Lead and Cadmium Interactions with Mackinawite: Retention Mechanisms and the Role of pH

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The reactive iron monosulfides including mackinawite are known for their ability to scavenge trace metals. Oxidation and reduction reactions in sediments and the types of metal bonding with mackinawite determine both the stability of the metal bonds and the susceptibility of the material to oxidation. Metal retention is important because it influences the availability of toxic metals to aquatic organisms. In this study, Pb and Cd interactions with mackinawite were investigated, and two major retention mechanisms were suggested. They are, first, that Pb and Cd displace up to 29% of the Fe from mackinawite by forming $(Pb,Fe)S$ and $(Cd,Fe)S$ on the surface of the mackinawite and, second, that 0.91 mmol/g of Pb and 2.03 mmol/g of Cd are adsorbed on the surface of the transformed mackinawite. The mixed ferrous sulfides are more insoluble and more stable than the pure mackinawite, while surface adsorption is a relatively weak and labile retention mechanism. Both reactions contributed toward a drop in pH, although the mackinawite containing Pb and Cd was stable at this lower pH.

Introduction

The mobility, availability to aquatic organisms, and burial of toxic metals is strongly influenced by their interactions with benthic sediments. Surficial oxic sediments are often transformed into anoxic sediments at a few centimeters of depth, as organic matter is decomposed. During this process oxygen is consumed, as it is of primary importance as a electron acceptor, and sulfate is reduced to sulfide. The sulfide dissolves ferric oxides (goethite, lepidocrocite, and hematite) to yield ferrous ions that react with hydrogen sulfide to form ferrous sulfides. This can release metals adsorbed by organic matter and oxide minerals, but the metals may be taken up by the newly formed sulfide minerals (*1−3*).

The iron sulfides include pyrite (FeS_2) and the more soluble monosulfides, mackinawite ($Fe_{0.995−1.023}$), pyrrhotite ($Fe_{1−x}$), greigite (Fe_3S_4), and "amorphous FeS", which may be pyrite precursors (*4−6*). The more unstable monosulfide fraction

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is also referred to as the acid volatile sulfide (AVS) fraction. Pyrite framboids can resist oxidation for months or years, pyrite grains can be oxidized within days, and complete mackinawite oxidation occurs in a few hours (*1, 7*). However, in a "sulfide-dominated system", without iron oxyhydroxides and with high solid and aqueous sulfide concentrations, there is greater resistance to sulfide oxidation, and if associated metals are released, they will likely have a short residence time (*8*).

Sediment metal associations are controlled by the state of redox, and like iron, trace metals are able to move through different sediment phases (*2*). As conditions become increasingly reducing, metals adsorbed by oxide minerals may become bonded with sulfide minerals, and Pb^{2+} and Cd^{2+} coprecipitated with mackinawite may be pyritized. During oxidation, the pyritized metals can be moved to the AVS phase, and metals bonded with mackinawite can be released to the aqueous phase (*1, 2, 9*).

In nature, mackinawite contains traces of Co, Ni, and Cu (*10*), and a metal with a lower sulfide solubility than mackinawite is able to displace a molar equivalent of Fe from the lattice of mackinawite (*7*). This reaction is rapid because in 5 min the displacement of Fe in mackinawite by Ag is complete (*11*). In addition, the exchange of AVS associated Fe by Cd takes place on a "time scale of minutes to hours" (*12*). This type of reaction, which was also observed experimentally between Fe and Cu, only affects the pH to the extent that the hydrolysis of the two metals is different (*13*). For a divalent metal Me, either $(Me,Fe)S$ is formed or MeS is formed, and these sulfides are more insoluble and less susceptible to oxidation than pure mackinawite (*11, 14*). The increasing insolubility of some metal sulfides is MnS < mackinawite < NiS < CoS < ZnS < CdS < PbS < CuS ≪ Ag_2S (*12, 15*).

Significant coprecipitation of Mn with mackinawite does not occur (*16*) as MnS is more soluble than mackinawite (*7*). However, complete surface adsorption of Mn by mackinawite occurs in 30 min (*16*), although the bonding mechanism is relatively weak and unstable. Mackinawite is similar to pyrrhotite, which has a zero point of charge at pH 3 (*17*). If mackinawite is variably charged and the pH exceeds the zero point of charge, there will be an electrostatic attraction between the negatively charged mackinawite surface and the Mn^{2+} ions.

