A

Sample ID	Time (days)	Flow rate (g/day)	pH	Cd (ppb) ±	Cr (ppb) ±	Cu (ppb) ±	Mn (ppb) ±	Ni (ppb) ±	Pb (ppb) ±	Zn (ppb) ±
SC4-11-A-1	0.47	a	8.01	0.78 0.02	0.75 0.51	3.82 0.11	42.5 1.6	2.98 0.08	1.26 0.01	16.45 0.37
SC4-11-A-2	1.42	41.92	7.78	2.12 0.03	0.44 0.24	1.29 0.10	22.0 0.7	2.20 0.03	1.92 0.02	11.39 0.10
SC4-11-A-3	2.35	42.65	7.81	3.95 0.05	0.24 0.13	1.34 0.04	17.5 0.4	1.79 0.03	2.67 0.03	16.59 0.29
SC4-11-A-4	3.34	42.97	7.82	6.50 0.09	0.31 0.11	1.47 0.05	16.1 0.4	1.42 0.04	2.98 0.01	17.55 0.23
SC4-11-A-5	4.41	43.47	7.87	na na	na na	na na	na na	na na	na na	na na
SC4-11-A-6	5.42	43.58	7.87	na na	na na	na na	na na	na na	na na	na na
SC4-11-A-7	6.39	43.91	7.83	11.20 0.14	0.22 0.11	1.85 0.13	18.7 0.8	1.55 0.03	2.84 0.01	17.16 0.37
SC4-11-A-8	7.37	43.75	7.81	na na	na na	na na	na na	na na	na na	na na
SC4-11-A-9	11.36	44.64	7.93	16.14 0.25	0.32 0.05	2.66 0.10	17.7 0.4	2.18 0.04	2.82 0.03	23.43 0.16
SC4-11-A-10	14.19	45.04	7.82	13.74 0.11	0.28 0.04	2.68 0.12	14.7 0.5	1.90 0.02	2.65 0.01	22.48 0.43
SC4-11-A-11	18.43	45.31	7.82	12.77 0.16	0.31 0.06	2.64 0.07	12.9 0.5	1.92 0.04	2.51 0.03	18.88 0.14
SC4-11-A-12	21.23	45.53	7.86	11.54 0.04	0.26 0.10	2.34 0.07	10.9 0.4	1.80 0.03	2.50 0.01	17.41 0.24
SC4-11-A-13	25.72	46.56	7.77	10.92 0.13	0.39 0.28	3.31 0.04	10.5 0.4	2.03 0.02	3.01 0.01	18.63 0.24
SC4-11-A-14	33.86	46.91	7.82	9.45 0.11	0.41 0.05	2.43 0.08	8.50 1.40	2.00 0.04	2.32 0.05	12.82 0.20
SC4-11-A-15	39.91	47.81	7.87	na na	na na	na na	na na	na na	na na	na na
SC4-11-A-16	47.75	41.16	8.05	na na	0.38 0.09	1.99 0.08	na na	2.21 0.30	2.30 0.28	na na
SC4-11-A-17	54.75	44.60	7.81	10.11 0.23	0.44 0.11	2.90 0.09	8.00 0.30	2.10 0.07	3.13 0.01	18.08 0.41
SC4-11-A-18	62.91	44.80	7.85	6.93 0.14	0.41 0.15	2.39 0.06	5.90 0.90	1.76 0.01	2.21 0.06	11.91 0.22
SC4-11-A-19	76.90	48.08	7.87	2.81 0.04	0.41 0.13	1.77 0.04	2.70 0.20	1.16 0.03	1.88 0.02	7.58 0.08
SC4-11-A-20	91.41	47.53	7.94	1.34 0.10	0.36 0.21	1.00 0.01	na na	0.88 0.02	1.02 0.05	3.91 0.36

