

Thermally Induced Release of Adsorbed Pb upon Aging Ferrihydrite and Soil Oxides

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Noncrystalline iron oxides are among the soil components that could limit Pb solubility and bioavailability in soils. Long-term changes in Pb solubility may occur after noncrystalline iron oxides transform into well-crystallized materials. In this study, thermally induced transformation products and the solubility of preadsorbed Pb were compared in a synthetic ferrihydrite and two natural materials containing iron oxides. The adsorbents were characterized initially and after heating for 60 days at 70 °C. Dissolved Pb was measured by differential pulse anodic stripping voltammetry (dpasv) in the supernatants after heating the suspensions for 60 days at 70 °C and compared to the solubility after adsorption for 15 days at room temperature. Lead activities were calculated from dpasv measurements. Surface area, FTIR, XRD analyses, and extraction with oxalate and pyrophosphate were used to characterize the solid phases. Iron oxide transformation products differed among the systems. The laboratory-synthesized ferrihydrite showed the most distinct transformation to goethite and hematite. Goethite formation was also evidenced from one natural (SMS-1) material. The other (SMS-2) material, with a low surface area initially and no FTIR or XRD evidence of crystalline or noncrystalline iron oxide, revealed limited transformation after thermal treatment. Despite these differences, Pb activity increased from all adsorbents after heating for 60 days at 70 °C. The amount of adsorbed Pb had no effect on iron oxide transformation products. Differences in the degree of transformation and in the identity of transformation products may be due to the presence of organic matter, Si, and Al in the pedogenic materials as well as to the initial Fe forms present in the samples. The results suggest that in addition to iron oxide recrystallization, thermally induced changes in other soil constituents (e.g., organic matter, noncrystalline ferro-alumino-silicates) may be responsible for increased Pb activities in solution.

Introduction

Iron oxides retain Pb very strongly and thus could limit its toxicity and bioavailability in soils. Lead reaction with iron oxides may be important when ferric salt-stabilized sludges are applied to soils and when metal-polluted soils are chemically remediated with iron oxides or metallic Fe.

Transformation of noncrystalline iron oxides, however, can result in long-term changes in metal solubility after aging and/or transformation of the original product into a well-crystallized material. Aging copper–ferrihydrite coprecipitates, for example, resulted in reduced Cu solubility after transformation to more crystalline materials (1, 2), while the aqueous solubility of coprecipitated Pb increased after ferrihydrite transformation to goethite (3). Thermal treatment of metal–ferrihydrite coprecipitates reduced soluble Cd and Zn whereas Pb appeared to be expelled from the solid phase (1). These changes in the solubility of coprecipitated metals were accompanied by the formation of mixed end products including ferrihydrite, hematite (Hm), and goethite (Gt)- and lepidocrocite (Lp)-like microcrystalline structures (1). Adsorption studies have also shown an aging effect on metal solubility. Ainsworth et al. (4) showed decreased Cd adsorption reversibility from ferrihydrite after aging for several weeks while no changes were observed for Pb.

Natural systems have a more complex makeup than those typically used in laboratory studies. The nature of ferrihydrite transformation products formed by aging depends on factors including pH, temperature, and the presence, quantity, and identity of foreign ions and organic matter (5–8). Ferrihydrite transformation may be kinetically hindered since goethite formation requires dissolution of the precursor, nucleation, and crystal growth while hematite formation involves internal rearrangement and dehydration (5). All these “partial” processes may be inhibited or drastically retarded in a highly impure system (pedoenvironment) such as soils. Metal cations (e.g., Al and Si) tend to retard ferrihydrite transformation when present at high metal/(metal + Fe) mole ratios (5, 9). Organic matter influences the ratio of hematite (Hm) to goethite (Gt) formed and strongly interferes with the formation of iron oxides, thereby influencing the types of oxides formed, their crystallinity, and their crystal morphology (5–8).

