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FORMATION OF CHLOROPYROMORPHITE IN A LEAD-CONTAMINATED SOIL AMENDED WITH HYDROXYAPATITE

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Abstract

To confirm conversion of soil Pb to pyromorphite [$Pb_5(PO_4)_3Cl$], a Pb contaminated soil collected adjacent to a historical smelter was reacted with hydroxyapatite in slurries of soil and hydroxyapatite separated by a dialysis membrane and incubated. A crystalline precipitate formed on the dialysis membrane in the slurry systems was identified as chloropyromorphite. Soluble species measured in the soil slurry indicated that dissolution of solid-phase soil Pb was the rate-limiting step for pyromorphite formation. Additionally samples reacted with hydroxyapatite were incubated at field-capacity moisture content. The sequential chemical extraction used to identify species in the field-moist soil incubation experiment showed that hydroxyapatite treatment reduced the first four fractions of extractable Pb and correspondingly increased the recalcitrant extraction residue fraction by 35% of total Pb at 0 d incubation and by 45% after 240 d incubation. The increase in the extraction residue fraction in the 240 d incubation as compared to the 0 d incubation implies that the reaction occurs in the soil but the increase in the hydroxyapatite amended 0 d incubated soil as compared to the control soil illustrates the chemical extraction procedure caused changes in the extractability. Thus, the chemical extraction procedure cannot easily be utilized to confirm changes occurring in the soil as a result of incubation. Extended x-ray absorption fine structure (EXAFS) spectroscopy indicated that the 240 d incubated hydroxyapatite treatment caused a change in the average, local molecular bonding environment of soil Pb. Low-temperature EXAFS spectra (chi data and radial structure functions - RSFs) showed a high degree of similarity between the chemical extraction residue and synthetic pyromorphite. Thus, confirming that the change of soil Pb to pyromorphite is possible by simple amendments of hydroxyapatite to soil.

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Introduction

In addition to the geochemical significance of Pb phosphates in regulating the levels of lead (Pb) in many natural water bodies, immobilization of lead in contaminated soils by formation of solid Pb phosphates has attracted interest as a potential alternative to current remediation technologies. The working hypothesis of Pb immobilization is that the soluble soil Pb, which exists in equilibrium with the solid species, can be converted into lead orthophosphates (pyromorphites) in situ by adding phosphate. Because pyromorphites, $Pb_5(PO_4)_3(Cl, OH, F...)$, are the most stable minerals in the group of Pb phosphate compounds found under normal environmental conditions encountered in nature, other solid phase species would be converted to pyromorphite by a dissolution-precipitation mechanism. Nriagu et al., (1-4) established a detail thermodynamic basis for the reaction of Pb(II) and phosphates in aqueous solutions. In the family of pyromorphite minerals, chloropyromorphite [$Pb_5(PO_4)_3Cl$] has the lowest solubility, which is several orders of magnitude less than that of hydroxyl-, bromo-, and fluoro-pyromorphites (3). Due to the abundance and wide distribution of chloride in nature, it is expected that chloropyromorphite is the dominant form in the pyromorphite mineral family. Accordingly, pyromorphite was reported in Pb-bearing mineral deposits, mine-waste contaminated soils (5), garden soil (6) and soils contaminated with Pb ore (galena) adjacent to a phosphoric acid plant (7). A recent report (8) has demonstrated the formation of pyromorphite in a highly Pb contaminated soil (3-4% Pb content) when amended with hydroxyapatite.

Recent research demonstrates that the addition of phosphates effectively attenuates the aqueous Pb concentration to low levels in Pb solutions or Pb-contaminated soil solutions (9, 10). Several Pb phosphates, e.g., $Pb_3(PO_4)_2$ and $Pb_4O(PO_4)_2$, whose solubilities are similar to hydroxypyromorphite [$Pb_5(PO_4)_3OH$] at pH 4 to 7 were not identified in the Pb-H₂O-P₂O₅ systems (2, 9, 11, 12). Furthermore, the concentration of cations and anions commonly found in soil solutions did not significantly affect formation of pyromorphite or its composition (11, 12). Thus, phosphate addition to Pb contaminated soil should result in the formation of pyromorphite.

The significant reduction of soluble Pb concentration in soil suspensions by addition of rock phosphate has been reported, and successes in the formation and identification of pyromorphites in the Pb aqueous solutions have been achieved; however, direct evidence for the formation of pyromorphite in Pb contaminated soils upon phosphate addition is limited. Laperch et al. (8) recently identified pyromorphite in the products obtained from the reaction of the Pb enriched fraction (82 g Pb/kg) of a highly contaminated soil (Pb content = 3-4% w/w) with a synthetic hydroxyapatite. Cerrusite ($PbCO_3$) was the dominant Pb mineral and the major source of soil Pb. However, a contaminated soil with a single Pb species is not often found. The diversity of species distribution and relatively low content (e.g., less than 10,000 ppm) of soil Pb makes the individual species identification and quantification difficult with ordinary chemical and instrumental techniques. However, in development and evaluation of remediation technologies, it is necessary to illustrate the behavior of the target pollutant in the chemical or physical treatment processes, and the intermediate(s) and final product(s) of the pollutant. Therefore, the feasibility of immobilization of Pb in contaminated soils by amendment with phosphates depends upon direct evidence of formation of pyromorphite in the phosphate treated soils, as well as inferences collected from soil and solution experiments.

