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Lead Immobilization in Thermally Remediated Soils and Igneous Rocks

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Abstract

This is the final report for a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The principal goal of this project was to investigate the speciation of lead in the environment at LANL and to determine the feasibility of using thermal remediation methods to immobilize lead in the environment. Lead occurs as pyromorphite $[\text{Pb}(\text{PO}_4)_3(\text{Cl},\text{OH})]$, cerussite (PbCO_3) and galena (PbS) in vapor-phase-altered Bandelier Tuff samples. LANL soils primarily contain cerussite and PbO . Thermal remediation experiments at high temperatures (up to $400\text{ }^\circ\text{C}$) suggest that thermal immobilization of highly-reactive Pb compounds in the environment may be feasible, but that this technique is not optimal for more refractory lead phases such as cerussite and PbO .

1. Background and Research Objectives

In recent years, there has been significant interest in potential human health risks

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resulting from environmental exposures to lead. The Agency for Toxic Substances and Disease Registry identified lead as the highest priority contaminant at Superfund sites nationwide. In many situations, lead contamination is strongly associated with organic contamination (e.g. where leaded gasoline has leaked from the former site of an underground storage tank), semi-volatile organic contamination (in association with lead paints), or with high explosives contamination (as at a firing site at LANL). On-site thermal treatment of organic and HE wastes is becoming a viable option for remediation because of the high costs and governmental regulations associated with waste transportation and landfilling. Thermal methods are particularly useful for destroying organic and HE wastes, because high temperatures break down complex organic contaminants; however, at many waste sites, these methods are ineffective for solving the associated problem of lead and other toxic metal contamination. We have investigated the feasibility of modifying one or more of these thermal-treatment methods so that they also provide protection against the mobilization of lead. This study required an investigation of the fundamental geochemical controls on lead mobility in contaminated rocks and soils at LANL followed by a technology development study designed to optimize thermal remediation to halt ingestible lead mobility in the environment.

Pb Partitioning in the Environment

Understanding the partitioning of a trace element between phases in a rock or soil is fundamental to geochemical modeling of environmental mobility of that element. Trace elements may be bound in soils and igneous rocks by a variety of mechanisms: they may be located in crystallographic sites in the minerals composing the soil or rock, they may be adsorbed on minerals surfaces, or they may occur on colloids with organic and inorganic particulates. Few detailed studies have examined the partitioning of trace elements such as Pb between materials within soil and felsic igneous rocks (Sisson, 1991) using methods other than qualitative leaching tests. Proton-induced X-ray emission (PIXE) and secondary ion

mass spectrometry (SIMS) are extremely powerful tools for studying trace-element distributions between minerals and other particulates. These methods have been applied to mafic igneous and high-grade metamorphic rocks (i. e., Hickmott et al. 1987; Rogers et al. 1987; Shimizu et al. 1978). This project represents one of the first quantitative investigations of Pb speciation in soils and felsic igneous rocks using such trace-element microanalytical methods.

Thermal Remediation of Metals - Conceptual Model

When rocks or soils are heated, particularly in the presence of fluids that can catalyze high-T reactions, they recrystallize to new mineral assemblages or melt to form glasses. The minerals that form during a subsolidus recrystallization process depend on the bulk composition of the soil or rock, the kinetics of the recrystallization reactions, the temperature and pressure during heating, and the nature of associated fluids.

Specific high-T recrystallization products will have affinities for different minor and trace metals such as Pb. Insoluble recrystallization products: (1) are resistant to fluid-induced transport by surface waters and groundwaters; (2) will not fail the Toxicity Characteristic Leaching Procedure, which is used to determine whether a soil is a characteristic hazardous waste; and (3) are minimally bioavailable to human or ecological receptors who may ingest metal-contaminated soils in the environment. The nature of high-T recrystallization phases can be controlled by amending soils with raw materials that stabilize insoluble high-T recrystallization products. This study focuses on stabilizing insoluble Pb-bearing minerals during thermal remediation.

2. Importance to LANL's Science and Technology Base and National R&D Needs

The significance of the results derived from this study is twofold. First, the study provides fundamental information concerning the geochemical distribution of lead in rhyolitic tuff, in soils derived from tuff, and in the low-grade vapor-phase metamorphic by-products of that material. This information is useful in studies concerned with remediation of these elements at a variety of contaminated sites and provides fundamental information for use in

petrogenetic studies. Second, if the concept of "mineralogic immobilizers" as a complement to existing thermal waste-treatment methods can be further optimized, we will be able to transfer the resultant technology to the private sector. We have implemented a CRADA with ICF-Kaiser Engineers that builds on the lead speciation work that was completed during the first two years of this project.

The results of this study support LANL's mission in 'Environmental Stewardship' and enhance LANL's core technical competencies in 'Earth and Environmental Systems', and 'Complex Experimentation and Measurements'. The CRADA and associated R&D 100 award developed as a follow-on to this project help LANL's 'Industrial Partnership' efforts. The research directly helps pursue LANL's newly-developed programmatic tactical goal in 'Environmental Science'. Publications resulting from the project enhance LANL's reputation as a 'center of excellence in environmental science' and 'improve our understanding of environmental processes'. Research methodologies and technical innovations developed during the project may help solve the staggering environmental problems facing the DOE complex.

3. Scientific Approach and Accomplishments

The principal goal of this study was to demonstrate that it is feasible to reduce the leach toxicity of lead from thermally remediated soils or rocks by tailoring the bulk composition of the remediation products to produce minerals that are resistant to dissolution and that strongly incorporate lead. Additional goals included: (1) to characterize the distribution of lead between primary minerals, grain boundaries, and alteration products of tuffs and mine wastes; (2) to determine lead distributions between minerals and other particles in thermally remediated tuffs and mine wastes; and (3) to parameterize the observed lead behavior using thermodynamic and kinetic models.

This project was divided into three phases. The first two phases are described briefly, because their results are published in the literature. The last phase is described in some detail because the data has not yet been published.

