Aqueous Solubility of Pb at Equilibrium with Hydroxypyromorphite Over a Range of Phosphate Concentrations

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ENVIRONMENTAL SIGNIFICANCE

The solubility, lability and bioavailability of Pb in soils and water can potentially be reduced by treatment with phosphate to produce the highly stable hydroxypyromorphite. Because past research has shown this Pb apatite to display incongruent dissolution behavior in water, we tested the classical thermodynamic model of constant solubility product for hydroxypyromorphite over a range of dissolved phosphate concentrations. Small additions of soluble phosphate reduced dissolved Pb as well as free Pb^{2+} activity. However, the measured ion activity products (IAPs) of the solution phase in equilibrium with crystalline pyromorphite varied widely as a function of pH and soluble phosphate, indicating that Pb solubility and free Pb^{2+} ion activity cannot be predicted accurately using the standard assumption of a constant solubility product.

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Abstract

Hydroxypyromorphite (HPM) is a low-solubility Pb phosphate mineral that has the potential to limit solubility and bioavailability of Pb in soils and water. Because of reported uncertainty regarding the solubility product of this important mineral, we re-evaluated the solubility of Pb and activity of the free Pb^{2+} ion in aqueous suspensions of microcrystalline HPM equilibrated up to 30 days over a wide range of added soluble phosphate. A small addition of phosphate (0.1 mM) reduced Pb solubility as measured by ICP-OES, but greater phosphate additions (up to 50 mM) had no further effect in lowering HPM solubility. However, free Pb^{2+} ion activity measured by ion-selective electrode progressively decreased from about $10^{-6.5}$ with no added phosphate to 10^{-9} as soluble phosphate was increased. The effect of soluble phosphate in lowering Pb^{2+} activity is attributed to inhibited dissolution of HPM as well as increased Pb^{2+}-phosphate ion pair formation in solution at higher solution concentrations of phosphate. Measurement of the ion activity products (IAP) of the solutions at equilibrium with HPM gave highly variable IAP values that were sensitive to pH and were generally not consistent with the reported solubility product of this mineral. The high variability of the IAPs for solutions with variable pH and phosphate concentrations indicates that dissolution-

precipitation reactions of HPM are not described by a constant solubility product at equilibrium, possibly because of the incongruent dissolution behavior of this mineral at near-neutral pH.

Keywords: Solubility product, incongruent dissolution, pyromorphite, Pb^{2+} ion activity

Introduction

Pyromorphites are low-solubility Pb phosphate minerals of the apatite-group that may limit Pb solubility in contaminated soils and water when significant concentrations of soluble phosphate are present.[1,2] For example, hydroxypyromorphite (HPM), $Pb_5(PO_4)_3OH$, is commonly formed under natural conditions in soils,[3] and is also reported to be involved in limiting Pb solubility in phosphate-treated drinking water.[4,5] Although chloropyromorphite, $Pb_5(PO_4)_3Cl$, is considered to be more stable than HPM in natural waters containing chloride based on its lower calculated solubility, the former mineral is not generally detected in phosphate-dosed "hard" water in lead pipes. In fact, mixed Ca-Pb apatite minerals tend to be formed rather than pure Pb mineral phases in these natural waters.[2,6] Solid solutions of Pb with Ca could theoretically limit Pb solubility to lower levels than pure $Pb_5(PO_4)_3OH$.[7]

HPM has a dissolution reaction which can be described as follows :

$$Pb_5(PO_4)_3OH \ (s) + 7 \ H^+ \ \rightleftharpoons \ 5 \ Pb^{2+} + 3 \ H_2PO_4^- + H_2O \qquad \log K_{SP} = -4.14 \qquad (1)$$

Therefore, the equation for the solubility product, K_{SP} , of HPM is expressed as :

$$\log K_{SP} = 5 \log (Pb^{2+}) + 3.0 \log (H_2PO_4^-) + 7 \ pH \ = \ -4.14 \qquad (2)$$