The focus of this effort is to identify the products of soil Pb and apatite reaction in a soil containing low levels of Pb ($Pb_{total} \cong 8,000 \text{ mg kg}^{-1}$). Untreated and hydroxyapatite treated soils were analyzed by a sequential extraction technique and synchrotron based X-ray absorption spectroscopy (XAS). The XAS analysis provides direct evidence of soil Pb forms which can not

be obtained by ordinary diffraction techniques. Furthermore, a dialysis system allowed physical separation of Pb and P sources, provides information on the plausibility of the reaction and allows determination if the reaction was controlled by dissolution of apatite, dissociation of solid associated Pb, or by Pb and P diffusion in the solution.

Materials and Methods

Soil. The soil used in this study was collected from the area of a historical lead smelting plant in Montana. Before any measurements were conducted, the bulk soil was air dried, passed through a 2 mm sieve and mixed. The contents of major and trace elements and selected soil properties are listed in Table 1.

Hydroxyapatite. The synthetic hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) was obtained from Bio-Rad laboratories (Bio-Gel). The Ca/P molar ratio of 1.625 is close to the ratio of 1.667 in an ideal hydroxyapatite crystal. Characteristic XRD peaks of hydroxyapatite were obtained for this material, both from this study and in the literature (13).

Chloropyromorphite. Chloropyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$), used as the reference, was synthesized by slowly mixing a $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ solution and a $\text{Pb}(\text{NO}_3)_2$ solution undervigorously stirring. The molar ratio of Pb/P = 1.664 which is very close to the theoretical ratio of 1.667 for pyromorphite. The results from chemical and instrumental analyses indicate that the precipitate is the crystallized chloropyromorphite.

Incubation Experiment. One kg of air-dried, less than 2.0 mm sieved soil was thoroughly mixed with 32.3 g of hydroxyapatite. The amount of apatite used yielded a 5/1 molar ratio of phosphate to lead in the soil. After thorough mixing, 200 g of water were added to the soil, simulating a moisture level of soil field capacity. Duplicate samples were placed in 1 L polyethylene containers. The weight of the container was monitored and adjusted to avoid a significance loss of soil water during the 240 day incubation period. In addition to the soil sample mixed with hydroxyapatite, another sample of the same soil without apatite was incubated under the same conditions to serve as an experimental control.

Dialysis Experiment. The fraction of prepared soil that passed a 180 μm sieve was used in the dialysis experiment. This fraction had a total Pb content of 12,111 (± 189) mg kg^{-1} . Two (2.0) grams of the soil were suspended in a 50 mL solution of 0.1 M NaNO_3 and 0.001 M NaCl , and placed in a dialysis tube (Sup/7 with a MWCO of 1,000). Six of the soil dialysis tubes were placed in a 2 liter polyethylene bottle containing a dialysis solution consisting of 1,600 mL of 0.1 M NaNO_3 and 0.001 M NaCl solution. To prevent the growth of microorganisms, 0.5 g of NaN_3 was added into the dialysis solution. Two dialysis tubes each containing one gram of hydroxyapatite suspended in 50 mL of the dialysis solution, were placed in the same bottle. The bottles were then rotated on a parallel rotator.

The dialysis solution was adjusted from its initial pH of 7.75 to pH of 5.50 or 6.50 (± 0.10) using a 0.1M HNO_3 solution. The pH was maintained during the 95 d dialysis period. The dialysis solution was monitored and sampled daily for the first week and then less frequently during the remainder of the dialysis period. The sampled solutions were acidified and stored in a cold chamber (-2°C) until analyzed.

A dialysis tube containing the soil was removed from the dialysis solution after 14, 28, 56 and 95 days. The soil was collected on a filter paper after rinsing with deionized water. The dialysis

membranes themselves were thoroughly rinsed with deionized water, air dried, and samples were prepared for SEM/EDX analysis.

Analytical Procedures

Acid Digestion. Acid digestion was used to determine the total Pb content in soils and the Pb in the extraction residual portion of the soil after sequential extraction. A sample (0.100 - 0.300 g) of dried soil was digested in 10.0 mL of concentrated HNO₃ in a microwave oven (CEM). A soil sample obtained from the National Institute of Standard and Technology (Standard Reference Material 2710) was digested with the experimental soil samples as an external standard for the procedure and analytical quality control. The diluted digest solution was analyzed for Pb with an atomic absorption spectrometer or inductively coupled plasma spectrometer.

Sequential Extraction. A sequential extraction procedure similar to that of Tessier et al., (14) and Rapiz et al. (15) was used in this study. One gram of soil was extracted in 10.0 ml of 1 M MgCl₂ solution at pH 7. After shaking for one hour, the suspension was centrifuged at 13,000 rpm and the supernatant solution collected. This fraction of Pb was considered as "exchangeable Pb". The soil residue from the exchangeable extraction was shaken for 3 hours with 10.0 ml of 1 M sodium acetate (NaOAc) solution at pH 5, adjusted using acetic acid (HOAc). This fraction of Pb was classified as "lead carbonates". The soil residue from the carbonate extraction was extracted for 3 hours with 10.0 ml of 0.04 M NH₂OH·HCl in 25% (v/v) HOAc in a water bath (95°C) with occasional agitation. This fraction of Pb was considered as Pb bound to Fe-Mn oxides. The Pb bound to organic matter and sulfide was obtained from extracting the soil residue with 3 ml of 0.02 M HNO₃ and 30% H₂O₂ adjusted to pH 2 with HNO₃ at a temperature of 85°C in a water bath. After 2 hours, a second 3 ml aliquot of H₂O₂ was added and the extraction continued for another 3 hours with intermittent agitation. After cooling, 5 ml of 3.2 M NH₄OAc in 20% (v/v) HNO₃ were added, and the total sample volume was then brought to 20 ml. The suspension was agitated on a shaker continuously for 30 min before centrifugation. The soil residue from the organic and sulfide bound extraction was digested by concentrated HNO₃ in a microwave oven to obtain the residual Pb fraction.