Previous in-depth research of trace metal interactions with mackinawite is scarce. Therefore, this study examines the retention of Pb and Cd by mackinawite and the role of pH. Both metals have a natural affinity for sulfur and are of environmental importance because of their toxicity.

Experimental Section

Preparation of Mackinawite. Experiments were conducted at room temperature (22 °C). Previous work (*18−20*) was referred to in developing a method to precipitate the mackinawite, and the method is described herein. The mackinawite was prepared in a fume hood because H_2S gas was produced. Inorganically produced mackinawite is indistinguishable from mackinawite formed by bacterial processes (*4*).

High-purity N_2 gas was bubbled through 120 mL of distilled water and 120 mL of 0.65 mmol/L CH_3COOH until the dissolved oxygen (DO_2) was 0.2 mg/L. The DO_2 was measured using a Cole Parmer model 9070 oxygen meter. The equivalent of 0.0834 mol/L of ferrous sulfate ($FeSO_4·7H_2O$) and 0.1468 mol/L of sodium sulfide ($Na_2S·9H_2O$) were

measured into two separate 100-mL flasks. These proportions of $FeSO_4$ and Na_2S were also used elsewhere (20). The Na_2S was crushed so it would dissolve rapidly. The $FeSO_4$ flask was filled to capacity with the deaerated distilled water, sealed, and agitated. The deaerated dilute CH_3COOH was filled to about 1 cm below the top of the Na_2S flask, and the contents were dissolved by mixing. Both solutions were combined, and the precipitate that formed immediately was centrifuged at 3000 rpm for 1 min. The precipitate was placed in a vacuum desiccator over P_2O_5 and evacuated 1 h on two consecutive days. Exposure to the atmosphere was minimized by working quickly, by bubbling N_2 gas through the solutions, and by ensuring zero airspace. The $\approx$0.5-g sample was stored in a desiccator over a drying agent. The dried sample was less susceptible to oxidation, and CH_3COOH also helps prevent oxidation of sulfide minerals (21).

Present with the dried mackinawite were some residual ferrous and sulfide ions remaining from the liquid phase. Mackinawite requires an excess of these ions for equilibrium to be maintained, and their removal would result in some dissolution of the mackinawite (12). Therefore, washing of the mackinawite was avoided, and instead the amount of Fe^{2+} ions that would be removed by distilled water alone was determined. The dried mackinawite and deaerated distilled water were agitated for 24 h. The supernatant was acidified to pH 1, and the total concentration of ferrous iron was measured on a Perkin-Elmer 3110 atomic absorption spectrometer.

Characterization Experiments. A Japanese Electro-Optics Laboratory (JEOL), model 6T100, scanning electron microscope was used to photograph the mackinawite. There was no sample pretreatment at the lower magnification, but at the higher magnification the sample was coated with Au dust to obtain a clearer image.

Qualitative X-ray diffraction (XRD) analysis of a powder sample of mackinawite, set on a zero background mount, was performed on a Rigaku D/MAX 2400 12-kW rotating anode automated powder diffractometer.

Metal hydroxide precipitation of Pb and Cd as a function of pH was determined. The pH of the metal solutions was raised with NaOH, and the metal in solution was measured at increments of pH.

Batch Equilibrium Tests. Batch tests were conducted to measure the retention of Pb and Cd by mackinawite. Solutions of Pb (as $PbCl_2$) and Cd (as $CdCl_2$) were adjusted with HCl to pH 3.6 and pH 3.8, respectively. High-purity N_2 gas was bubbled through distilled water and the metal solutions until the DO_2 was 0.3 mg/L. The proportions for each test were 0.042 g of mackinawite and 42 mL of solution or 0.001 g/mL. A centrifuge tube was half filled with deaerated distilled water, the mackinawite was added, and the pH was measured. The centrifuge tube was then filled to capacity with the metal salt solution, sealed with Parafilm, and placed on a roller for 24 h. The solid and liquid phases were separated by centrifuging at 6000 rpm for 10 min. Some of the supernatant was extracted, and the pH of the remaining mixture was measured. The supernatant was acidified to pH 1 with HCl, and the metal in solution was measured by atomic absorption spectrophotometry. The total initial metal minus the metal in the supernatant was taken as the metal retained by the mackinawite. Some evaporation of the metal solution occurred during deaeration, and an adjustment was made to account for this. The tests were assumed to reach equilibrium within 24 h because of the rapidity with which metal interactions with mackinawite are reported to occur.