The solubility and dissolution kinetics of this mineral could be of great importance in limiting human exposure to Pb. The equilibrium constant given in equation (1) originates from the early research of Nriagu,[8,9] and has persisted in the thermodynamic database of a number of computer programs used to calculate speciation of metal ions in water such as

Visual MINTEQ[10] despite the fact that it was measured at high ionic

strength and chloride concentration and extremely low pH (< 3), and therefore might not

be expected to be valid under natural conditions of soils or water. The above reaction is

written with $H_2PO_4{}^-$ for convenience in calculations because it is the predominant form of

phosphate in the environmentally relevant pH range of 3 to 7.

Despite their potential importance to human health and the environment, the solubilities and

dissolution characteristics of Pb phosphates, and more specifically the pyromorphite minerals,

remain uncertain. Solubilities of pyromorphites and reports of congruent dissolution behavior have

been based on behavior in solution at very low pH (2-3), conditions of little relevance in most soil

and water environments.[8,11,12] Furthermore, chloropyromorphite, $Pb_5(PO_4)_3Cl$, has been frequently

reported to have a solubility product several orders of magnitude greater than the value published in

various standard compilations of mineral stabilities and employed in chemical speciation

calculations.[12-14] These experimental discrepancies in measured solubility products have led some

researchers to conclude that the widely accepted assumption of invariant solubility products for

minerals of the apatite group, including pyromorphite, is invalid, and that a surface coating

compositionally different from the ideal mineral phase forms and controls solubility.[15,16] A recent

study of HPM precipitation and solubility over a range of pH at high dissolved phosphate is

consistent with this hypothesis,[17] as is an earlier study of Pb phosphates revealing discrepancies

between ion activity products (IAPs) in solution and the actual minerals precipitated from solution.[18]

Measuring the true ion activity products (IAPs) of solutions in equilibrium with pyromorphites

(and other relatively insoluble Pb minerals) under environmentally realistic conditions (e.g., pH 5-8)

where Pb solubility and Pb^{2+} ion activities are expected to be very low is difficult for a number of

reasons. First, because few methods are available to directly measure or estimate the activity of the

free Pb^{2+} cation in solution, IAPs are typically estimated by calculating the Pb^{2+} activity from total

dissolved Pb after estimating the fraction of dissolved Pb in soluble complexes with phosphate,

bicarbonate, hydroxide and other ligands that might complex or pair with the metal cation. Incorrect

estimates of the formation constants of one or more of these ion pairs or complexes would lead to

erroneous values for ion activity products of solutions. In addition, very fine colloidal forms of Pb that

bypass filtration could be erroneously included in the measure of dissolved Pb by methods such as

ICP-MS and ICP-OES, leading to overestimation of the true dissolved concentration. The filtration

procedure itself further introduces uncertainty about true Pb solubility because Pb^{2+} ions are

particularly prone to retention on filter membranes, a process that seems to relate to cation

exchange properties of the membrane materials.[19,20] An additional difficulty with the definition of

solubility products for mineral structures of the apatite group is the tendency of these structures to

dissolve incongruently as a result of the exchange of surface metal cations (Ca^{2+} and Pb^{2+}) into

solution by H^+ ions.[21] As a consequence, the measured IAPs of solutions in equilibrium with Pb

phosphates are commonly not in accordance with the reported solubility products of the mineral

phases actually present,[18] and the assumption of invariant solubility products for the apatite mineral

structural group including pyromorphites may be invalid.[15]