Solution. An atomic absorption spectrophotometer (AA, Perkin-Elmer Zm4000) equipped with a flame head (FAA) and graphite furnace (GFAA) was used to analyze Pb in the dialysis solutions. An inductively coupled plasma spectrometer (Trace 61E, Thermal Jerrel Ash) was also employed to analyze P, Ca and Pb concentrations in the solutions. Detection limits are 0.5 and 2.0 µg L⁻¹, for GFAA and ICP, respectively. Solution and suspension pH values were measured using a combination glass electrode and a pH meter (Acumen). The distribution of Pb, PO₄, Ca, CO₂, NO₃ and Cl species in the solutions was established using a geochemistry computer code, EQ3/6 (16).

Solids. An X-ray diffractometer (Scintag, XDS 2000) with Cu K α radiation produced at 30 KV and 20 mA was used for mineralogical analysis of solids. Solids used for XRD and SEM/EDX analysis were air dried, crushed and mounted on a glass sample holder. Step-scanning with 1 s per 0.04° 2 θ was employed to obtain the XRD patterns. Solids and the dialysis tube films were placed on sample holders and coated with carbon, or Au, for SEM/EDX analysis. The SEM/EDX measurements were conducted using a JEOL Scanning Electronic Microscope (JSM 5300) equipped with an Energy Dispersive X-ray Spectrometer.

X-ray absorption spectroscopy (XAS) analyses were completed on beamline X-11A at the National Synchrotron Light Source, Brookhaven National Laboratory. Air-dried soil samples were ground to $< 125 \mu\text{m}$ using a mortar and pestle and stainless-steel sieve. Soil samples receiving various treatments and reference samples of chloropyromorphite and hydroxypyromorphite were analyzed in transmission mode at approximately 10 K. Data were collected across the energy region bracketing the Pb L_{III} edge at 13,055 eV. A Displex cryogenic unit was used for temperature control. Fourier transforms and data fitting of extended x-ray absorption fine structure (EXAFS) spectra were used to determine whether pyromorphite was present in the soil samples, and for determining relative distances between Pb and surrounding atoms. Data were subjected to standard normalization, background correction, baseline correction, and data analysis techniques (17, 18). The University of Washington FEFF programs were used for fitting (19).

Results

The Dialysis Experiment. The dialysis systems used in this study were designed to study the dissolution of phosphate and solid-phase Pb, dissociation of Pb, and formation of Pb-P compounds (20). Although it has been demonstrated that hydroxyapatite is able to provide sufficient phosphate to immobilize Pb in solutions as pyromorphite (9, 13), Pb adsorbed on goethite (20), and Pb primary minerals (21-23), this process has not been demonstrated in a complex soil system. In addition, the dialysis system used in this study helps isolate the reaction product(s) for a direct observation with proper instruments as illustrated in related studies in our laboratory (20).

The concentrations of total P, Ca and Pb in the two dialysis solutions with a pH 5.5 and 6.5, respectively, in a 95 day dialysis period are presented in Fig. 1. In both systems, the total Pb concentration in the dialysis solutions increased during the first 6 days then decreased rapidly during the next 14 days and then maintained a relatively constant level of 10 to 20 $\mu\text{g L}^{-1}$ after 30 days. In contrast, results from agitated systems, in which a contaminated soil and hydroxyapatite were in direct contact in suspension, the soluble Pb decreased to less than 10 $\mu\text{g L}^{-1}$ in a time period of several minutes (9, 10). Thus, soluble Pb in the dialysis solution takes a longer time to reach steady state. It should be noted that in the dialysis system, there was no direct contact between the soil and hydroxyapatite and no intensive agitation, therefore, the dissolution of hydroxyapatite and the solid Pb species would not be promoted by abrasion between particles in the suspension as occurs during shaking in extraction experiments. The pH and the measured concentrations of P, Pb, Ca, Na, NO₃ and Cl of the dialysis solutions were used as input into the geochemical code, EQ3 (16) in order to model the distribution of Pb and phosphate species and mineral formations in the dialysis solutions. Two solids that could precipitate from both dialysis solutions were chloropyromorphite and chloroapatite [$\text{Ca}_5(\text{PO}_4)_3\text{Cl}$], the latter is less soluble compared to the added hydroxyapatite. The soluble phosphate concentrations, therefore, were likely influenced by the presence of both hydroxyapatite and chloroapatite. The amount of phosphate used to precipitate the dissolved Pb was negligible and the dissolved phosphate will not become the limiting factor in terms of supplying P to form chloropyromorphite in these systems.

To identify the reaction products of soil Pb and hydroxyapatite, the challenge is to separate the precipitated chloropyromorphite particles from their soil matrices. The chloropyromorphite becomes strongly attached to a host, e.g., chloropyromorphite was found on the dialysis film or glassware walls in this study and related experiments (20). Similarly, it has been found (9, 13) that