Phase I - Characterization of Pb Distribution

The first stage of this project involved detailed bulk and microanalytical characterization of soils and altered tuffs, and Pb-contaminated mine wastes to determine the partitioning of lead between primary minerals, volcanic glass, vapor-phase minerals, and low-T alteration phases. This phase of the study considered both lead-contaminated and clean material. The overall goal of this phase of the study was to determine the mineralogic siting of trace metals in different rock and soil types and how such siting affects the leaching of these materials.

We analyzed samples of Bandelier Tuff — glassy material, devitrified samples, and highly vapor-phase altered materials — to determine naturally-occurring lead speciation in the vadose zone at LANL (Stimac et al. 1996). Igneous minerals and glasses contained significant amounts of lead (Figure 1). However, lead was also found in minute (< 20 micrometer) vapor-phase Pb-bearing minerals such as pyromorphite, cerussite, and galena. This result was surprising; it had not previously been recognized that much of the budget of a moderately volatile metal, such as lead, could be tied up in secondary, vapor-phase minerals in felsic igneous volcanics. Soluble vapor-phase lead minerals such as cerussite are both bioavailable and susceptible to leaching by infiltrating groundwaters. Results of our study should prompt a reinvestigation of mechanisms of trace-element mobilization in the Earth's crust, particularly in igneous-associated ore deposits.

Similar investigations of Pb speciation in mine-tailings material from the Kelly Mine, Magdalena District, NM were completed. Here, scanning electron microscopy suggested much simpler lead speciation than in the Bandelier Tuff. Most lead was contained either in the primary lead mineral (galena) or in secondary Pb-sulfate rimming the primary ore material (Larocque et al. 1995).

Many lead-contaminated soils at LANL firing sites are extremely heterogeneous. To focus our investigations of lead-contaminated soils onto materials with the highest lead concentrations, we investigated the application of laser-induced breakdown spectroscopy

(LIBS) to lead-contaminated soils (Eppler et al. 1996). LIBS was shown to be an effective analytical tool for soil studies — provided that both bulk-compositional and Pb-phase speciation between standards and unknowns were similar. This study attracted the interest of an industrial partner (ICF Kaiser Engineers) and a CRADA to pursue this work was completed.

Phase II - Identification of Pb-immobilizing Minerals

The second phase of the study involved optimization of the compositions of thermally remediated soils to stabilize lead-bearing minerals resistant to dissolution. This phase focused on three tasks: (1) evaluation of the proclivity of a wide-range of high-T minerals to partition Pb based on crystal chemical constraints; (2) simulation of human gastrointestinal tract dissolution of Pb-contaminated materials, and (3) calculation of changes in bulk composition needed to stabilize lead-bearing minerals using chemical mass transfer codes such as EQ 3/6 (Wolery 1992). This phase of the investigation was designed to focus on the most likely modified-rock compositions that stabilize Pb.

Proton-induced X-ray emission studies of naturally occurring altered minerals identified the minerals epidote (Hickmott et al. 1992) and alkali feldspar (Stimac et al. 1996) as strongly partitioning lead in high-T alteration environments. Although epidote is known to be relatively insoluble in surficial fluids, alkali feldspars are quite soluble over geologic time-scales (Blum and Stillings 1995). Epidote is typically stable at higher pressures than those common in thermal remediation systems. Neither of these silicate phases was identified as a good candidate as a mineralogic immobilizer.

Contaminated tuff samples, soils samples, and mine-tailings samples were all subjected to a two-stage dissolution test that simulates exposure of soils to the human gastrointestinal tract (Ruby et al. 1993). This test mimics the bioavailability of lead to humans. Soils from mine tailings sites have much lower bioavailability at a given level of contamination than do most tuff or soil samples (Figure 2). Tuff samples display a wide range in bioavailability (Figure 2). Samples containing vapor-phase pyromorphite (Figure 3)

have the lowest bioavailability of any tuff samples. Pyromorphite has been previously identified as a low-solubility Pb mineral (Ruby et al. 1994; Xu 1994). However, its existence as a vapor-phase mineral suggested that it could potentially be formed in high-temperature thermal remediation systems, provided the thermally-treated material had an appropriate bulk composition.

Phase III - Experimental Investigations of Pb Immobilizers

Introduction: Phase II studies suggested that pyromorphite [Pb(PO₄)₃(OH,Cl)] combined: 1) a very strong affinity for Pb; 2) low-solubility in the human gastrointestinal tract, and 3) stability at high temperatures and low pressures in felsic bulk compositions.

An experimental program was conducted to investigate conditions under which Pb compounds combine with phosphates to yield insoluble Pb-phosphates. The goal was to find thermal and/or aqueous treatment methods to react Pb oxide, carbonate, or dissolved lead with a source of phosphate to yield pyromorphite, the least soluble and bioavailable of the known Pb-bearing compounds. The experiments were conducted using simple Pb and phosphate chemical systems, so that the extent of reaction and nature of reaction products would be evident. Experiments on Pb-contaminated soils were limited in scope because X-ray diffraction and electron microscopy showed that the mineralogic speciation of Pb-bearing phases was difficult to determine at typical contamination levels (hundreds or thousands of parts per million).

Experimental Approach: Thermal and aqueous reactions were investigated in an effort to create pyromorphite by reaction of Pb compounds with phosphates. A variety of Pb compounds were chosen to reflect the potential diversity of compounds occurring in an oxidizing soil environment (Davis et al. 1993; Larocque et al. 1995; Stimac and Hickmott 1994). PbCl₂ was used as a highly soluble and reactive source of Pb. PbO and PbCO₃ were used as low solubility, low reactivity sources of Pb. A variety of phosphates were used to investigate their reactivity with Pb compounds. These phosphates included hydroxyapatite

($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), monetite (CaHPO_4), and disodium hydrogen phosphate (Na_2HPO_4). The desired reaction product in all of these cases was pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) or hydroxy-pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{OH}$). NaCl was used in a number of experiments as a source of Cl for the formation of pyromorphite. The extent of reaction was determined primarily by comparison of X-ray diffraction (XRD) data for reactants and experimental products. This technique could not easily detect minor degrees of reaction ($<$ several percent). Additional characterization was conducted by scanning electron microscopy (SEM) and electron microprobe analysis (EMPA). It was found that these techniques were also ineffective in the determination of minor degrees of reaction due to the fine-grained character of reactants and products in cases where little reaction was detected by XRD.