A final likely source of apparent solubility product variability of pyromorphites is the inability

to accurately estimate concentrations of the various ion pairs formed with Pb^{2+} in solution, a difficulty

caused in large part by the very low solubility of Pb phosphate in water over the pH range of

environmental relevance. Consequently, there are no published direct measurements of the stability

constants of dissolved $PbHPO_4^0$ and $PbH_2PO_4^+$ ion pairs, species that could be very important in

controlling Pb solubility in aqueous solutions with large phosphate/Pb mole ratios. Instead, these

constants have been estimated in databases of chemical equilibrium programs by analogy with the

measured stabilities of other presumeably analogous metal-phosphate ion pairs.[22] Although Nriagu [8]

reported log formation constants of 1.50 and 3.10 for $PbH_2PO_4^+$ and $PbHPO_4^0$, respectively, these

estimates were calculated from solutions equilibrated in very acidic solutions (pH 2-4) that would be

unfavorable to ion pair formation. Nriagu [8] considered the calculated constants to be reasonable given their similarity to earlier estimates of phosphate ion pair stabilities with divalent metals such as Ca^{2+} (log formation constants for $CaH_2PO_4^+$ and $CaHPO_4^0$ are reported to be 1.40 and 2.74, respectively). However, this analogy must be questioned given later evidence that Pb^{2+} bonding with organophosphates is stronger than that of alkaline earth metals.[23] Saha et al.[24] determined the stability constants of metal-HPO_4 ion pairs (K_{MHPO4}) by potentiometric titration, finding metals such as Cu^{2+} and Cd^{2+} to have K_{MHPO4} constants at least one log unit greater than Ca^{2+}. Although they did not report a stability constant for $PbHPO_4^0$, it seems likely that K_{PbHPO4} would be at least as large as the stability constant for $CdHPO_4^0$.

Pb^{2+}-nitrate ion pair formation constants in databases of speciation programs, obtained from quite old studies, indicate that Pb^{2+} complexes more strongly than most other divalent metal ions with nitrate.[25,26] More recent spectroscopic studies have confirmed that Pb^{2+} has a stronger tendency to form inner-sphere ion pairs with NO_3^- than Ca^{2+} or Mg^{2+}.[27,28] The fact that the formation constants for $PbNO_3^+$ and $Pb(NO_3)_2^0$ are reported to be nearly 6 log units greater than those for the analogous Ca-nitrate ion pairs [25] means that other more strongly basic oxyanions such as phosphate are also likely to form ion pairs with Pb^{2+} much more strongly than with Ca^{2+}, and that the commonly assumed stability constants for Pb-phosphate ion pairs have underestimated Pb^{2+} complexation with this anion.

The solubilities of Pb measured in high-phosphate solutions at pH 6-8 are greater than predicted from the reported solubility product of HPM,[17] suggesting that the contribution of $PbH_2PO_4^+$ and particularly $PbHPO_4^0$ ion pairs to the solubility of Pb has been underestimated in chemical speciation programs. Miller found that the addition of phosphate to water at pH 9.0 beyond 1.0 mg L^{-1} increased Pb solubility, reversing the trend for reduced Pb solubility by dosing drinking water with phosphate.[29] In addition, as greater phosphate concentrations (3 and 5 mg L^{-1}) were introduced into

the water, the dissolved Pb increasingly exceeded that expected from the solubility product of HPM. Zhao et al.[5] concluded that dosing drinking water with excess phosphate lowers dissolved Pb concentrations but may increase concentrations of particulate Pb by increasing Pb phosphate particle charge and inhibiting aggregation. These variable effects of phosphate addition on measured soluble Pb levels are of concern to human health because phosphate addition to municipal water is the primary treatment method used to reduce human exposure to Pb in drinking water.

The uncertainties that exist about factors involved in limiting the aqueous solubility of Pb by HPM precipitation need to be better understood. Therefore, the present investigation of HPM solubility was designed to test whether the widely employed model of constant ion activity product (IAP) is valid for this mineral over a range of phosphate concentrations in the solution phase in the pH range of 6-7.