the precipitates of pyromorphite attached to the surface of hydroxyapatite. Soil provides many surfaces, e.g., clays, oxides, organics, etc., for chloropyromorphite to crystallize on, making isolation of the newly formed mineral difficult in light of the small amount of solid formed and its very fine grain size. However, after 49 d of dialysis, a gray precipitate was observed to have accumulated on the surface of the dialysis membrane. The precipitate was so fine grained that it was difficult to resolve using SEM/EDX analysis, however, the dialysis film collected after 95 d of dialysis allowed the determination of the hexagon-shaped cross-section of chloropyromorphite crystals by SEM imaging (Fig. 2a). The chemical composition of the precipitate surface was determined by the energy dispersive X-ray spectroscopy, (Fig. 2b), and was similar to that of the synthetic chloropyromorphite. The similarity of the two EDX spectra provided further evidence for the formation of chloropyromorphite on the soil dialysis tube. The solids filtered from the dialysis solution were also examined with SEM/EDX, and no chloropyromorphite was identified. The dialysis tubes containing hydroxyapatite were examined at the end of the 95 d dialysis and no precipitate was observed. The dialyzed hydroxyapatite was also analyzed by SEM/EDX and XRD and there was no difference found from that of the hydroxyapatite prior to dialysis. In the reaction of aqueous Pb with hydroxyapatite, either newly formed hydroxyapatite (9) or chloropyromorphite (13) was attached to the apatite surfaces. Thus, the hydroxyapatite served as the phosphate source and the nucleation site for pyromorphite growth. It has also been illustrated that the effectiveness of Pb removal from solution decreased because of the coverage of newly formed chloropyromorphite on the hydroxyapatite surface when the soluble Pb salt was used as the Pb source (13). In the dialysis system using soil as the source of Pb, the rate of Pb released from soil appeared slower than that of the dissolution of hydroxyapatite after the initial 6 days of reaction, thus the dissolved phosphate diffused into the dialysis tube containing soil and precipitated with the Pb in the solution near the Pb source as it was released from the soil. There was no Pb detected on the hydroxyapatite surface either by EDX or acid digestion analysis, suggesting that hydroxyapatite is able to provide sufficient phosphate to precipitate the dissolved Pb.

Changes in Pb Species by Sequential Extraction. Soil Pb was classified into five fractions based on its extractability as described by Tessier et al. (14). Though the species are operational definitions of species. These operationally defined species are related to the degree of stability of the soil metal. A recent example (24) related the results from a sequential extraction of Pb-contaminated soils to bioaccessibility of the Pb in the soils which were treated with various materials to reduce the soil Pb bioavailability in situ.

The mass balance of Pb extracted in this five step sequential extraction procedure indicated that the overall recovery relative to total soil Pb, obtained by acid digestion, was 94% (± 3) for soils regardless of hydroxyapatite treatment or length of incubation. The hydroxyapatite treatment and length of incubation caused changes in amount and percentage of each fraction of soil Pb recovered by the sequential extraction procedure (Fig. 3).

For the soil samples without hydroxyapatite, the 240 d incubation caused no significant change in Pb distribution among the five fractions ($P = 0.05$, Fig. 3), indicating that the distribution of Pb in the soil had reached a steady state in the field and was not subject to further change under the experimental incubation conditions. As compared to the control the addition of hydroxyapatite to the soil caused significant changes in the Pb distribution both in the 0 d and 240 d incubation samples. Except for Pb in the extraction residue, the amount of Pb in each of the four fractions was reduced in the hydroxyapatite treated soil as compared to the untreated soil (Fig 3).

The water soluble Pb is important for Pb transformation, transport, and bioavailability, however, it represented an insignificant amount of the total soil Pb (< 0.025%). Further, water soluble Pb was rapidly removed from the soil solution when soil is mixed with hydroxyapatite (9, 10). Thus, it was not reported here.

The $MgCl_2$ extractable Pb fraction in the untreated soil samples was 12 to 14% of the total soil Pb, and it decreased to 2 to 3% of the total soil Pb in the soil treated with hydroxyapatite. It has been well demonstrated that Pb adsorption is through a mechanism of inner-sphere surface complex formation (25). Unlike the *readily exchangeable ions*, which are the fully solvated ions or diffuse-ion swarm adsorbed on soils (26), the interaction between the adsorbed Pb and the soil particle surfaces is relatively strong and involves a direct association between Pb and the adsorbent surface. However, comparing the dissociation constant of adsorbed Pb on a hydrous ferric oxide surface ($10^{-4.1}$) (27) with the solubility products (K_{sp}) of cerussite ($PbCO_3$, $10^{-12.8}$) and anglesite ($PbSO_4$, $10^{-7.7}$), respectively (28), the adsorbed Pb is readily equilibrated with Pb in solution.

In the untreated soil this lead carbonate fraction was the highest among the five Pb fractions analyzed and accounted for 40% of the total Pb. This result was in agreement with lead carbonates being hypothesized to be the major component among the soil Pb species (28). In the hydroxyapatite treated soil incubated for 0 d, about 24% of the original lead carbonate had disappeared from this fraction, resulting in 28% of the total soil Pb remaining in this fraction. In comparison in the 240 d incubated soil amended with hydroxyapatite, about 37% of the original lead carbonates disappeared, resulting in 25% of the total soil Pb remaining in this fraction (Fig. 3). Assuming that the disappearance of soil Pb from this fraction caused accumulation in the residual Pb fraction, then lead carbonate was a major source of the increased residual Pb after hydroxyapatite treatment.

It was found that in the untreated sample, the Fe and Mg associated Pb fraction accounted for 20% of the total soil Pb. In the 0 d incubated hydroxyapatite treated soil about 17% of the original Pb in this fraction had disappeared, resulting in 16% of the total soil Pb remaining in this fraction. In the 240 d incubated hydroxyapatite treated soil, about 47% of Pb in this fraction had disappeared, reducing this fraction to 12% of the total soil Pb (Fig. 3).

The fraction of Pb associated with organic matters accounted for 13 to 15% of total soil Pb in the untreated soil (Fig. 3). In both the 0 d and 240 d incubated soil treated with hydroxyapatite, this fraction was reduced by 75% relative to the untreated soil samples, and accounted for only 3% of total soil Pb (Fig. 3).