Metal concentrations of 250, 500, 1000, 1500, 2000, and 2500 ppm were tested, but the results were expressed in units of mmol/L in order to show an equal molar exchange of Fe for Pb or Cd. As 2500 ppm of Pb = 12.1 mmol/L and 2500
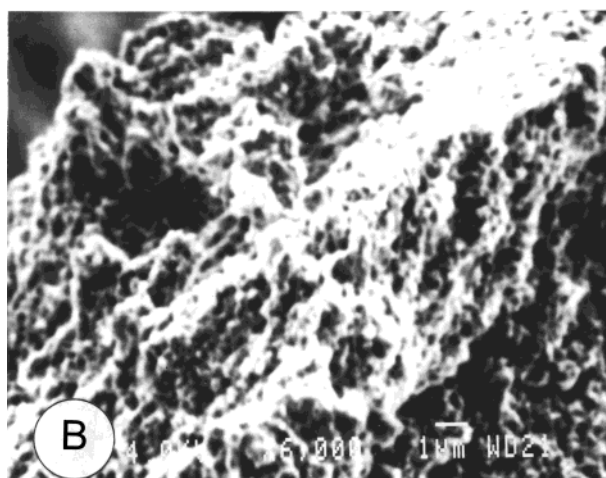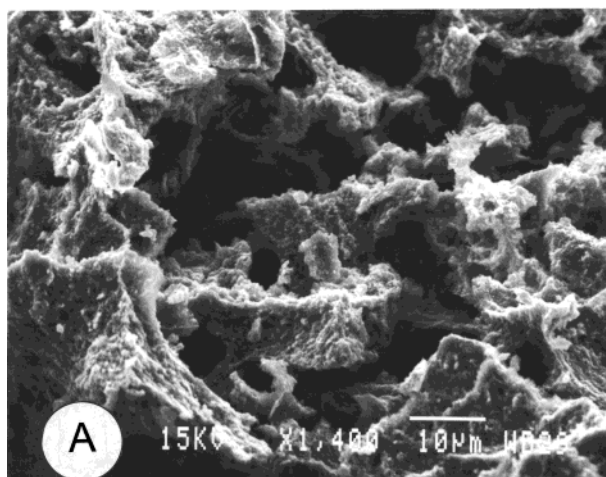

FIGURE 1. Scanning electron micrographs of mackinawite (a) at $1400\times$ magnification and (b) at $6000\times$ magnification.

ppm of Cd = 22.2 mmol/L, the range of metal concentrations that appears on the graphs is different for the two metals.

Results and Discussion

Properties of Mackinawite. Dried samples of the mackinawite used in this study resemble the natural material. In Figure 1a, the mackinawite has a texture similar to that of naturally occurring greigite and mackinawite found as coatings on pyrite framboids (22). Mackinawite appears as "small, wormlike grains" (5) with a particle size of less than 1 μm (13), and the mackinawite in Figure 1b completely fits this description.

Positive identification of the mackinawite was established through XRD. The XRD scan in Figure 2 reveals that the mackinawite has a small particle size and that there is a lack of amorphous FeS, indicated by the broadness of the peaks and the absence of background curvature, respectively. Sample oxidation appeared to be minimal as no iron oxides were identified.

Precipitation of Pb and Cd. The effect of pH on the formation of $Pb(OH)_2$ and $Cd(OH)_2$ is shown in Figure 3. Precipitation increases with pH, is greater at higher metal concentrations, and occurs at about 2 pH units lower for Pb than for Cd. These values agree within 0.5−1 pH unit of experimental values reported elsewhere, and differences are probably due to procedural dissimilarities (23, 24).