Thermal Experiments: Elevated-temperature experiments were conducted by mixing reagent-grade reactants in an automatic mortar and pestle, loading the mixture in a ceramic crucible, and placing them in a calibrated oven for a period of days to weeks. The experimental conditions and results are given in Table 1. Most experiments were conducted at 400°C . These conditions were used to simulate temperatures of many thermal treatments, yet they also avoided significant volatilization of Pb . Several experiments were conducted using soil or clay amendments in an effort to discover a catalyst for the conversion of Pb compounds to pyromorphite.

Aqueous Experiments: A series of experiments were conducted in aqueous solutions by mixing Pb -bearing and phosphate-bearing compounds. The experiments were conducted at room temperature ($\sim 22^\circ\text{C}$) and at 140°C under hydrothermal conditions. The reactants were mixed in an automatic mortar and pestle and placed in Teflon containers for periods ranging from 2 days to more than 3 weeks. The experimental conditions and results are given in Table 2. The ratio of Pb to Ca was varied in many of the experiments to investigate the effect of available lead on the precipitation of pyromorphite. (A value of $\text{Pb}/\text{Ca} = 2.77 \text{ g/g}$ permits a stoichiometric conversion of calcium phosphate to pyromorphite).

Discussion of Thermal Treatment Results: The most reactive source of phosphate was disodium hydrogen phosphate. This yielded pyromorphite when combined with lead chloride, and it produced NaPbPO_4 when reacted with lead oxide or carbonate. The solubility of NaPbPO_4 is not known; however it is likely to be more soluble than PbHPO_4 . Lead carbonate decomposed to lead oxides in many of the experiments, indicating that the net effect of the thermal treatment of lead carbonate was essentially the same as that for the lead oxides. Hydroxyapatite and lead compounds reacted to only a minor extent and produced no pyromorphite. It appears that hydroxyapatite is an insufficiently reactive source of phosphate to produce pyromorphite in thermal treatment systems.

Discussion of Aqueous Treatment Results: Hydroxyapatite readily converted to pyromorphite in the presence of lead chloride in aqueous solutions. The high concentrations of lead produced by the dissolution of lead chloride yielded beautiful crystals of pyromorphite with sizes approaching a millimeter in length (Figure 5). Large pyromorphite crystals formed at a variety of ratios of Pb/Ca, but the most abundant crystals were formed at the stoichiometric ratio of 2.77 g/g as determined by SEM analysis. The crystals contain minor quantities of Ca and indicate little tendency for the formation of chemical intermediates between apatite and pyromorphite. Although the X-ray diffraction data indicated a well-crystallized pyromorphite, several features of the chemical analysis indicated unusual chemical substitutions in the experimental materials (Table 3). Relative to stoichiometric pyromorphite, the experimental materials have excess Pb and Cl, suggesting a solid solution that incorporates excess lead chloride. It is unclear how this chemical substitution can be accommodated by the pyromorphite crystal structure.

Lead carbonate and lead oxide did not react to form pyromorphite, even in the presence of sodium chloride. However, other reaction products formed including $\text{Pb}_7\text{O}_6\text{Cl}_2$ and NaPbHPO_4 . The solubility of these compounds is unknown, and the relative thermodynamic stability of these compounds compared to pyromorphite is also unknown. However, it is possible to conclude that the crystallization of these materials must reduce the availability of dissolved Pb relative to the starting oxides and carbonates.

Analysis of Results: The thermal experiments indicate that formation of pyromorphite from apatite reactants is difficult to achieve. Calculations using thermodynamic data show that apatite and chloro-apatite are stable relative to pyromorphite at room temperature using oxide or chloride species. Unfortunately, enthalpy data are not available for pyromorphite, although data for hydroxy-pyromorphite have been published recently (Ntahomvukiye et al. 1995). Using the latter data to provide an estimate of the enthalpy of pyromorphite allows calculation of the expected equilibrium among pyromorphite, apatite, and oxides or chlorides of Pb and Ca. These data suggest that pyromorphite is stabilized at moderately, elevated temperatures (the precise temperature cannot be quantified due to the nature of the thermodynamic approximations). Evidently, these temperatures were not achieved in the thermal experiments and may be difficult to realize in practice due to volatilization of lead.

The aqueous experiments demonstrate that pyromorphite is readily formed from apatite in Pb-rich solutions. This result is consistent with thermodynamic calculations. However, lead oxide and carbonate systems did not yield pyromorphite, perhaps because of the relatively low concentrations of Pb. The lead oxide and carbonate systems produced other phases, which have poorly understood properties. These results were somewhat unanticipated because reaction calculations show that pyromorphite crystallizes from aqueous solutions in the presence of lead oxide or carbonate (Figure 6).

Reaction path calculations for hydroxyapatite and lead oxide/carbonate systems were made using EQ3/6 (Wolery 1992) (Figure 6). In order to perform the calculations, it was found necessary to suppress the formation of Pb^{4+} , which would consume all of the Pb^{2+} and produce plattnerite (PbO_2). The reaction path calculations clearly demonstrate that pyromorphite forms as lead oxide and lead carbonate dissolve, resulting in a reduction of the concentration (5×10^{-6} m) of Pb that would form by simple dissolution of PbO . However, the calculation also shows that the stable state of the system may involve phases other than pyromorphite. In the calculation depicted in Figure 6, pyromorphite eventually reacts-out to produce $(Pb(OH)_2)_3 \cdot PbCl_2$ plus $Pb_4O(PO_4)$. Neither of these phases were observed in the experiments. Instead, other Pb-bearing phases that are not in the EQ3/6 database

precipitated. At this stage, it is unknown whether these phases represent a stable thermodynamic state in the Pb-Ca-PO₄-Cl-H₂O system.

Conclusions: An effective thermal treatment of Pb-contaminated soils will require the use of a highly reactive source of phosphate, for example Na₂HPO₄. However, there are no thermodynamic or solubility data for the Pb-bearing products that are likely to form in these thermal environments. While it is likely that these compounds are more stable than lead oxide or lead carbonate, solubility or calorimetric data are required to establish the efficacy of such treatments.