Laboratory-synthesized iron oxides are widely used as model systems in metal adsorption studies. Yet, there is little evidence to support the hypothesis that trace metal retention and solubility in synthetic iron oxides is comparable to that of their natural counterparts in soils. Although noncrystalline materials spontaneously transform to more crystalline phases, it is not known if the mineral transformations observed in synthetic systems occur in soil environments within realistic time frames or if the solubility of adsorbed trace metals follows a similar trend. Thus, in this study we compare thermal transformation products and the activity of preadsorbed Pb from a laboratory-synthesized ferrihydrite and two natural iron oxide-containing materials.

Experimental Section

Adsorbents and Their Characterization. The adsorbents used were a synthetic ferrihydrite and two natural iron oxide-containing materials (labeled SMS-1 and SMS-2). Ferrihydrite was prepared by titrating an $\text{Fe}(\text{NO}_3)_3$ solution with alkali in the presence of CO_2 (10). A rapid titration (6.2 mL of base min^{-1}) was used to obtain a 2-line ferrihydrite similar to the one present in the SMS-1 material (Figure 1). The natural iron oxide-containing materials were collected from acidic forest soils in St-Michel-des-Saints, QC, Canada (details about their origin and collection can be found in ref 11). Chemical and physical properties of the adsorbents were determined in the freeze-dried materials and are reported in Tables 1 and 2. Elemental analyses were performed by inductively coupled plasma emission spectrometry (ICP) of concentrated HNO_3 digests (Table 1). The organic carbon content was

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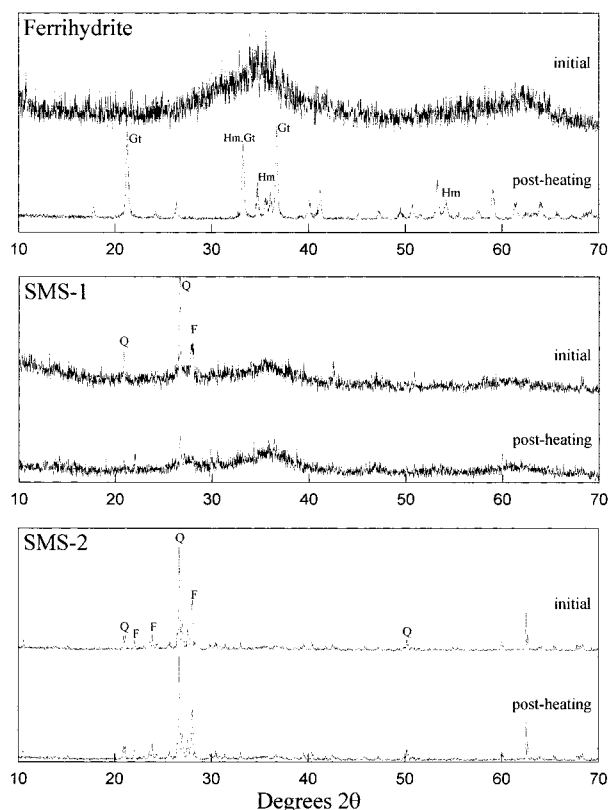


FIGURE 1. X-ray diffraction (XRD) patterns of ferrihydrite, SMS-1, and SMS-2 at initial conditions and after heating the suspensions for 60 days at 70 °C. Identification: Gt, goethite; Hm, hematite; Q, quartz; F, feldspar.

TABLE 1. Chemical Properties of the Adsorbents^a

adsorbent	organic C (g kg ⁻¹)	Fe (g kg ⁻¹)	Al (g kg ⁻¹)	Si (g kg ⁻¹)	P (g kg ⁻¹)	Pb (mg kg ⁻¹)
ferrihydrite	na ^b	572	nd ^c	nd	0.4	2.7
SMS-1	95.4	454	2.6	5.1	2.4	67
SMS-2	59.4	100	7.8	0.9	1.4	96

^a Elemental analyses of HNO₃ digests. ^b na, not analyzed. ^c nd, not detected.