Table 1 shows species distributions for solutions of Pb^{2+}, Cd^{2+}, and Fe^{2+} as calculated from stability constants (25) and metal concentrations in mmol/L. This table shows 50%
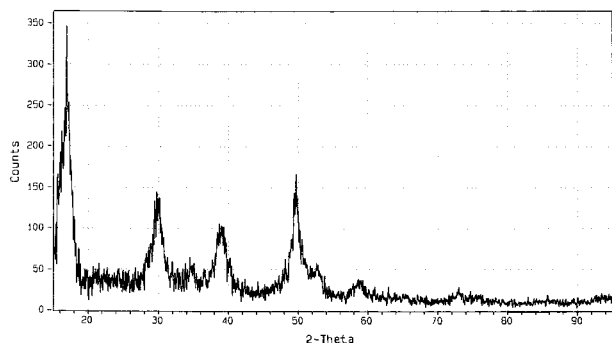
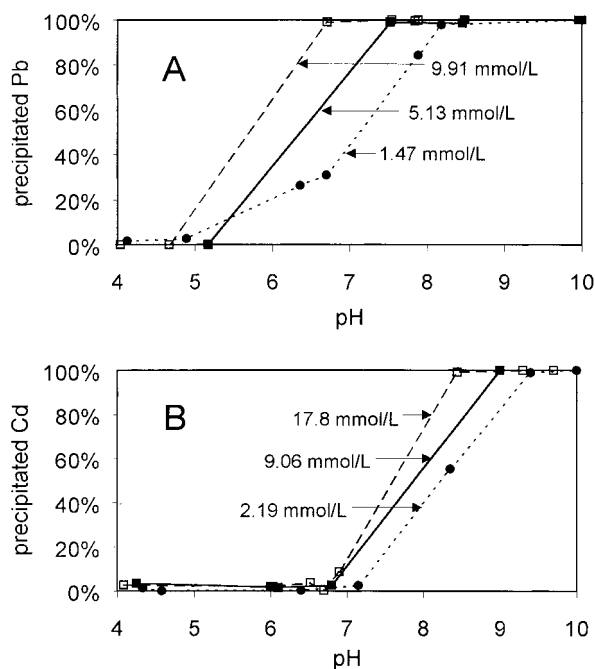**FIGURE 2. X-ray diffraction pattern for mackinawite.**

FIGURE 3. Precipitation of (a) Pb and (b) Cd as a function of pH. Three metal concentrations for each metal are shown, and each point on the curves represents a single test.

Pb precipitation occurring at pH 9.5 and 50% Cd precipitation occurring at pH 10.5. In Figure 3, 50% Pb precipitation is occurring between pH 5.5 and pH 7, and 50% Cd precipitation is occurring between pH 7.5 and pH 8.5. However, the Figure 3 results also indicate that metal precipitation occurs at a higher pH when metal concentrations are lower. It would therefore be expected that experimentally determined precipitation of more dilute metal solutions would agree well with Table 1.

In Figure 3, the curves for Pb are spaced further apart than the curves for Cd, indicating that changes in the metal concentration affect the formation of $Pb(OH)_2$ more than the formation of $Cd(OH)_2$. This is consistent with the difference of 2 pH units between precipitation of Pb and Cd in Figure 3 and the difference of 1 pH unit between Pb and Cd precipitation in Table 1, assuming that the Table 1 values are for more dilute solutions. Therefore, the trends in Figure 3 and Table 1 are fundamentally the same.

Batch Equilibrium Test Results. The batch equilibrium test results are presented in Figures 4 and 5. The pH values of the mackinawite suspensions after 24 h and as a function of the initial Pb or Cd concentrations are shown in Figure 4. At a zero metal concentration, the mackinawite suspension is at pH 6.3. The decrease in pH increases as the metal concentration increases, and it is greater for the Cd suspensions than for the Pb suspensions.

The uptake of Pb and Cd by mackinawite, as a function of the initial metal concentration is plotted in Figure 5a. For metal concentrations of ≤ 4 mmol/L, the uptake of Pb and Cd is close to linear, and almost all of the Pb and Cd is retained. At >4 mmol/L, less of the total metal is retained, and eventually the uptake becomes relatively constant and attains average maximum values of 4.07 mmol/g of Pb and 5.19 mmol/g of Cd.

The amount of Fe released from the mackinawite as a result of the retention of Pb and Cd is shown in Figure 5b. The amount of Fe found in distilled water after mixing with the mackinawite was determined to be 0.555 mmol/g. This Fe represents residual Fe deposited from the liquid phase during drying and may include Fe dissolved from the mackinawite by the distilled water. This amount was deducted from the total Fe found in solution when the mackinawite was contaminated because it does not represent the portion of Fe removed by the Pb or Cd. Figure 5b reveals that the amount of Fe displaced from the mackinawite is virtually the same whether the mackinawite is contaminated with Pb or with Cd. For initial Pb or Cd concentrations ≤ 4.0 mmol/L, the Fe removed from the mackinawite increases almost linearly, and for Pb or Cd concentrations >4.0 mmol/L, the Fe released from the mackinawite becomes approximately constant at 3.16 mmol/g.