The residual Pb in the soil without hydroxyapatite was about 11 to 15% of total soil Pb. However, in the 0 d incubated soil treated with hydroxyapatite the extraction residue accounted for 49% of the total soil Pb and in the 240 d incubated soil treated with hydroxyapatite the residual fraction accounted for 60% of the total soil Pb (Fig. 3). The amount of Pb gained in the residual portion was approximately equal to the total Pb lost in the previous four extractions. This implies that the Pb was transformed into substance(s) that can only be extracted with a vigorous acid digestion. Metals in the residual fraction are considered to be species that generally do not dissolve under conditions encountered in nature (14).

To verify the stability of chloropyromorphite in the sequential extraction process a synthetic chloropyromorphite was spiked into the incubated hydroxyapatite-soil mixture before proceeding with the sequential extraction. The results (not shown here) indicated that there was no significant difference in the amount of Pb extracted by the first four extractants between the unspiked soil and spiked soil. Approximately 92% of chloropyromorphite spiked Pb was recovered in the residual portion by acid digestion. Illustrating that chloropyromorphite is highly stable and is not

extractable even under the harsh high acidic, high temperature conditions of the sequential extraction process used, but rather remains in the residual fraction.

The assumption that soil Pb was transformed into pyromorphite by hydroxyapatite addition was consistent with the results obtained from the sequential extraction experiment where soil Pb reductions in the first four fractions of soil lead sequential extraction were accounted for by the increase in the residual fraction. Approximately 38 to 45 % of the total soil Pb had been converted to pyromorphite. However, as an increase in the residual fraction in both the 0 d and 240 d incubated soil treated with hydroxyapatite occurs, it is apparent that the extraction processes formed pyromorphite. A rapid reaction between soluble Pb and hydroxyapatite to precipitate solid pyromorphite has previously been demonstrated (9, 20-23). The increase in Pb in the residual fraction of the 240 d incubated soil treated with hydroxyapatite as compared to the 0 d incubated soil treated with hydroxyapatite implies that a conversion of soil Pb to pyromorphite happens during soil incubation. Thus, the reaction of conversion of soil Pb to pyromorphite does occur in soils amended with hydroxyapatite. As a conversion of soil Pb to pyromorphite occurs in both the extraction process and within the soil upon incubation with hydroxyapatite it is impossible to use sequential extraction to quantify the amount of pyromorphite formed. However, it is possible to conclude that at least 10% and maybe as much as 45% of the soil Pb was converted to pyromorphite during the 240 d incubation period.

X-ray Absorption spectroscopic (XAS) analysis. To confirm that pyromorphite has been formed in the soil system requires identification of the forms of lead in the residual fraction. To further illustrate the changes in Pb forms in the treated soils, X-ray absorption spectroscopy (XAS) was employed to examine the untreated and treated soils as well as the extracted soil residue. XAS, a non-destructive, element-specific analytical technique that probes the average local molecular bonding structure of a heavy metal, was used to investigate the nature of the reaction products of soil Pb and hydroxyapatite. Figure 4 shows the magnitudes and imaginary parts of radial structure functions (RSFs) obtained by fourier transformation of EXAFS spectra for samples of untreated soil, hydroxyapatite-treated soil (0 or 240 d incubation periods), the residual fraction from chemically extracted hydroxyapatite-treated soil, and the synthetic pyromorphite standards. These spectra are uncorrected for phase shift; therefore, the peak positions do not correspond to actual bond lengths between Pb and neighboring atoms. Results for the sample containing a physical mixture of hydroxyapatite and soil without incubation (0 d treatment) showed a decrease in the amplitude and resolution of peaks, but the overall structure of the RSF was similar to the sample receiving no treatment (Fig. 4).

Incubating the soil with hydroxyapatite for 240 d significantly changed the RSF features, indicating that this treatment induced changes in the average, local molecular bonding of soil Pb. By comparing features in the imaginary parts of the RSFs in relation to the dominant (1st-shell) peak near 1.8 Å, it is apparent that the spectrum for the sample incubated for 240 d is more similar to that of the hydroxypyromorphite standard than either the soil sample receiving no treatment or the sample incubated for 0 d. Also peaks between 2.1 and 4.0 Å were weaker in the sample incubated for 240 d compared with the samples receiving no treatment or a 0-d incubation. Although the RSFs suggest that some hydroxypyromorphite formed in the incubated soil (240 d), fitting results showed an average first shell bond length of 2.27 to 2.29 Å (± 0.02 Å) for all soil samples (Table 2). First-shell hydroxypyromorphite and chloropyromorphite bond lengths were longer (2.33 and 2.42 Å). However, the soil incubated for 240 d showed a second-shell Pb-O distance that was greater than those of the other soil samples (Table 2). Fitting was not done on the broad, higher-shell spectral region for hydroxypyromorphite standard. Likewise,

a 3rd-shell Pb-O peak in the soil incubated for 240 d had a distance (3.17 Å) that was consistent with that of the Pb-P distance in chloropyromorphite. Third-shell fitting of the soil RSF using oxygen was better than when using phosphorus. Collectively, the data suggest that some pyromorphite formed in the soil incubated with hydroxyapatite for 240 d.

The soil sample (residue) that underwent sequential chemical extraction, had an RSF and fitting results that were similar to chloropyromorphite (Fig. 4, Table 2). Particularly note the correspondence of the imaginary parts of the Fourier transform and the first-shell Pb-O bond length near 2.4 Å. Again, 3rd-shell oxygen yielded a better fit than with phosphorus. The results indicate that chloropyromorphite formed during the sequential extraction.