measured using a combustion method. The adsorbents were characterized by surface area, extraction with oxalate and pyrophosphate, infrared (FTIR), and X-ray diffraction (XRD) analyses. Surface area (BET) was determined by three-point N₂ adsorption measurements after an outgas procedure with dry N₂ of 1 h at 100 °C. Oxalate-extractable Fe was measured by mixing 0.03–0.05 g of freeze-dried solid with 20 mL of 0.2 M acid ammonium oxalate (pH 3) solution at room temperature. The samples were shaken for 2 h in the dark and centrifuged for 15 min at 15000 rpm (27000 rcf), and the supernatants were filtered through a 0.2-μm polycarbonate membrane filter. Extraction with oxalate provides an estimate of the noncrystalline iron oxides and organically complexed Fe present in the samples. Pyrophosphate-extractable Fe was measured by mixing about 0.04 g of freeze-dried solid with 20 mL of 0.1 M sodium pyrophosphate solution at room temperature for 16 h. The suspensions were then centrifuged for 15 min at 27000 rcf, and the supernatants were filtered through a 0.2-μm polycarbonate membrane filter. Extraction with pyrophosphate gives an estimate of the Fe complexed by organic matter. Iron in the oxalate and pyrophosphate extracts was analyzed by atomic absorption spectroscopy (AAS). Dissolved organic carbon (DOC) was measured in the supernatants using a OI Analytical model 1010 TOC analyzer.

Infrared spectra were obtained using a pellet containing 2 mg of sample mixed with 170 mg of KBr. Measurements were made using a Perkin-Elmer Fourier transform 1720-x spectrometer at 2 cm⁻¹ resolution and 100 co-added scans. X-ray diffraction analyses were made using a Scintag, Inc. τ - τ diffractometer with a solid-state intrinsic germanium detector.

Pb Adsorption and Thermal Treatment. A batch-type reaction experiment was used to monitor the solubility of preadsorbed Pb and changes in the solid phases after heating the suspensions for 60 days at 70 °C to accelerate their transformation. The solids were weighed (0.35 g) into polypropylene centrifuge tubes; spiked with Pb solutions (as Pb(NO₃)₂) to give concentrations of 0, 400, 1000, 1500, 2500, 6000, 15 000, and 60 000 mg of Pb (kg of solid)⁻¹; small aliquots (<0.5 mL) of base were added to adjust the pH to 6; and the total volume was made to 35 mL in 0.01 M KNO₃. Separate suspensions (two sets) were prepared and equilibrated at room temperature for 15 days. After this equilibration, one of the sets was subjected to thermal treatment (60 days at 70 °C). The centrifuge tubes were capped during the equilibration time but not completely sealed (to avoid anaerobic conditions). Small water losses occurred during thermal treatment, thus the centrifuge tubes were "filled to the mark" every 5–7 days. The initial and final volumes were identical. Heating the suspensions resulted in decreased pH. Thus, periodically, the pH of the suspensions was readjusted to 6. At the end of the equilibration period (15 days at room temperature or 60 days at 70 °C), the suspensions were centrifuged (27 000 rcf for 10 min), the final pH was measured, the supernatants were filtered (0.2 μm polycarbonate membrane filter), and Pb in solution was analyzed by differential pulse anodic stripping voltammetry (dpasv). DPASV measures labile Pb (12) and can be used to calculate free Pb²⁺ (11). The measured dpasv Pb was partitioned into those inorganic ion pairs calculated to be most prevalent in solution (PbOH⁺, Pb(OH)₂⁰, Pb(OH)₃⁻, PbHCO₃⁺, PbCO₃⁰, Pb(CO₃)₂²⁻, PbNO₃⁺, PbCl⁺, PbSO₄⁰), and an estimate of free Pb²⁺ was obtained by difference (14). Calculation of Pb inorganic ion pairs is relatively simple, and it is based on the constants and default values reported by Lindsay (13). The process of crystallization and transformation of the adsorbents was characterized by surface area, extraction with oxalate and pyrophosphate, FTIR, and XRD analyses on freeze-dried materials as described previously.