The abscissa on each graph in Figures 4 and 5 is the initial metal concentration, and these axes are to the same scale, so a visual comparison of the results is possible. The trends are similar for all the curves in Figure 5. For metal concentrations ≤ 4.0 mmol/L, the uptake of Pb and Cd is only slightly greater than the amount of Fe displaced. At >4.0 mmol/L, there is a greater discrepancy between the Pb and Cd retained and the Fe released, although all the curves eventually level off.

Discussion and Interpretation. The primary retention mechanism suggested by the data in Figure 5 is an exchange of Pb and Cd for the Fe in the mackinawite. Either ion exchange at the surface of the mackinawite is occurring and resulting in the formation of (Pb,Fe)S and (Cd,Fe)S or the separate metal sulfide phases PbS and CdS are forming. Metal sulfide or hydroxide precipitation is approximately predicted by solubility product constants, and the order of increasing insolubility of some selected compounds is $Cd(OH)_2 <$ Fe$(OH)_2 < Pb(OH)_2 <$ FeS $\ll$ CdS $<$ PbS (*26*). Pb and Cd are strongly chalcophilic, tending to precipitate as metal sulfides under reducing conditions (*27*), and this is supported by the relative insolubility of CdS and PbS that is shown. This provides some explanation as to why the Pb and Cd are reacting primarily with the sulfide phase and not the hydroxide phase.

While the formation of either (Pb,Fe)S and (Cd,Fe)S or PbS and CdS is possible, the former and not the latter mechanism seems to be the most strongly supported. First, mackinawite is quite insoluble, and the solubility product constant or $K_{sp} = 7.94 \times 10^{-19}$ (*15*). Mackinawite is not easily dissolved except by oxidation and by acid. As the formation of PbS and CdS would require the decomposition of mackinawite by Pb and Cd, this process seems less likely. Second, as the same amount of Fe is being replaced by Pb as by Cd, this implies that equal amounts of PbS and CdS are precipitating. If the two metals were controlling the reaction, it is unlikely that they would react in an identical manner.

Therefore, the predominant retention mechanism seems to be surface ion exchange and the formation of (Pb,Fe)S and (Cd,Fe)S, although negligible amounts of PbS and CdS could also be forming. The fact that the same amount of Fe is exchanged whether mackinawite is contaminated with Pb or Cd, points to a surface controlled reaction. Any bulk exchange with the attendant diffusion of Pb and Cd into the

TABLE 1. Fractions of Lead, Cadmium, and Ferrous Iron Species for Selected pH Values[a]

	Pb^{2+}	$Pb(OH)^+$	$Pb(OH)_2$	Cd^{2+}	$Cd(OH)^+$	$Cd(OH)_2$	Fe^{2+}	$Fe(OH)^+$	$Fe(OH)_2$
pH 4	1			1			1		
pH 5	0.998	0.002		1			1		
pH 6	0.98	0.02		1			1		
pH 7	0.833	0.166	0.001	0.999	0.001		0.997	0.003	
pH 8	0.325	0.649	0.026	0.992	0.008		0.969	0.031	
pH 9	0.035	0.691	0.274	0.922	0.073	0.005	0.758	0.240	0.002
pH 10	0.001	0.201	0.798	0.436	0.346	0.218	0.227	0.716	0.057
pH 11		0.025	0.975	0.017	0.134	0.849	0.017	0.548	0.435
pH 12		0.003	0.997		0.016	0.984		0.111	0.889

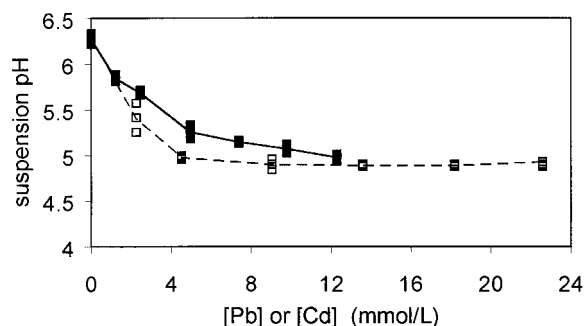[a] Values calculated with stability constants obtained from ref 25.