To more precisely compare local molecular bonding of Pb between the soil residue and chloropyromorphite, Fig. 5 shows EXAFS spectra collected at about 10 K. Decreasing the sample temperature increases the sensitivity of EXAFS spectroscopy to higher-shell x-ray backscattering interactions by decreasing the contribution of thermal motion to local molecular bonding disorder (18). To obtain a fairly uniform amplitude of the EXAFS oscillations across the entire k range shown in Fig. 5, it was necessary to use different k -weighting factors for each sample spectrum. We attribute this discrepancy to a higher sample temperature (> 10 K) for the chloropyromorphite sample during data collection, apparently due to poorer thermal contact between the mineral and the cryogenic sample holder. (The soil residue sample consisted of one thicker layer of material sandwiched between two pieces of Kapton[®] tape, while the chloropyromorphite sample consisted of multiple thin layers of material separated by tape folded onto itself). The frequencies of oscillations in the EXAFS spectra in Fig. 5 show a high degree of similarity between the two samples, even out to a wavevector of 18 \AA^{-1} . These results provide strong evidence that the soil extraction residue was dominated by chloropyromorphite. The unique peak at 4.4 \AA^{-1} in the chloropyromorphite spectrum is likely a multiple scattering peak (30). The RSFs for k -weighted data from low-temperature (~ 10 K) analysis of the soil residue and chloropyromorphite reference sample (see Supporting Information) showed similar spectral features, with a number of high-amplitude peaks present up to a radial distance of 5 Å. These data also support our conclusion that the Pb in the soil residue was predominantly chloropyromorphite. The fact that more peaks were resolved in the RSF from the soil residue was consistent with our assumption that this sample was at a lower temperature during data collection.

Overall, the EXAFS data are consistent with the sequential extraction data indicating that incubation of contaminated soil with hydroxyapatite for 240 d did alter the chemical speciation of soil Pb. The fact that the extraction residue contained chloropyromorphite provides supporting evidence for the formation of chloropyromorphite during the incubation; however, we cannot rule out the possibility that chloropyromorphite formed as a result of the chemical extraction itself.

Discussion

The EXAFS spectra for the 0 d incubated soil treated with hydroxyapatite and the control soil implies they are not different. Whereas, the sequential extraction data indicates the forms of soil Pb contained in the two samples was different. The high ratio of water to solid, relatively low pH, and continuous agitation in the extraction process created a favorable environment for both soil Pb and apatite P release into the extraction solution. Reported data (9, 20-22, 30) illustrate that the precipitation of pyromorphite is rapid when both Pb and P are in the solution. Thus, pyromorphite formation during extraction offers a plausible explanation for the differences observed by the two measurements and raises concern about the use of extractions to determine if

amendments have altered the species of Pb present in the sample.

A comparison of the sequential extraction for 0 d and 240 d incubation of the hydroxyapatite treated soil illustrated that changes in soil Pb occurred during the incubation. If we except the difference in the residual fraction of the sequential extraction as the amount converted to pyromorphite then at least 10 % (difference between hydroxyapatite amended samples at 240 d and 0 d) and maybe as much as 45% (difference between hydroxyapatite amended samples at 240 d and control at 0 d) of the soil Pb had been altered during the incubation. The EXAFS spectra for the 240 d incubated soil treated with hydroxyapatite indicated that this treatment induced changes in the average, local molecular bonding of soil Pb. The extracted soil residue had an RSF and fitting results that were similar to chloropyromorphite indicate that chloropyromorphite may have formed during incubation, but its formation during the sequential extraction to get the residue cannot be ruled out. The confirmation of chloropyromorphite formation in the dialysis experiment would support that its formation occurred during the incubation.

The hypothesis that various fractions of soil lead were transformed into chloropyromorphite and remained in the residual Pb fraction seems apparent from the results obtained from the dialysis experiment (Fig. 1 & 2), the sequential extraction experiment (Fig. 3), and the EXAFS spectra for the 240 d incubated soil treated with hydroxyapatite and the extracted soil residue (Fig. 4 and 5). But at this time we are unable to quantify the rate and extent of the transformation in more than very general terms.

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Table 1. Total elemental concentrations and suspension pH of the used soil[@]

SOM [*]	Si	Al	Fe	Ca	K	Mg	P
%							
2.1	25.8	6.88	3.50	1.55	2.60	0.85	0.14
Pb	Mn	Ba	Zn	Cu	Ni	Cd	pH [#]
mg/kg							
8,106	673	751	2,432	1255	19.4	158	6.78

^{*} Soil organic matter;

[#] Measured in 1:2 soil: water suspensions after 24 hours

[@] Except Pb, the data listed in this table were provided by Dr. L. Ma, University of Florida