Results and Discussion

Adsorbents at Initial Conditions. Iron is an important constituent of all the adsorbents, while SMS-1 and SMS-2 (pedogenic materials) are also high in organic matter (Table 1). Characterization of the laboratory-synthesized iron oxide by X-ray diffraction (XRD) at initial conditions demonstrated the presence of a noncrystalline (2-line) ferrihydrite (Figure 1). A high surface area and high Fe extractability by oxalate are also indicators of the presence of noncrystalline materials (Table 2). A 2-line ferrihydrite was also present in the SMS-1 material (Figure 1). The surface area of SMS-1 was high, comparable to that in the synthetic ferrihydrite (Table 2). All the Fe in SMS-1 was extracted by oxalate, indicating a high degree of noncrystallinity. However, about 25% of Fe in SMS-1 was complexed by organic matter as indicated by the pyrophosphate extraction (Table 2). SMS-2 has a XRD pattern and a surface area typical of a crystalline material. X-ray diffraction presents peaks at positions corresponding to quartz (Q) and feldspar (F) with no evidence of crystalline or noncrystalline iron oxides (Figure 1). Although the SMS-2 material has a considerable amount of total Fe, all was extracted by oxalate (Tables 1 and 2). Furthermore, about 50% of the oxalate-extractable Fe was extracted by pyrophosphate, thus indicating that much of the total Fe was

TABLE 2. Surface Area and Oxalate- and Pyrophosphate-Extractable Fe

adsorbent	surface area ($\text{m}^2 \text{g}^{-1}$)		oxalate-extractable Fe (g kg^{-1})		pyrophosphate-extractable Fe (g kg^{-1})	
	initial	postheating	initial	postheating	initial	postheating
ferrihydrite	170	27.4	617	9.44	0.56	nd ^a
SMS-1	97.9	128	413	432	116	186
SMS-2	26.4	31.9	106	115	46.9	47.3

^a nd, not detected (below 0.28 g of Fe (kg of solid^{-1})).

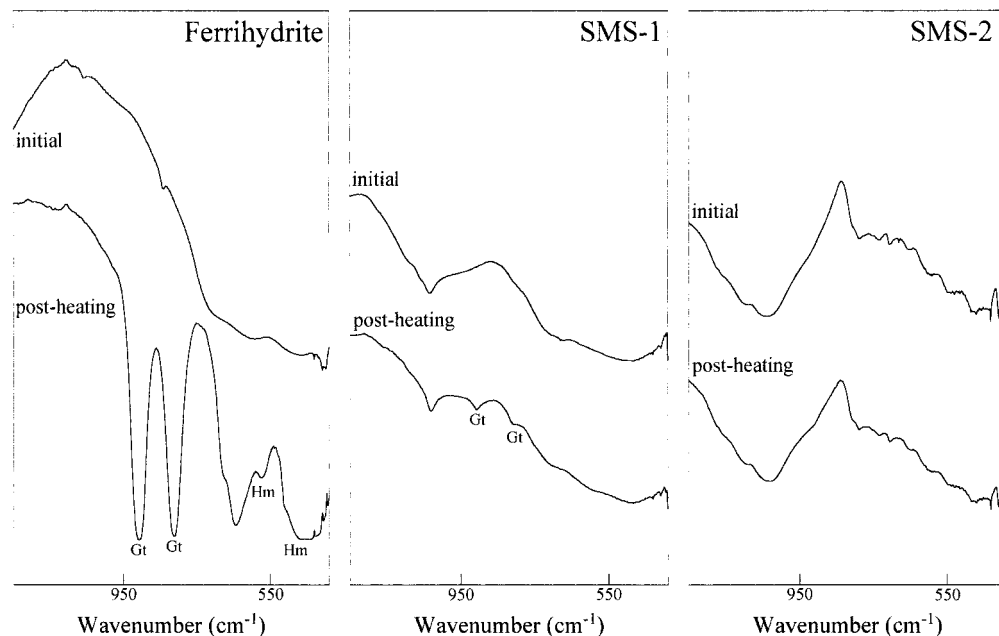


FIGURE 2. Fourier transform infrared (FTIR) spectra of ferrihydrite, SMS-1, and SMS-2 at initial conditions and after heating the suspensions for 60 days at 70 °C. Identification: Gt, goethite; Hm, hematite.