FIGURE 4. Final pH values of mackinawite suspensions as a function of the initial Pb (■) or Cd (□) concentration. These tests were conducted in duplicate, and each measurement and the mean value are shown. The lines connect the mean values.
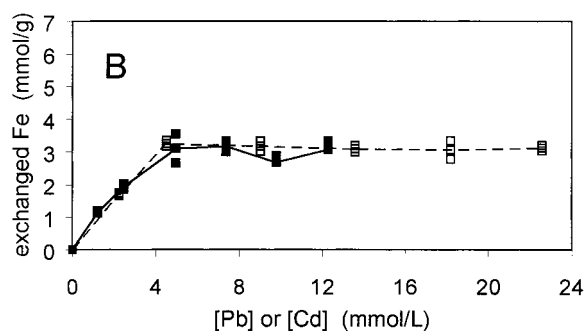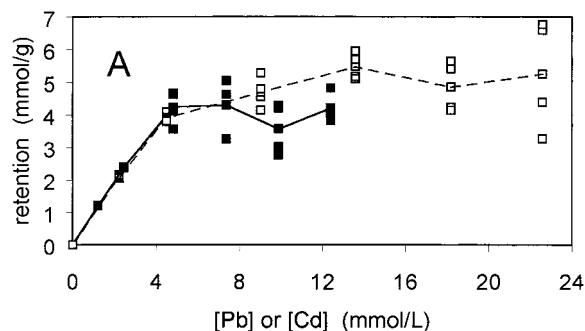

FIGURE 5. (a) Retention of Pb (■) and Cd (□) by mackinawite as a function of the initial metal concentration. Four sets of tests were conducted, and each value and the mean are shown. (b) Exchange of Fe for Pb (■) and Cd (□) as a function of the initial metal concentration. The tests were conducted in duplicate, and each measurement and the mean value are shown. On both graphs, the lines connect the mean values.

crystal lattice is also unlikely as then differing amounts of released Fe would be expected for the two metals. According to Table 1, $Fe(OH)_2$ formation starts at pH 9 and probably only soluble Fe species would be present during the

experiments in this study. Therefore, the displaced Fe and the measured Fe should be identical.

The exchanged Fe reaches a maximum at ≈ 4 mmol/L (Figure 5b) when all of the Fe at the surface of the mackinawite is removed (28). This maximum is 3.16 mmol/g or $\approx 29\%$ of the Fe composition of the mackinawite. If the mackinawite is represented by FeS and assuming a surface ion exchange reaction, then $Fe_{1-x}Cd_xS$ and $Fe_{1-x}Pb_xS$ are formed. In this study x reached a maximum of ≈ 0.29, but this value should increase as the particle size of the mackinawite decreases.

The mixed iron sulfides (Pb,Fe)S and (Cd,Fe)S (as well as the pure sulfides PbS and CdS) are more insoluble and less susceptible to oxidation than the FeS mackinawite (14). In addition, the toxic Pb and Cd are being retained in exchange for the more abundant and less toxic Fe. The long term stability of the mixed iron sulfides will be more likely if there is a dominance of sulfides in the system (8). The metals could become pyritized and enter a more stable form (9), or they could remain incorporated in the mackinawite phase, if anoxic conditions persist. If burial of the sulfides makes them less susceptible to oxidation, then permanent removal of the contaminants may be accomplished. Otherwise, in the event of oxidation due to seasonal changes, storm activity, or dredging, the metal bonding will be temporary, and the released metals may diffuse upward through the surficial sediments and enter the overlying waters (12). The metals are then more available to aquatic organisms unless they can become associated with another sediment phase under oxic conditions. To what extent trace metals would be exchanged for Fe in real sediments and in the presence of competing ions is unknown. However, these results indicate that $\approx 29\%$ of the Fe is exchanged if the mackinawite has a particle size similar to the material used in this study.

A secondary retention mechanism is also suggested by the data in Figure 5. At the higher metal concentrations where the total metal uptake is approximately constant, the average Pb and Cd retention, in excess of the Fe displaced, is 0.91 and 2.03 mmol/g, respectively. This additional retention could be due to surface adsorption or surface precipitation, but surface adsorption may be more probable for the following reasons.