Materials and methods

Hydroxypyromorphite (HPM) was prepared according to a method modified from Zhu et al.[21] Specifically, 4.14 g of $Pb(NO_3)_2$ and 0.9905 g of $(NH_4)_2HPO_4$ salt (5/3 mole ratio of Pb to P) were dissolved in 100 ml of 0.62 M NH_4 acetate (pH 4.8). The white suspension formed immediately was adjusted to pH to 7.5 with concentrated NH_4OH and stirred for 10 minutes. The suspension was placed in a pressure bomb at 100° C for 72 hours, then washed 4 times in deionized water to remove salts, and finally dried to a powder at $70^\circ C$. The mineral product consisted of micron–sized columnar crystallites as shown by optical microscopy (Figure 1A), and confirmed by XRD analysis using a Brucker D8 Advance diffractometer with Cu Kα radiation (λ = 1.54060 Å) to be crystalline HPM (Figure 1B). This mineral product was used for all subsequent studies of Pb phosphate dissolution in aqueous solutions containing a range of phosphate concentrations.

Stock aqueous solutions of 0.50 M Na_2HPO_4 and 0.50 M $NaNO_3$ were prepared from reagent

grade salts. The 0.50 M Na_2HPO_4 stock was adjusted to pH 7.00 using concentrated NaOH, and a

0.10 M Na_2HPO_4 solution was prepared from this stock. Quantities of the 0.50 M $NaNO_3$ and 0.10 M

Na_2HPO_4 were pipetted into 125 ml. Erlenmeyer flasks containing 0.100 g of the synthetic OH-
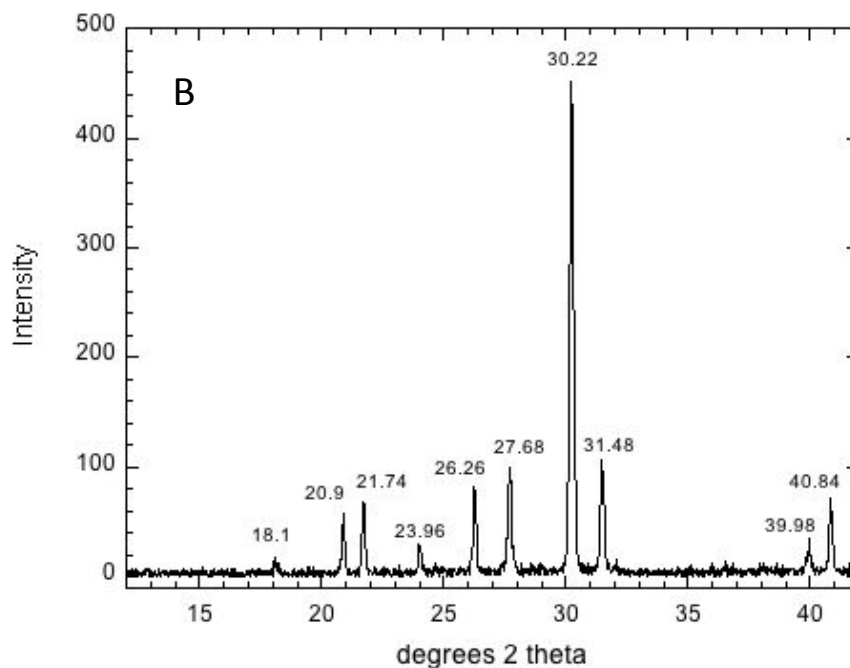
Figure 1: Optical microscopic image (A) and XRD pattern (B) of synthetic hydroxypyromorphite.

pyromorphite and diluted to 100 ml. total volume with deionized water to create 3 replicates each at

phosphate concentrations of 0, 0.1, 1.0, 10 and 50 mM, all in a electrolyte medium of 0.05 M $NaNO_3$.