Sediment SC4-11-B

Sample ID	Time (days)	Flow rate (g/day)	pH	Cd (ppb) ±	Cr (ppb) ±	Cu (ppb) ±	Mn (ppb) ±	Ni (ppb) ±	Pb (ppb) ±	Zn (ppb) ±
SC4-11-B-1	0.47	a	7.98	0.42 0.02	nd nd	0.91 0.04	36.9 0.7	1.26 0.04	1.83 0.05	6.88 0.25
SC4-11-B-2	1.42	41.52	7.85	na na	na na	na na	na na	na na	na na	na na
SC4-11-B-3	2.35	42.12	7.82	4.89 0.05	nd nd	1.06 0.06	18.6 0.5	1.86 0.05	3.51 0.03	13.66 0.16
SC4-11-B-4	3.34	42.59	7.86	9.71 0.11	0.32 0.113	1.41 0.09	19.1 0.7	2.21 0.04	3.87 0.04	17.59 0.26
SC4-11-B-5	4.41	43.10	7.86	na na	na na	na na	na na	na na	na na	na na
SC4-11-B-6	5.42	a	7.86	na na	na na	na na	na na	na na	na na	na na
SC4-11-B-7	6.39	43.73	7.86	11.59 0.13	0.37 0.114	2.07 0.06	15.4 0.6	1.45 0.05	3.03 0.02	19.62 0.33
SC4-11-B-8	7.37	43.84	7.84	12.12 0.42	0.28 0.074	1.85 0.12	13.8 0.4	nd nd	2.54 0.08	19.94 1.06
SC4-11-B-9	11.36	44.77	7.93	18.20 0.18	0.36 0.053	2.57 0.12	13.7 0.3	2.04 0.03	3.69 0.04	23.71 0.28
SC4-11-B-10	14.19	45.36	7.79	19.87 0.15	0.37 0.045	2.85 0.12	12.7 0.3	2.12 0.07	3.72 0.05	24.53 0.16
SC4-11-B-11	18.43	46.43	7.80	21.20 0.24	0.33 0.057	3.01 0.07	11.2 0.2	2.25 0.04	3.61 0.04	24.59 0.17
SC4-11-B-12	21.23	46.81	7.80	23.01 0.09	0.45 0.096	2.96 0.11	9.16 0.16	2.22 0.04	3.38 0.04	22.65 0.18
SC4-11-B-13	25.72	47.68	7.80	18.43 0.29	0.33 0.276	2.66 0.11	6.17 0.37	2.17 0.06	2.99 0.06	19.27 0.32
SC4-11-B-14	33.86	48.92	7.81	14.20 1.41	0.38 0.050	2.66 0.10	na na	1.85 0.04	3.09 0.29	22.52 3.77
SC4-11-B-15	39.91	50.83	7.86	8.27 0.09	0.37 0.045	3.31 0.07	3.73 0.22	1.61 0.01	2.62 0.07	15.25 0.25
SC4-11-B-16	47.75	41.34	7.86	7.42 1.28	0.42 0.087	2.35 0.06	na na	1.84 0.13	3.11 0.35	na na
SC4-11-B-17	54.75	44.49	7.79	7.74 0.28	0.40 0.112	2.61 0.11	4.60 0.54	1.70 0.05	3.68 0.10	19.64 1.02
SC4-11-B-18	62.91	44.76	7.80	6.70 0.74	0.44 0.148	2.49 0.08	na na	1.46 0.05	3.36 0.23	15.42 2.17
SC4-11-B-19	76.90	42.20	7.87	3.49 0.06	0.38 0.134	2.08 0.06	2.28 0.14	1.10 0.04	2.57 0.06	8.68 0.12
SC4-11-B-20	91.41	49.85	7.87	15.24 0.29	0.46 0.214	1.84 0.03	2.83 0.42	4.16 0.05	2.62 0.21	13.79 0.36