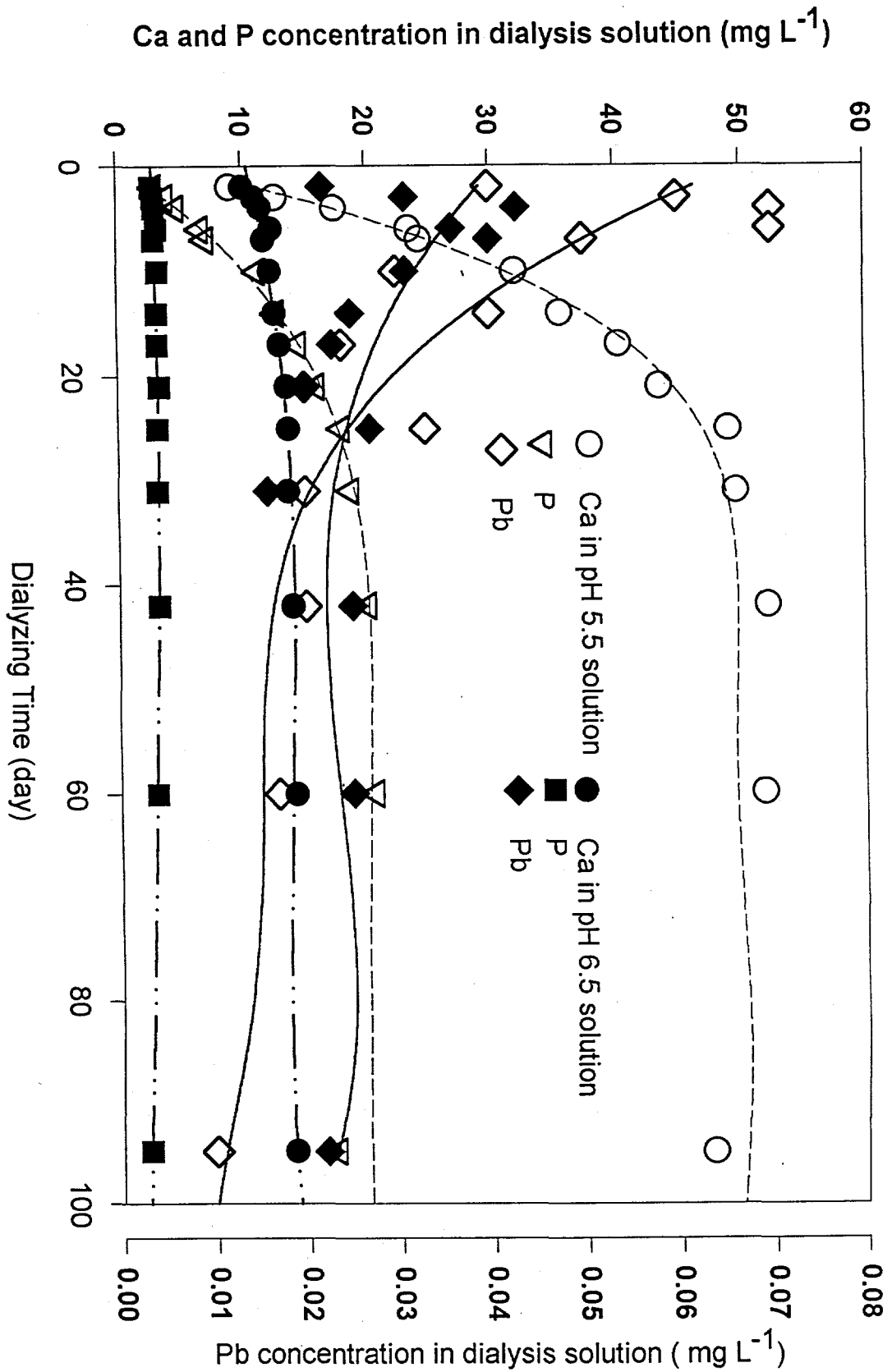


Fig. 1. Concentrations of Ca, P and Pb in the dialysis solutions with pH 5.5 and 6.5, respectively.