Aqueous treatment of Pb-contaminated soils is likely to be much more effective for the immobilization of lead. All Pb-compounds were found to be reactive in aqueous media with hydroxyapatite. Pyromorphite was produced only in the presence of highly soluble forms of lead. In addition to pyromorphite, Pb₇O₆Cl₂ and NaPb₄(PO₄)₃ were precipitated in NaCl-bearing solutions with lead oxides and carbonates. Again, thermodynamic and solubility data are required to confirm that these Pb-phases effectively reduce aqueous concentration of lead.

Many experiments failed to produce any observable reaction. It is possible that reaction in these experiments was limited to thin surface layers. If this was the case, treatments based on these experimental conditions may be effective in the soil environment where the Pb-phases are minute and have high surface areas.

These experiments were designed to determine effective remediation strategies for soils contaminated with lead and organic residues. The results indicate that simple addition of hydroxyapatite or other phosphate to contaminated soil prior to thermal treatment is not likely to effectively reduce the bioavailability of Pb in the soil: pyromorphite does not readily crystallize from the reaction of PbO and hydroxyapatite at elevated temperature under dry conditions. However, it may be possible to design a post-thermal treatment strategy to immobilize lead. For example, thermally treated soils could be cooled by application of phosphate- and chloride-bearing solutions. The aqueous experiments indicate

that pyromorphite or another insoluble Pb-compound will readily precipitate under these conditions.

Publications

1. Eppler, A., Cremers, D. A., Hickmott, D. D., Ferris, M. J., and Koskelo, A. C., "Matrix effects in the detection of Pb and Ba in soils using a laser plasma," *Applied Spectroscopy*, **50**, 1175-1181 (1996).
2. Hickmott, D. D., Herrin, J. M., Abell, R., Stimac, J., and Gauerke, E. R., "Environmental applications of the LANL nuclear microprobe," *Nuclear Instruments and Methods in Physics Research* (submitted).
3. Larocque, A. C. L., Chapin, C. E., Laughlin, A. W., and Hickmott, D. D. "Metal-residence sites in mine tailings in the Magdalena District, NM. USA." *Mineral Deposits: From Their Origin to Their Environmental Impacts*, J. Pasava, B. Kribek, and K. Zak, eds., A.A. Balkema, Rotterdam, 661-664 (1995).
4. Stimac, J., Hickmott, D., Abell, R., Larocque, A. C. L., Broxton, D., Gardner, J., Chipera, S., Wolff, J., and Gauerke, E., "Redistribution of Pb and other volatile trace metals during eruption, devitrification, and vapor-phase crystallization of the Bandelier Tuff, NM.," *Journal of Volcanology and Geothermal Research*, **73**, 245-266 (1996).
5. Werner, C., Stimac, J. A., and Hickmott, D. D. "Trace element distributions in the upper Bandelier Tuff, New Mexico: Zircon zoning and implications for magmatic evolution of the Valles system." *The Jemez Mountains Region*, F. Goff, B. S. Kues, M. A. Rogers, L. D. McFadden, and J. N. Gardner, eds., New Mexico Geological Society, Socorro, N.M., 285-293 (1996).

References

- [1] Blum, A. E., and Stillings, L. L. "Feldspar dissolution kinetics." *Chemical Weathering Rates of Silicate Minerals*, A. F. White and S. L. Brantley, eds., Mineralogical Society of America, Washington, D.C., 291-346 (1995).
- [2] Davis, A., Drexler, J. W., Ruby, M. V., and Nicholson, A., "Micromineralogy of mine wastes in relation to lead bioavailability, Butte, Montana," *Environmental Science and Technology*, **27**, 1415-1425 (1993).
- [3] Eppler, A., Cremers, D. A., Hickmott, D. D., Ferris, M. J., and Koskelo, A. C., "Matrix effects in the detection of Pb and Ba in soils using a laser plasma," *Applied Spectroscopy*, **50**, 1175-1181 (1996).
- [4] Hickmott, D. D., Shimizu, N., Spear, F. S., and Selverstone, J. E., "Trace element zoning in a metamorphic garnet," *Geology*, **15**, 573-576 (1987).

- [5] Hickmott, D. D., Sorensen, S. S., and Rogers, P. S. Z., "Metasomaism in subduction complexes: Constraints from microanalysis of trace elements in minerals from garnet amphibolite, Catalina Schist," *Geology*, **20**, 347-350 (1992).
- [6] Larocque, A. C. L., Chapin, C. E., Laughlin, A. W., and Hickmott, D. D. "Metal-residence sites in mine tailings in the Magdalena District, NM. USA." *Mineral Deposits: From Their Origin to Their Environmental Impacts*, J. Pasava, B. Kribek, and K. Zak, eds., A.A. Balkema, Rotterdam, 661-664 (1995).
- [7] Ntahomvukiye, I., Khattech, I., and Jemal, M., "Synthesis and determination of the standard enthalpy of formation of lead hydroxyapatite," *Annales de Chimie - Science des Materiaux*, **20**, 1-8 (1995).
- [8] Rogers, P. S. Z., Duffy, C. J., and Benjamin, T. M., "Accuracy of Standardless Nuclear Microprobe Trace Element Analyses," *Nuclear Instruments and Methods in Physics Research*, **B22**, 133-137 (1987).
- [9] Ruby, M. V., Davis, A., Link, T. E., Schoof, R., Chaney, R. L., Freeman, G. B., and Bergstrom, P., "Development of an in vitro screening test to evaluate the in vivo bioaccessibility of ingested mine-waste lead," *Environmental Science and Technology*, **27**, 2870-2877 (1993).
- [10] Ruby, M. V., Davis, A., and Nichololon, A., "In situ formation of lead phosphates in soils as a method to immobilize lead," *Environmental Science and Technology*, **28**, 646-654 (1994).
- [11] Shimizu, N., Semet, M. P., and Allegre, C. J., "Geochemical applications of quantitative ion-microprobe analysis," *Geochimica et Cosmochimica Acta*, **42**, 1321-1334 (1978).
- [12] Stimac, J., Hickmott, D., Abell, R., Larocque, A. C. L., Broxton, D., Gardner, J., Chipera, S., Wolff, J., and Gauerke, E., "Redistribtion of Pb and other volatile trace metals during eruption, devitrification, and vapor-phase crystallization of the Bandelier Tuff, NM.," *Journal of Volcanology and Geothermal Research*, **73**, 245-266 (1996).
- [13] Stimac, J., and Hickmott, D. D., "Trace-element partition coefficients for ilmenite, orthopyroxene, and pyrrhotite in rhyolite determined by micro-PIXE analysis," *Chemical Geology*, **117**, 313-330 (1994).
- [14] Wolery, T. J., "EQ3/6, A Software Package for Geochemical Modeling of Aqueous Systems: Package Overview and Installation Guide (Version 7.0)." *UCRL-MA-110662-PT-I*, Lawrence Livermore National Laboratory, Livermore, CA, (1992).
- [15] Xu, Y., Schwartz, FW, "Lead immobilization by hydroxyapatite in aqueous solutions," *Journal of Contaminant Hydrology*, **15**, 187-206 (1994).