Table 7 (continued) Sediment SC4-11-C

Sample ID	Time (days)	Flow rate (g/day)	pH	Cd (ppb) ±	Cr (ppb) ±	Cu (ppb) ±	Mn (ppb) ±	Ni (ppb) ±	Pb (ppb) ±	Zn (ppb) ±
SC4-11-C-1	0.47	a	7.96	0.52 0.01	1.00 0.51	13.71 0.26	43.2 1.3	4.96 0.12	2.13 0.02	22.43 0.31
SC4-11-C-2	1.42	41.64	7.66	1.15 0.01	0.30 0.24	2.09 0.10	22.0 0.5	1.97 0.06	1.96 0.00	10.96 0.15
SC4-11-C-3	2.35	42.49	7.84	2.50 0.00	0.34 0.13	2.07 0.06	21.2 0.5	1.65 0.03	2.21 0.02	13.31 0.13
SC4-11-C-4	3.34	43.00	7.85	4.55 0.02	0.32 0.11	2.02 0.07	19.8 0.4	1.49 0.05	2.06 0.01	12.71 0.13
SC4-11-C-5	4.41	43.67	7.85	na na	na na	na na	na na	na na	na na	na na
SC4-11-C-6	5.42	43.84	7.86	14.59 0.20	0.45 0.07	1.38 0.07	17.3 0.6	1.17 0.03	3.97 0.03	21.49 0.16
SC4-11-C-7	6.39	44.19	7.84	16.04 0.06	0.29 0.11	1.54 0.05	16.1 0.3	1.67 0.06	4.09 0.04	21.71 0.13
SC4-11-C-8	7.37	44.33	7.86	15.70 0.07	0.27 0.07	1.54 0.08	14.1 0.4	na na	3.63 0.04	20.65 0.23
SC4-11-C-9	11.36	45.42	7.91	23.54 0.11	0.28 0.05	2.05 0.12	13.6 0.3	2.30 0.03	6.34 0.05	29.54 0.33
SC4-11-C-10	14.19	46.02	7.83	22.85 0.24	0.39 0.04	2.43 0.15	14.4 1.0	2.33 0.08	4.73 0.06	31.06 0.37
SC4-11-C-11	18.43	47.27	7.80	19.52 0.17	0.29 0.06	2.80 0.19	9.88 0.21	2.21 0.02	6.30 0.07	28.26 0.36
SC4-11-C-12	21.23	47.04	7.74	19.52 0.10	0.26 0.10	2.97 0.06	8.88 0.12	na na	4.18 0.03	25.56 0.09
SC4-11-C-13	25.72	48.10	7.81	23.94 3.95	nd 0.28	5.95 0.22	na na	2.07 0.11	3.94 0.41	na na
SC4-11-C-14	33.86	50.50	7.86	13.77 0.26	0.41 0.05	3.73 0.14	5.15 0.18	2.08 0.03	4.41 0.04	21.81 0.11
SC4-11-C-15	39.91	54.43	7.85	10.33 1.13	0.43 0.04	2.37 0.06	na na	na na	2.97 0.23	13.58 2.22
SC4-11-C-16	47.75	39.49	7.89	na na	0.51 0.09	4.10 0.19	na na	na na	4.26 0.54	na na
SC4-11-C-17	54.75	45.85	7.87	10.53 0.21	0.40 0.11	3.54 0.11	5.41 0.97	2.57 0.09	4.59 0.15	29.81 0.57
SC4-11-C-18	62.91	46.58	7.83	3.61 0.07	0.57 0.15	3.69 0.10	3.62 0.11	1.76 0.04	5.19 0.04	24.20 0.26
SC4-11-C-19	76.90	51.01	7.88	1.59 0.28	0.38 0.13	2.17 0.05	na na	1.13 0.10	3.37 0.40	12.89 3.12