Cd precipitation begins at >pH 6.7 (Figure 3b), and all the Cd suspensions are at <pH 6.3 (Figure 4). This is an indication of surface adsorption, although soil and sediment materials may alter precipitation behavior. In the presence of oxide minerals and clays, greater than predicted surface precipitation can occur (29). At pH 5 and an initial Pb concentration of 12 mmol/L, $\approx 20\%$ Pb precipitation is expected (Figure 3a). Deducting the Pb already exchanged for Fe, 20% precipitation ≈ 1.8 mmol/L, but the additional Pb uptake is only ≈ 0.9 mmol/g. If surface hydroxide precipitation is occurring, then the amount is less than predicted.

Under similar conditions Pb precipitates at a lower pH than Cd (Figure 3 and Table 1). If the secondary retention

mechanism was due largely to metal hydroxide precipitation, then greater Pb than Cd retention should be expected, but the reverse is observed (Figure 5a). Also, normally surface adsorption occurs on a surface before surface precipitation (*30*). Therefore, it seems improbable that surface hydroxide precipitation is important. The sulfide phase may be influencing metal uptake more than the hydroxide phase, and the sulfide concentration is higher than the hydroxide concentration. Therefore, it seems most reasonable that the secondary retention mechanism is predominantly surface adsorption, as was observed with Mn^{2+} (*16*).

The surface adsorption of Cd is double that of Pb, and this may be related to metal speciation trends that are illustrated in Table 1. This table shows that the formation of $Pb(OH)^+$ precedes that of $Pb(OH)_2$ by 2 pH units, while the formation of $Cd(OH)^+$ precedes that of $Cd(OH)_2$ by 0.5 pH unit. At initial metal concentrations >4 mmol/L, the pH of the suspensions is close to pH 5 (Figure 4). Extrapolating between Figure 3 and Table 1, it appears that at pH 5, $Pb(OH)^+$ is the dominant Pb species, while Cd is virtually exclusively present as Cd^{2+}. $Pb(OH)^+$ is double the size of Cd^{2+} and with the monovalent Pb species and divalent Cd species dominating, there will only be half as much space at the surface of the mackinawite for the Pb as for the Cd, resulting in more Cd than Pb being adsorbed. Soft bases (i.e., S^{2-}) are most attracted to soft acids (i.e., Cd^{2+}) (*31*). This may also encourage greater surface adsorption of Cd. Surface adsorbed metals will be more labile and more easily removed from the mackinawite than coprecipitated metals.

At a metal concentration of 4 mmol/L, the higher final pH of the Pb suspensions as compared to the Cd suspensions (Figure 4) can be explained partly by the difference in hydrolysis of the two metals involved in the surface ion exchange reaction (*13*). Extrapolating between Table 1 and Figure 3, it is estimated at pH 3.6 that 10% of the Pb is present as $Pb(OH)^+$, but at pH 3.8, none of the Cd is present as $Cd(OH)^+$. When the metal solutions are mixed with the mackinawite, most of the hydrated Cd and Pb ions enter the mackinawite lattice and lose their surrounding sheaths of water molecules. The OH^- ions will be removed from the Pb and this will cause a slight rise in pH relative to the Cd suspensions.

Some decrease in suspension pH is due to the more acidic metal solutions being added to the mackinawite and also due to the surface adsorption reactions. The negatively charged mackinawite attracts H^+ ions to its surface. The surface adsorption of Pb^{2+} and Cd^{2+} ions displaces H^+ ions into solution, lowering the pH. The greater surface adsorption of Cd is consistent with the lower final pH of the Cd suspensions.

Pb and Cd retention by mackinawite appears to involve primarily surface controlled ion exchange resulting in the displacement of Fe, and secondarily, surface adsorption at the (Pb,Fe)S and (Cd,Fe)S surfaces. This study has demonstrated mackinawite's considerable ability to scavenge trace metals. The potential exists for mackinawite to be used practically for this purpose. Some decrease in pH accompanies the metal retention, but the mixed iron sulfides appear to be stable at the lower pH. In natural sediments, comprised of various geochemical components, the highly reactive mackinawite may bind with other sediment materials as well as with trace metals, and interactions with mackinawite could be shared among a number of sites.

Acknowledgments

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