Table 1. Thermal treatment of lead and phosphate compounds. Products identified by X-ray diffraction.

Reactants	Temp (°C)	Time (days)	Products
$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCO}_3$	400	10	$\text{PbO}_{1.37} + \text{Pb}_3\text{O}_4 + \text{Ca}_5(\text{PO}_4)_3\text{OH}$
$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCl}_2$	400	34	$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCl}_2 + \text{minor Pb}_5(\text{PO}_4)_3\text{Cl}$
$\text{Na}_2\text{HPO}_4 + \text{PbCO}_3$	400	34	$\text{Pb}_3\text{O}_4 + \text{NaPbPO}_4 + \text{Na}_2\text{H}_2(\text{PO}_3)_4$
$\text{PbCl}_2 + \text{Na}_2\text{HPO}_4$	400	34	$\text{Pb}_5(\text{PO}_4)_3\text{Cl} + \text{NaCl}$
$\text{PbO} + \text{Ca}_5(\text{PO}_4)_3\text{OH}$	400	24	$\text{PbO}_{1.37} + \text{Pb}_3\text{O}_4 + \text{Ca}_5(\text{PO}_4)_3\text{OH}$
$\text{PbO} + \text{Na}_2\text{HPO}_4$	400	24	$\text{Pb}_3\text{O}_4 + \text{NaPbPO}_4 + \text{Na}_2\text{H}_2(\text{PO}_3)_4$
$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCl}_2 +$ smectite	400	22	$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCl}_2$
$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCl}_2 + \text{Pb-}$ bearing soil	400	22	$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCl}_2$
$\text{PbO} + \text{CaHPO}_4$	400	22	Pb_3O_4
$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCl}_2$	950	1	$\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{Cl})$ (Pb phases volatilized)

Table 2. Aqueous reaction of lead and phosphate compounds. Products identified by X-ray diffraction.

Reactants	Pb/Ca (g/g)	Temp (°C)	Time (days)	Products
$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCl}_2$	2.77	RT	24	$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$
$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCl}_2$	2.77	RT	24	$\text{Pb}_5(\text{PO}_4)_3\text{Cl} + \text{PbCl}_2$
$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCl}_2$	0.35	RT	24	$\text{Pb}_5(\text{PO}_4)_3\text{Cl} + \text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCl}_2$
$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCl}_2$	0.69	RT	24	$\text{Pb}_5(\text{PO}_4)_3\text{Cl} + \text{Ca}_5(\text{PO}_4)_3\text{OH}$
$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCl}_2$	1.39	RT	24	$\text{Pb}_5(\text{PO}_4)_3\text{Cl} + \text{Ca}_5(\text{PO}_4)_3\text{OH}$
$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCl}_2$	2.00	RT	24	$\text{Pb}_5(\text{PO}_4)_3\text{Cl} + \text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCl}_2$
$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCO}_3$	2.77	RT	24	$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCO}_3$
$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCO}_3 + \text{NaCl}$	2.77	RT	24	$\text{PbCO}_3 + \text{NaPb}_4(\text{PO}_4)_3$
$\text{PbO} + \text{Ca}_5(\text{PO}_4)_3\text{OH}$	2.77	RT	24	$\text{PbO} + \text{Ca}_5(\text{PO}_4)_3\text{OH}$
$\text{PbO} + \text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{NaCl}$	2.77	RT	24	$\text{Pb}_7\text{O}_6\text{Cl}_2 + \text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{amorphous} + \text{minor } \text{Pb}_5(\text{PO}_4)_3\text{Cl}$
$\text{PbO} + \text{Ca}_5(\text{PO}_4)_3\text{OH}$	2.77	140	2	$\text{PbO} + \text{Ca}_5(\text{PO}_4)_3\text{OH}$
$\text{PbO} + \text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{NaCl}$	2.77	140	2	$\text{Pb}_7\text{O}_6\text{Cl}_2 + \text{PbO} + \text{minor } \text{Pb}_5(\text{PO}_4)_3(\text{Cl}, \text{OH})$
$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCO}_3$	2.77	140	2	$\text{PbCO}_3 + \text{Pb}_3(\text{CO}_3)_2\text{OH} + \text{minor } \text{Ca}_5(\text{PO}_4)_3\text{OH}$
$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{PbCO}_3 + \text{NaCl}$	2.77	140	2	$\text{PbCO}_3 + \text{Pb}_3(\text{CO}_3)_2\text{OH} + \text{NaPbHPO}_4 + \text{minor } \text{Ca}_5(\text{PO}_4)_3\text{OH}$

Table 3. Chemical analyses (by electron microprobe) of experimental and reference samples of pyromorphite expressed as number of atoms

	Experimental R=0.69	Experimental R=2.77	Standard	Ideal
Na atoms	0.00	0.00	0.00	
Ca atoms	0.18	0.06	0.10	
Pb atoms	23.34	23.40	24.96	25.00
P atoms	13.08	12.89	14.91	15.00
Cl atoms	6.92	7.54	4.74	5.00
XPb	0.99	1.00	1.00	1.00
(Pb+Ca)/P	1.80	1.82	1.68	1.67
Cl/P	0.53	0.59	0.32	0.33