Table 7 (continued) Blank

Sample ID	Time (days)	Flow rate (g/day)	pH	Cd (ppb) ±	Cr (ppb) ±	Cu (ppb) ±	Mn (ppb) ±	Ni (ppb) ±	Pb (ppb) ±	Zn (ppb) ±
B-1	0.47	a	8.01	0.621 0.020	0.37 0.51	2.56 0.05	2.77 0.51	3.70 0.21	0.301 0.010	20.1 1.2
B-2	1.42	40.14	8.04	0.202 0.003	0.32 0.24	1.58 0.03	1.98 0.24	0.88 0.02	0.124 0.002	6.07 0.15
B-3	2.35	41.16	8.02	0.185 0.003	0.46 0.13	1.09 0.05	1.75 0.13	0.67 0.02	0.089 0.002	4.51 0.06
B-4	3.34	41.55	8	0.120 0.002	0.22 0.11	0.92 0.05	1.77 0.1	0.75 0.02	0.077 0.002	4.43 0.10
B-5	4.41	42.10	8.02	0.141 0.003	0.29 0.17	0.86 0.02	1.87 0.173	0.68 0.03	0.075 0.002	3.78 0.06
B-6	5.42	a	7.97	0.127 0.005	0.27 0.07	0.65 0.04	1.77 0.07	0.73 0.04	0.047 0.001	2.86 0.07
B-7	6.39	42.87	7.96	0.103 0.004	nd nd	0.52 0.03	1.61 0.11	0.55 0.03	0.041 0.001	2.74 0.04
B-8	7.37	42.96	8.1	0.124 0.004	0.22 0.07	0.50 0.03	1.73 0.08	0.68 0.02	0.062 0.001	3.28 0.04
B-9	11.36	44.27	7.96	0.103 0.005	0.35 0.05	0.44 0.04	1.72 0.05	0.91 0.03	0.041 0.001	2.45 0.04
B-10	14.19	44.61	8	0.126 0.002	0.32 0.05	0.46 0.03	1.54 0.05	0.89 0.03	0.039 0.001	2.75 0.02
B-11	18.43	45.35	7.94	0.110 0.002	0.22 0.06	0.47 0.02	1.69 0.06	0.88 0.02	0.032 0.001	2.43 0.03
B-12	21.23	45.53	8	0.205 0.007	0.94 0.10	0.76 0.04	2.50 0.10	1.31 0.03	0.043 0.001	3.00 0.04
B-13	25.72	46.33	7.9	0.097 0.014	nd nd	0.46 0.02	1.68 0.28	0.96 0.08	nd nd	1.24 0.39
B-14	33.86	47.11	7.92	na na	0.10 0.05	0.37 0.03	0.70 0.05	0.94 0.15	nd nd	2.07 0.37
B-15	39.91	49.35	7.92	na na	0.11 0.05	0.37 0.03	0.60 0.05	na na	nd nd	na na
B-16	47.75	39.18	7.87	0.107 0.017	nd 0.09	0.37 0.02	1.22 0.09	na na	na 0.000	na na
B-17	54.75	41.97	7.89	0.107 0.017	0.21 0.11	0.43 0.03	0.84 0.11	0.98 0.11	0.027 0.002	1.52 0.45
B-18	62.91	43.29	8.06	0.097 0.014	0.20 0.15	0.39 0.02	1.20 0.15	0.98 0.09	nd nd	na na
B-19	76.90	46.33	8	0.113 0.016	0.23 0.13	0.44 0.03	1.47 0.13	1.07 0.06	nd nd	3.47 0.65
B-20	91.41	49.13	7.92	0.087 0.002	0.20 0.21	0.64 0.02	1.26 0.21	0.92 0.01	0.013 0.000	3.53 0.11

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7.0 Figure Captions

Figure 1. Location map of field study. Star indicates general location where the sediment cores were sampled.

Figure 2. Chemical composition of porewaters extracted from core SC4. Dissolved carbon data is from core SC2. Both cores were collected on July 10, 1997.

Figure 3. Chemical composition of Seaplane Lagoon sediments from cores SC2, SC3, SC4, C1, C2, and C3.