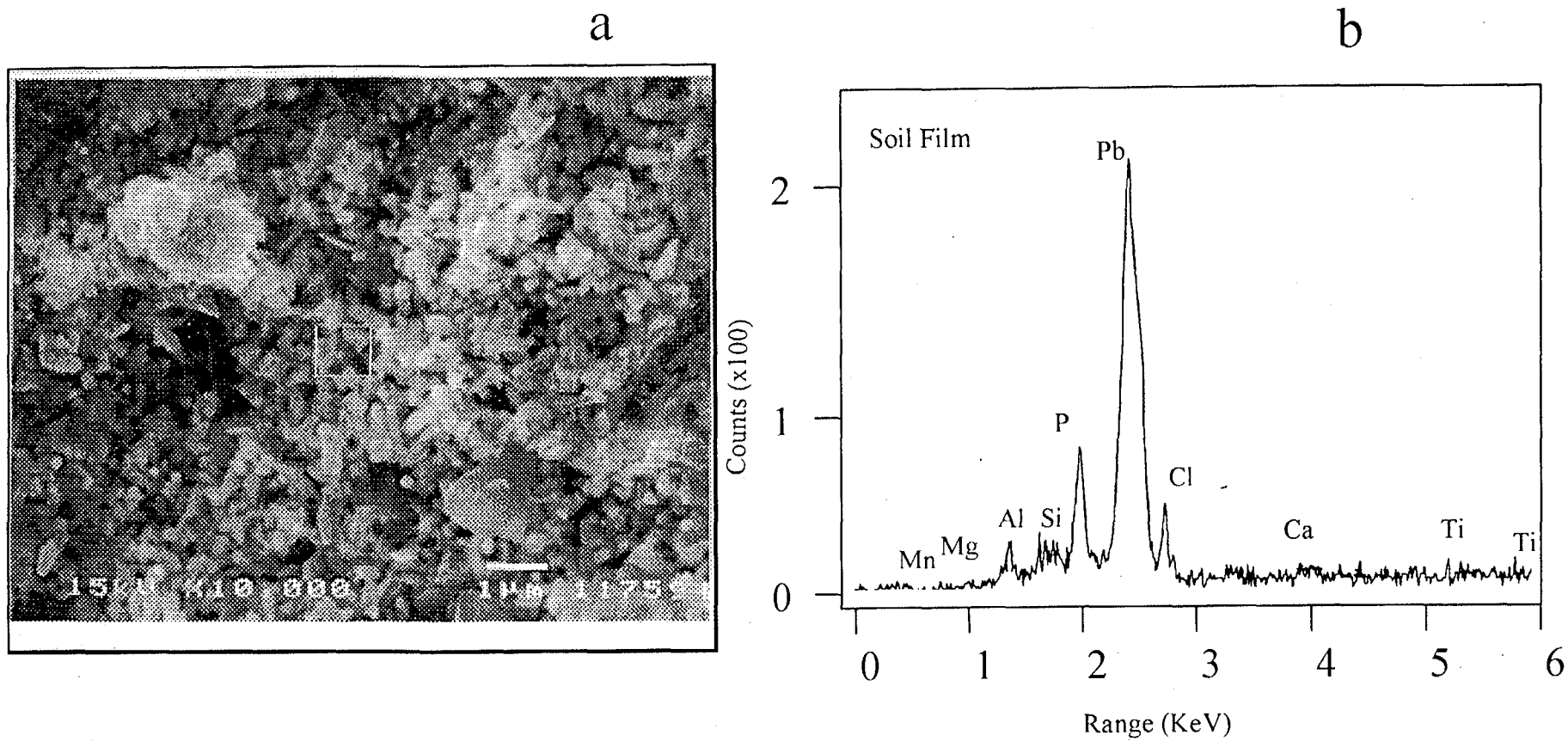


Fig. 2. Precipitate accumulated on the soil dialyses membrane, SEM image (a) and elemental spectra of surface by EDX (b).

Percent of Total Soil Pb

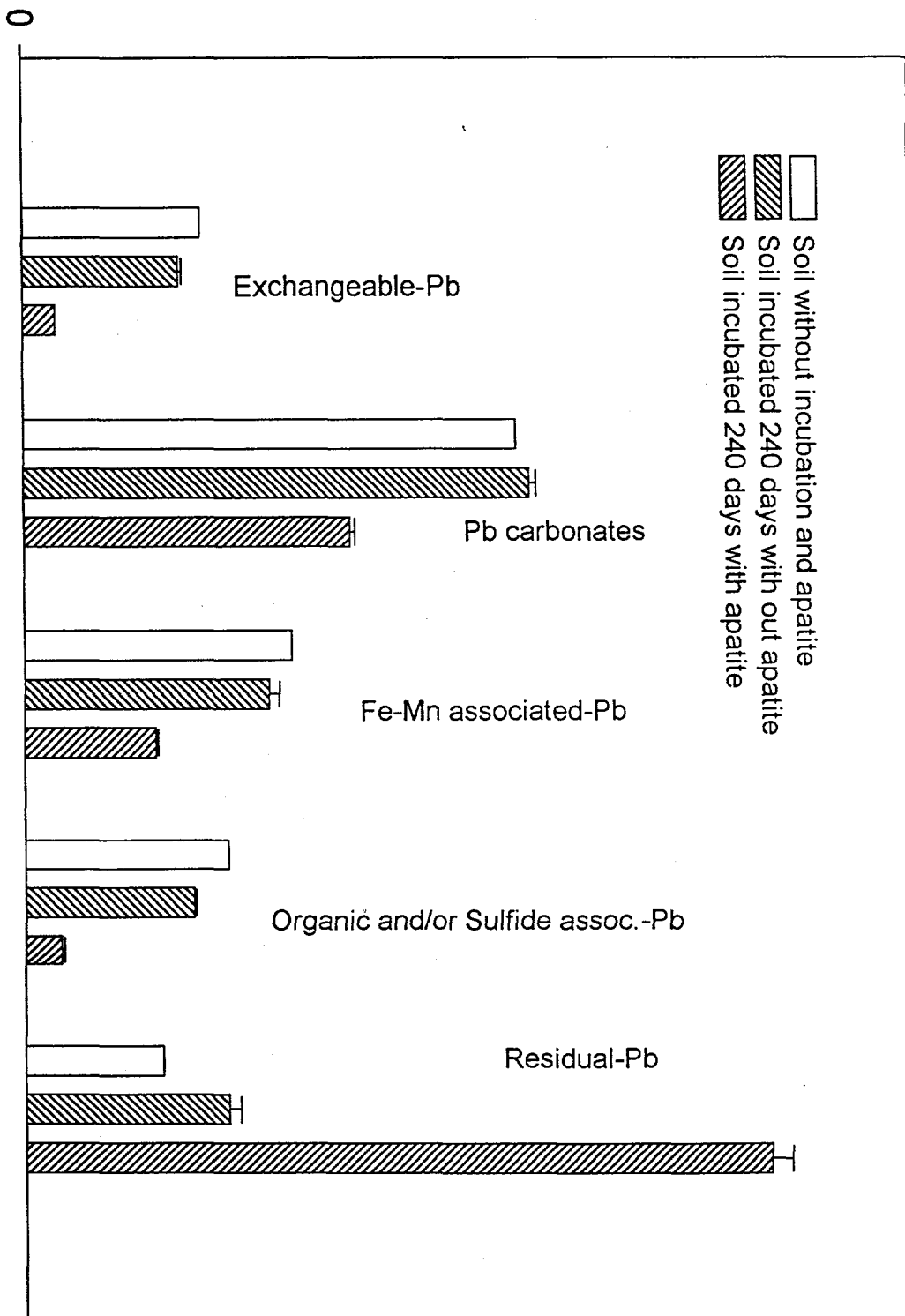


Figure 3. Sequential chemical extraction of Pb from soils treated and untreated with hydroxyapatite.

Fourier Transform Amplitude (w=3)