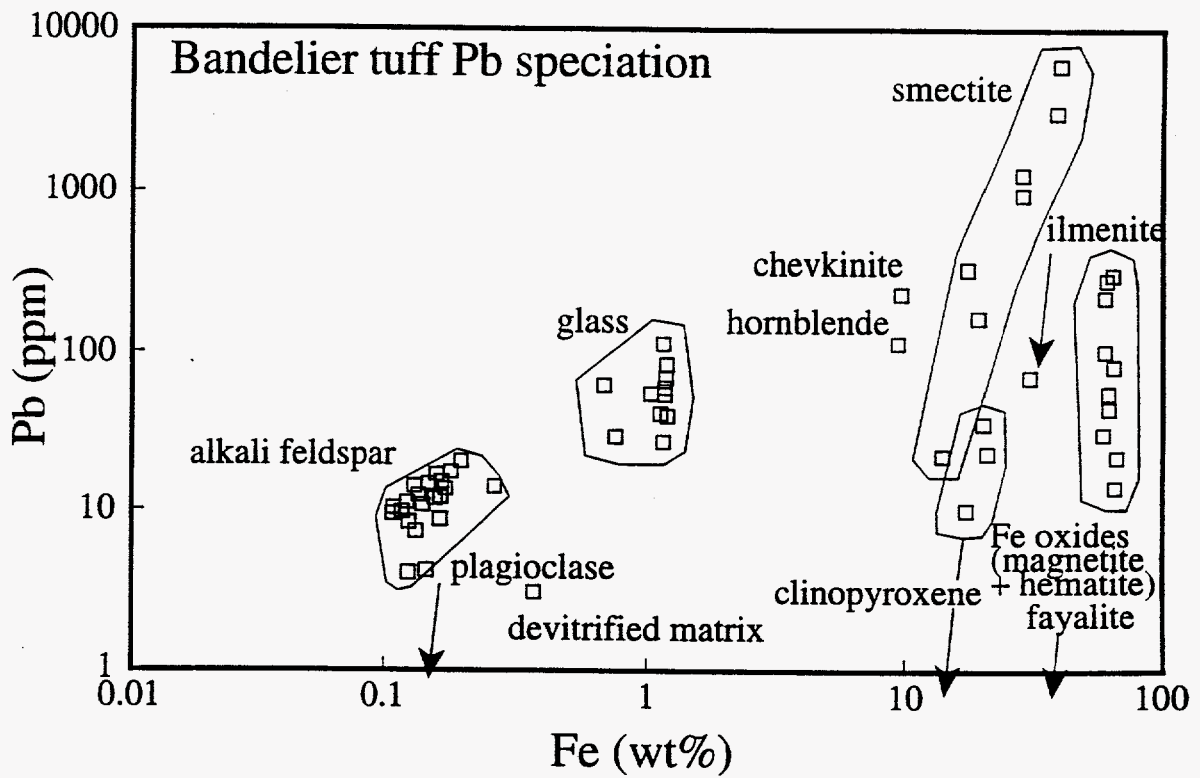


Figure 1. Lead (ppm) determined by PIXE versus Fe (wt.%) determined by electron microprobe analysis for minerals, glass and matrix for the Tshirege Member of the Bandelier tuff. Arrows indicate that some mineral grains have Pb concentrations below PIXE detection limits.

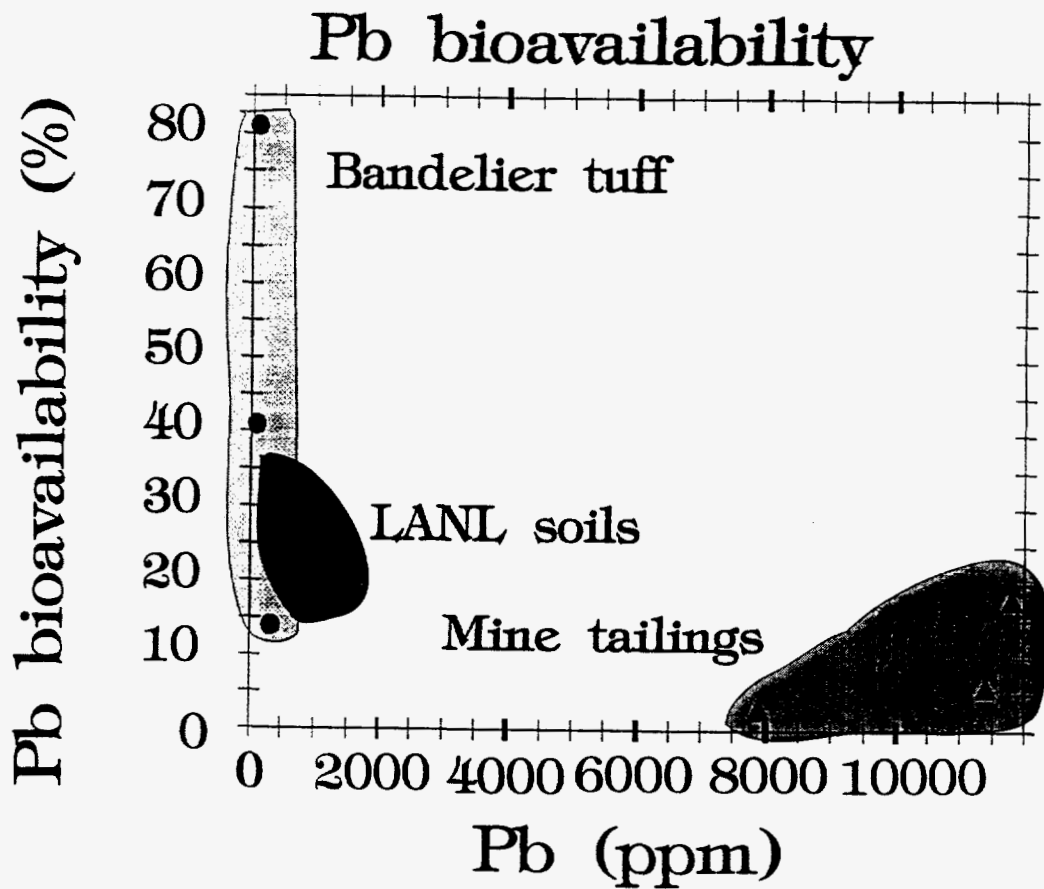


Figure 2. Bulk lead abundance (ppm) versus PTI bioavailability measurement (% bioavailability). Highest bioavailability is in cerussite-bearing Bandelier Tuff. Lowest bioavailability Bandelier Tuff material contains pyromorphite.