Fig. 4. (a) Normalized EXAFS and corresponding radial structure functions (uncorrected for phase shift of backscattering atoms) for cadmium in two NAS Alameda sediment samples from core SC4-12 (34.5 cm) and core C1-2 (5.5 cm) compared to reference precipitates, cadmium sulfide ($\text{CdS}(\text{ppc})$) and a mixture of cadmium and iron sulfide (CdS-FeS) precipitated from solution immediately before data collection, and crystalline cadmium sulfate ($\text{CdSO}_4(\text{s})$). Dashed red line is the non-linear least-squares best fit. (b) Normalized EXAFS and corresponding radial structure functions (uncorrected for phase shift of backscattering atoms) for zinc in sediment samples from core SC4 (at 1.5 and 34.5 cm) and core C3-9 (55 cm) compared to a reference spectrum of crystalline sphalerite ($\text{ZnS}(\text{s})$). Dashed red line is the non-linear least-squares best fit; green line is the fit component corresponding to sphalerite; blue line is the fit for a zinc-oxygen component that probably represents zinc substitution in detrital phyllosilicate or oxide minerals. (c) Normalized XANES spectra and corresponding first-derivative spectra for chromium in samples from cores SC4 (at 1.5 and 34.5 cm), SC9 (at 2.5 and 30 cm) and SC7 (at 18.5 cm) compared with reference spectra for crystalline chromium sulfide and potassium chromate compounds. (d) Normalized EXAFS and corresponding radial structure functions (uncorrected for phase shift of backscattering atoms) for chromium in sediment samples SC2-7, SC4-1, and SC4-12 compared to reference crystalline potassium chromate. Dashed red line is the non-linear least-squares best fit. Oxidation of Cr(III) to Cr(VI) results in a significant shift of the first-shell oxygen peak to shorter interatomic distance. (e) Normalized XANES spectra for lead in samples from core SC4 (at 1.5, 31.5, and 34.5 cm) compared with reference spectra for crystalline lead sulfide, oxide, and carbonate compounds.

Fig. 5 (a) Normalized XANES spectra and corresponding first-derivative spectra for manganese in samples from cores SC4 (at 1.5, 17.0, and 31.5 cm) and SC9 (at 0.0 and 10.2 cm) compared with reference spectra for synthetic manganese(IV) oxide (MnO_2 , pyrolusite), birnessite (layered Mn(III,IV) oxide) precipitated on quartz (birnessite/ SiO_2), a natural Mn-phosphate ($\text{Li}(\text{Fe}, \text{Mn})\text{PO}_4$, ferrisicklerite), and Mn(II) sulfide (MnS). (b) Normalized EXAFS and corresponding radial structure functions (uncorrected for phase shift of backscattering atoms) for iron in sediment samples from core SC4 (at 1.4 and 34.5 cm) compared to reference spectra of crystalline pyrite ($\text{FeS}_2(\text{s})$) and of iron substituted in reference illite IMt-1 (Clay Minerals Source Repository). Dashed red line is the non-linear least-squares best fit; green line is the fit component corresponding to pyrite; blue line is the fit for an iron-oxygen component that probably represents iron substitution in phyllosilicate or oxide minerals.

Figure 6. Oxidation rates of reduced sediments (SC4-11) in seawater plotted as the metal concentration dissolved per day normalized to the remaining metal concentration in the sediment (right side) and as the total metal concentration dissolved normalized to the initial metal concentration in the sediment (left side).

Fig. 7 (a) Normalized EXAFS and corresponding radial structure functions (uncorrected for phase shift of backscattering atoms) for cadmium in unleached and leached sediment samples from core SC4 at approximately the same depth (34 cm). Dashed red line is the non-linear least-squares best fit; green line is the fit component corresponding to CdS ; blue line is the fit for a cadmium-oxygen component that probably represents cadmium adsorption on iron-(oxy)hydroxides that form from pyrite oxidation. (b) Normalized EXAFS and corresponding radial structure functions (uncorrected for phase shift of backscattering atoms) for cadmium in unleached and leached sediment samples from core SC4. Dashed red line is the non-linear least-squares best fit; green line is the fit component corresponding to sphalerite; blue line is the fit for a zinc-oxygen component that probably represents zinc adsorption on iron-(oxy)hydroxides that form from pyrite oxidation and zinc substitution in phyllosilicate or oxide minerals noted previously. (d) Normalized XANES spectra for lead in samples in unleached and leached sediment from core SC4 compared to reference crystalline lead carbonate (PbCO_3). (e) Normalized XANES spectra for manganese in samples in unleached and leached sediment from core SC4 compared to a reference manganese phosphate ($\text{Fe}, \text{Mn}(\text{PO}_4)$). (f) Normalized EXAFS and corresponding radial structure functions (uncorrected for phase shift of backscattering atoms) for iron in unleached and leached sediment samples from core SC4. Dashed red line is the non-linear least-squares best fit; green line is the fit component corresponding to pyrite; blue line is the fit for an iron-oxygen component that probably represents formation of an iron-(oxy)hydroxide in addition to iron substitution in phyllosilicate or oxide minerals discussed previously.