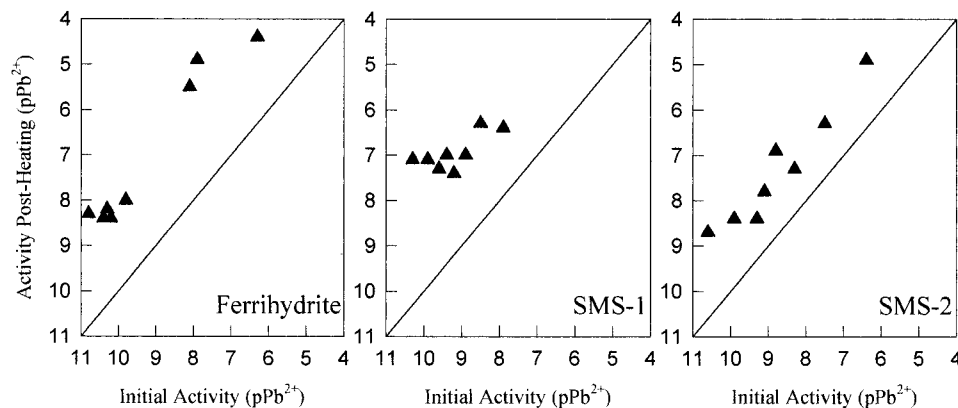


FIGURE 3. Relationship between initial (after equilibration for 15 days at room temperature) and postheating (60 days at 70 °C) Pb activity (pPb^{2+}) in solution. The solid line represents a 1:1 relationship (equal solubility).

complexed with organic matter (Table 2). The concentration ratio of Si to Al dissolved in the HNO_3 digest (Table 1) suggests the presence of noncrystalline ferro-alumino-silicates in the SMS-2 material, as no layer silicates were detected by XRD.

After Thermal Treatment: Solid-Phase Transformations and Pb Activity. Thermal treatment resulted in decreased suspension pH, especially in the ferrihydrite system. The degree of pH change followed the order: ferrihydrite > SMS-1 > SMS-2, indicative of the buffering capacity of the natural systems and suggesting different rates of transformation. X-ray diffraction and IR spectroscopy show ferrihydrite transformation to goethite and hematite after heating the suspensions (Figures 1 and 2). The surface area of ferrihydrite decreased to that of crystalline materials after thermal

treatment (Table 2). Clearly, ferrihydrite transformation to goethite and hematite resulted in increased Pb in solution, with free Pb^{2+} activity about 2 orders of magnitude higher after heating the suspensions (Figure 3). Presumably, Pb was ejected from the noncrystalline (very porous) laboratory-synthesized material during its transformation. This phenomenon was observed previously (1, 3) and could be explained by a reduction in the number of sorption sites for Pb, thus resulting in a lower retention capacity (15). The amount of Fe extracted by oxalate was greatly reduced after thermal treatment, further indicating the transformation of noncrystalline iron oxides (Table 2).

Lead activity increased after heating the pedogenic SMS-1 material as well (Figure 3). SMS-1 contains noncrystalline

iron oxides as evidenced by the 2-line ferrihydrite shown in its initial and postheating XRD patterns (Figure 1). Although not all the noncrystalline iron oxide initially present was transformed, IR provides evidence for the formation of goethite-like microcrystalline structures that are not well-enough ordered to produce a sharp XRD pattern (Figure 2). This transformation may be partially responsible for the postheating increase in Pb activity, although other constituents (e.g., organic matter) may be involved. Several studies have indicated that metals become more available after incubation of soils amended with metal-contaminated organic materials such as sewage sludge (16–18). In these studies, increases in metal availability were related to organic matter decomposition. Similarly, in a previous study, we observed a time-dependent increase in dpassv-labile Pb, suggesting that the decomposition of organic matter in a mixed ferrihydrite–organic matter system could increase metal solubility or toxicity (12). In the present study of the SMS-1 material, there were no significant changes in surface area or oxalate-extractable Fe after heating the suspensions (Table 2), further indicating that ferrihydrite transformation was partially hindered. An increase in dissolved organic carbon (DOC) occurred after heating the SMS-1 suspensions. In the absence of added Pb, DOC increased from 37 to 104 mg of C L⁻¹ after thermal treatment. Unlike the laboratory-synthesized ferrihydrite, this natural material contains high concentrations of Al, Si, and organic matter, all of which tend to retard ferrihydrite transformation (5–9).