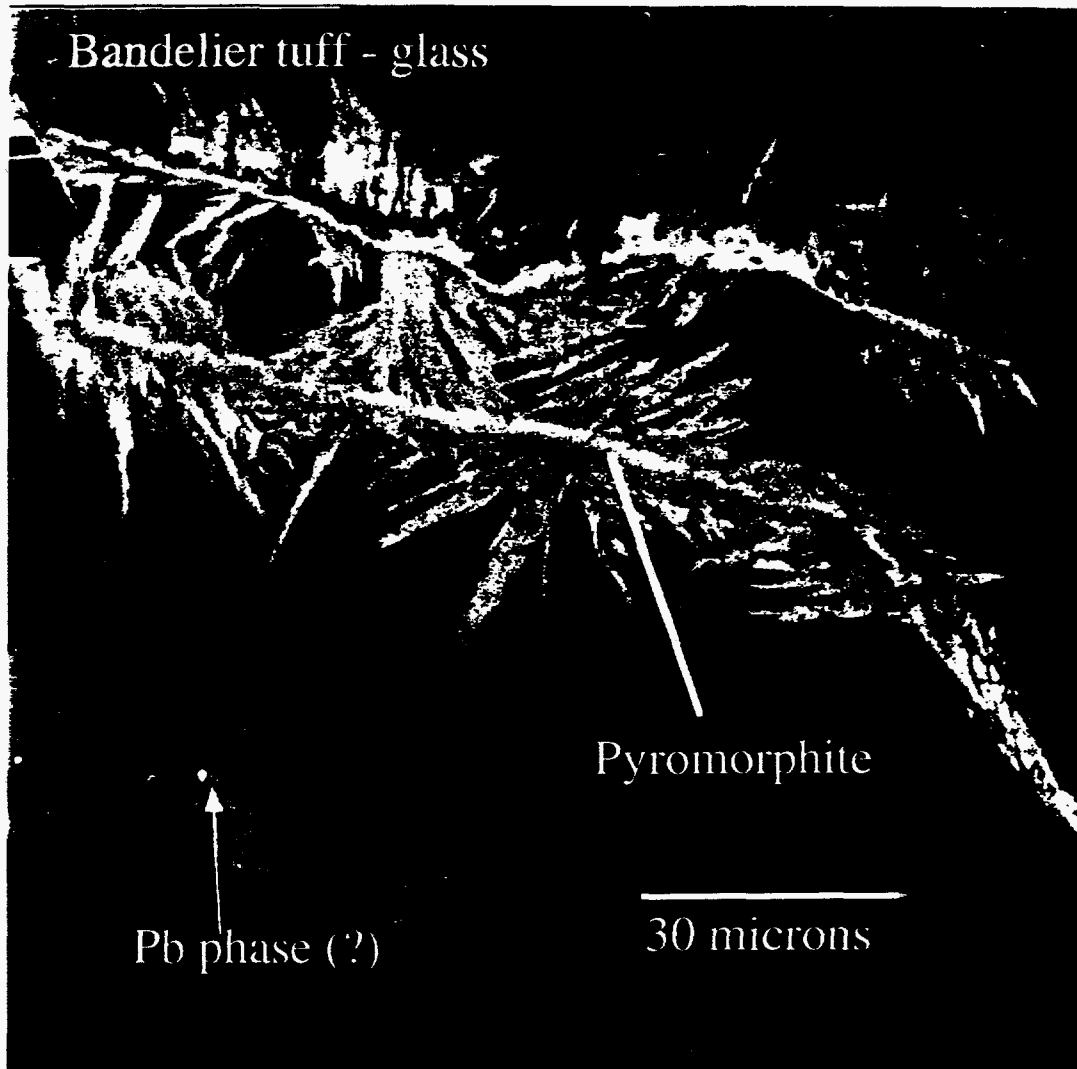


Figure 3. Scanning electron microscope photomicrograph of pyromorphite crystals found in Bandelier Tuff vapor-phase altered sample.

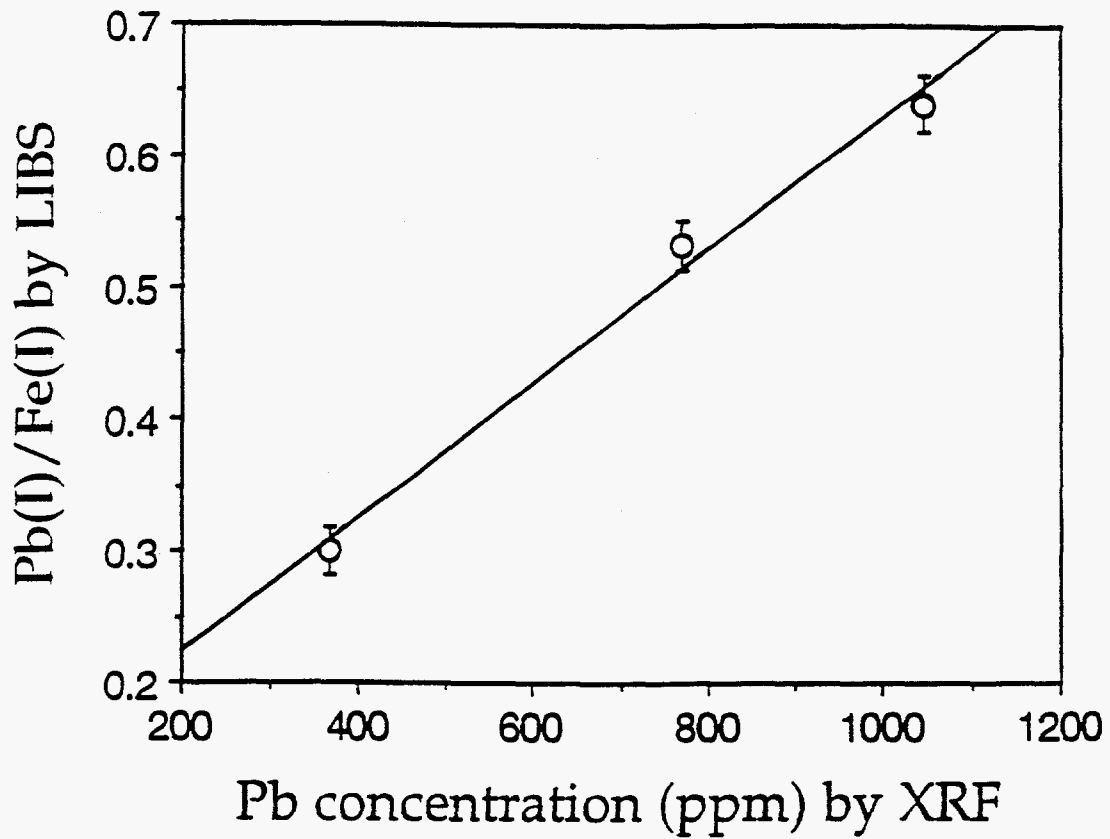


Figure 4. Working curve (Pb determined by LIBS versus Pb determined by XRF) for LIBS analysis of Pb in soils. Note excellent linear correlation between XRF results and LIBS results.



Figure 5. Scanning electron microscope photomicrograph of a pyromorphite crystal grown at room temperature from an aqueous solution containing lead chloride and hydroxyapatite. The image was taken with a backscattering electron detector. The granular material is unreacted hydroxyapatite and lead chloride.

Results of Reaction of 1 mole of PbO and 1 mole of Hydroxyapatite
in 0.01 m NaCl, pH=7, 1 liter of H₂O. Pb⁴⁺ suppressed.

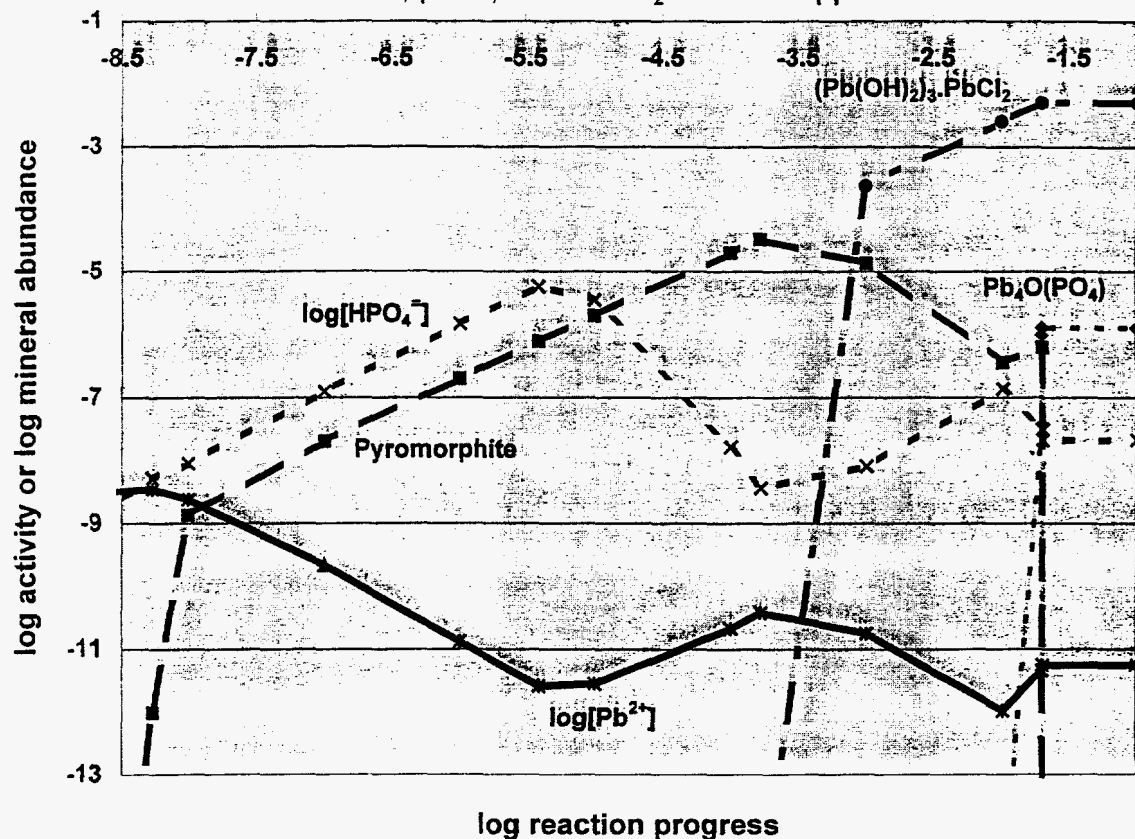


Figure 6. Results of an EQ3/6 calculation of the reaction of hydroxyapatite and litharge (PbO). The calculation simulates reaction at 25 °C with 1 mole each of litharge and hydroxyapatite in one liter of water. The initial pH was 7.0 and the solution contained one molal NaCl. The oxidation of Pb⁺² to Pb⁺⁴ was suppressed because this reaction was not observed in any experiment. At the end of the reaction (equilibrium achieved) about 2% of the litharge had dissolved, an insignificant amount of hydroxyapatite had dissolved, about 0.03 mmol of pyromorphite had precipitated and then redissolved, and about 5 mmol of (Pb(OH)₂)₃PbCl₂ and 0.2 mmol of Pb₄O(PO₄) had precipitated. During the reaction the lead concentration in solution decreased from 10⁻⁶ to 10⁻¹¹ molal.