Heating the suspensions did not produce a measurable change in the XRD pattern and FTIR spectra of SMS-2 (Figures 1 and 2). In addition, no changes were observed in surface area and oxalate- and pyrophosphate-extractable Fe after thermal treatment (Table 2). Elevated Pb activity, however, was consistently observed over the range of total Pb levels (Figure 3). Iron oxides (noncrystalline or crystalline) were not detected by FTIR or XRD analyses. Although SMS-2 has a substantial concentration of Fe (Table 1), the difference between oxalate- and pyrophosphate-extractable Fe is the only evidence of the existence of noncrystalline iron oxides in this material. This difference (about 50 g of Fe (kg of solid)⁻¹) is relatively small when compared to the concentration found in the synthetic ferrihydrite and SMS-1 systems (Table 2). Oxalate- and pyrophosphate-extractable Fe remain essentially unchanged after heating the suspensions (Table 2). Therefore, in the SMS-2 material, the increase in Pb activity cannot be explained by crystallization of iron oxides. Since SMS-2 is a more crystalline material containing low levels of noncrystalline iron oxides, Pb complexation with organic matter may be the most important retention mechanism.

The soil microbial population represents an organic surface capable of binding large quantities of different metals (19–20). Walker et al. (20) demonstrated that *Bacillus subtilis* walls and *Escherichia coli* envelopes have a higher Pb-binding capacity than some clay minerals. Only a relatively small fraction of this cellular material would need to be disrupted and solubilized to account for a large increase in soluble Pb. Heating the suspensions may have accelerated certain organic matter dissolution reactions and/or caused cell disruption and thus increased Pb activity (12, 16–20). An increase in DOC was also observed from the SMS-2 material after heating the suspensions, further supporting this hypothesis. Dissolved organic carbon increased from 56 to 85 mg of C L⁻¹ (no Pb added) as a result of thermal treatment. Noncrystalline ferro-alumino-silicates (their presence suggested by the low Si/Al ratio in SMS-2) may also provide reaction sites for Pb adsorption. Heating the SMS-2 suspensions may cause changes in this constituent, which might result in higher Pb activity. These hypotheses, however, need further investigation. For all adsorbents, the presence of Pb (up to a maximum

of 60 000 mg of Pb (kg of solid)⁻¹ had no effect on their surface areas, XRD patterns, or FTIR spectra. At the highest Pb loadings (>6000 mg of Pb (kg of solid)⁻¹), DOC values were generally reduced relative to the values at lower Pb loadings. This may be the result of DOC flocculation by high concentrations of Pb in solution.

Aging Effects. Heating the suspensions (thermal treatment) is used to accelerate spontaneous long-term transformations of the solid phases and to assess possible changes in the long-term activity of preadsorbed Pb. Although thermal treatment may not equate to natural aging processes in soils, it accelerates solid-phase transformations that are predicted on the basis of thermodynamic principles in both laboratory and natural systems. The degree of transformation differed among the materials studied, being less complete in the natural systems, which may have been a result of stabilization of noncrystalline minerals in soils by adsorbed materials such as silica or organic matter. Thermal treatment increased the solution Pb²⁺ activity of preadsorbed Pb from a pure system (ferrihydrite), a natural system containing high concentrations of noncrystalline iron oxides (SMS-1), and a natural system with little evidence of the presence of iron oxides (SMS-2). The results suggest that solid phases in addition to noncrystalline iron oxides (such as organic matter and/or noncrystalline ferro-alumino-silicates) may release adsorbed Pb into solution in the long-term. Lead activities measure the degree of biological toxicity of total Pb in soils, with Pb²⁺ activities above 10⁻⁸ M affecting plant growth and microbial processes in soils (ref 21 and references therein). In this study, the levels of Pb in solution (activities) obtained after thermal treatment are sufficiently high (at total Pb >1500 mg of Pb (kg of solid)⁻¹) that toxicity to plants and effects on microbial processes could be expected if these activities occurred in soils.

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