The flasks containing these suspensions were shaken continuously on an orbital shaker at 22°C,

with pH measured with a Thermo Scientific combination glass electrode and Pb activity measured

using a Cole Parmer solid-state ion-selective combination electrode at 8,15 and 30 days reaction

time. The pH electrode was calibrated using commercial pH 4.00 and 7.00 buffers, while the Pb

electrode was calibrated using six Pb^{2+} activity buffers (with calculated free Pb^{2+} activities varying

from $10^{-4.04}$ to $10^{-9.43}$) prepared from oxalate solutions of different concentrations with Pb in 0.01 M

Na acetate buffer at pH 5.0. The free Pb^{2+} ion activities were calculated for these solutions using

Visual MINTEQ and corrected stability constants for Pb-oxalate 1:1 and 1:2 complexes taken from

Xiong et al.[30] The relationship between millivolt (mV) response of the Pb electrode and calculated -

log Pb^{2+} ion activity (pPb) varied somewhat from day to day, with a representative electrode

response averaged over a week being:

$$pPb = -0.207 (\pm 0.134) - 0.0356 (\pm 0.00028) \, mV \qquad\qquad R = 0.994 \qquad (3)$$

As shown by equation (3), the slope of the millivolt response is quite stable over several days, but

the absolute mV reading as reflected by the variability in the intercept of the equation can differ from

day to day. Therefore, calibration of the electrode was done immediately before and after sample

measurements.

At each of the sampling times up to 30 days equilibration, replicate (n=3) 10 ml. samples of

the supernatants were taken, passed through Whatman #42 paper filters (pore size 2.5 μm),

stabilized with 0.1 ml. concentrated HNO_3 and analyzed for dissolved Pb by ICP-OES (Spectro

Arcos) at 220.35 nm. Although smaller pore size membrane filters were also tested for their ability to

remove all Pb phosphate particles from the solution phases, preliminary experiments using 0.2 μm

nitrocellulose membrane filters showed high variability in replicated measurements of dissolved Pb

in filtrates at all dissolved phosphate levels tested. Because this result suggested a contamination

issue with the nitrocellulose filters or filter holders, a systematic test of Pb mineral filtration by nylon

0.2 μm membrane filters was undertaken. It was found during the filtration of Pb sulfate suspensions

that 90% or more of dissolved Pb in the first 10 ml passed through the filter was retained by the

membrane filter at pH 4-5, and this removal efficiency increased to nearly 100% at higher pH (6-8).

Retention of Pb decreased markedly as additional 10 ml volumes of the same solutions were passed

through the filters, indicating saturation of the adsorptive capacity of the filter membranes, with little

or no additional Pb retention once 30 ml total volume passed through the filters. Thus, the 0.2 μm

membrane filters were determined to be unsatisfactory for Pb filtration in the present experiment,

producing non-reproducible results in measuring soluble Pb of filtered Pb mineral suspensions.

Conversely, filtrates collected from Whatman #42 filters showed very good reproducibility in replicate

samples at all phosphate concentrations except the lowest (no added phosphate). In fact, measured

Pb approached the detection limit of the ICP-OES instrument (4 μg L^{-1}) when phosphate

concentrations were adjusted to 0.1 mM and greater. Nevertheless, a statistically significant

correlation (R = 0.891) between measured Pb and P in the filtrates collected from the Pb phosphate

suspensions with zero added phosphate suggests that some of the smaller pyromorphite particles

may have passed through the Whatman filters at the lowest phosphate level tested. However, with

0.1 mM phosphate added, filtration using Whatman #42 paper appeared to be effective as indicated

by reproducibly low filtrate Pb concentrations and the fact that shaking time (8,15, 30 days) had no

measurable effect on dissolved Pb or P. Also, increasing or decreasing the quantity of HPM in

suspensions had no discernible effect in changing the measured Pb or P in filtrates at the 0.1 mM

phosphate level.

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The logarithm of the ion activity product (IAP) for OH-pyromorphite from the mineral dissolution

reaction (equation (1)) is given by the expression :

$$\log IAP = 5 \log (Pb^{2+}) + 3 \log (H_2PO_4^-) + 7 \text{ pH} \tag{4}$$

and Is reported to be equal to -4.14 for a saturated solution at equilibrium with HPM.[8,13,25] In order to

calculate the log IAP for each solution equilibrated with HPM, we first measured the solution pH

directly using a glass electrode. The $H_2PO_4^-$ activity was calculated from the ICP-measured total

dissolved phosphate using the chemical speciation simulation program Visual MINTEQ [10] to correct

for pH-dependent speciation and ionic strength effects. Finally, the free Pb^{2+} ion activity in

equilibrated aqueous suspensions of HPM was calculated by 2 methods:

1. using the Pb ion-selective electrode to measure free Pb^2

2. using Visual MINTEQ to speciate the total dissolved Pb in solution measured by ICP

The Visual MINTEQ program was additionally used to predict dissolved Pb as a function of soluble

phosphate based on the solubility product of HPM in the database and the inputs of measured pH

and dissolved phosphate. It is worth noting that the stability constants for Pb phosphate minerals

and ion pairs of Pb with anions such as phosphate and nitrate imbedded in the thermodynamic

databases of Visual MINTEQ, MINEQL+, and other commonly used chemical speciation programs

are derived in most cases from quite old experimental studies,[8,25] many of which have not been

verified by more recent research.

Visual MINTEQ predicts that the presence of dissolved carbonate species as a result of

equilibration of the HPM suspensions with atmospheric CO_2 at 400 ppmv would have only a minor

effect on Pb speciation and solubility. Specifically, in the absence of atmospheric CO_2, the

predominant species of dissolved Pb at equilibrium with HPM at pH 6.7 in 0.1 mM phosphate with

0.05 M $NaNO_3$ are predicted to be free Pb^{2+}(69.9%), $PbNO_3^+$ (23.3%), $PbOH^+$ (4.90%) and $PbHPO_4^0$

(0.54 %). Assuming equilibrium of the same system with 400 ppmv CO_2 only slightly alters soluble

Pb speciation to 68.7 % free Pb^{2+}, 22.9% $PbNO_3^+$, 4.82% $PbOH^+$ and 0.53% $PbHPO_4^0$.

Furthermore, Visual MINTEQ predicts that equilibration with CO_2 at pH 6.7 would only slightly raise

Pb solubility from 8.40 x 10^{-8} to 8.52 x 10^{-8}. Thus, the aqueous suspensions investigated in this study

were allowed to equilibrate with atmospheric CO_2.

To confirm accuracy and reproducibility of ICP-OES measurement of dissolved Pb at low Pb

concentrations over the wide range of Na phosphate concentrations present in the experimental

solutions, Pb standards at 100 µg L^{-1} were prepared from a certified $Pb(NO_3)_2$ stock solution. These

were acidified with 2.0 ml ultrapure concentrated HNO_3 added per liter. The solutions were spiked

with appropriate quantities of 0.10 M Na_2HPO_4 solution to create triplicate 100 µg L^{-1} Pb standards

ranging from 0 to 10 mM Na phosphate. The final pH of all solutions were measured and found to be

1.65 or lower. The Pb standard solutions containing 0, 0.10 mM , 1.0 mM , and 10 mM Na_2HPO_4 ,

were determined by ICP-OES, to contain 113±6 , 110±0, 103±6 , and 97±6 µg Pb L^{-1}, respectively,

indicating good accuracy and precision with only a small apparent matrix effect of relatively high

concentrations of phosphate and Na on Pb measurement by ICP-OES.

Results and Discussion

The measured pH, free Pb^{2+} activities, and solubilities of Pb and phosphate in filtered solutions

after equilibration of the Na phosphate solutions with HPM for 8,15 and 30 days are

summarized in Table 1. These results are further analyzed and discussed in the following

sections.

Table 1: Measured pH, dissolved phosphate, dissolved Pb and free Pb^{2+} ion activity of solutions
equilibrated with OH-pyromorphite for 8,15 and 30 days.

Solution property	Added PO_4 (mM)	Equilibration Time (days)		
		8	15	30

pH	0.0	5.91 ±0.27	5.86 ±0.11	6.04 ±0.08
	0.1	6.69 ±0.03	6.71 ±0.09	6.77 ±0.07
	1.0	6.49 ±0.07	5.67 ±0.05	5.86 ±0.04
	10	6.80 ±0.11	5.70 ±0.06	5.80 ±0.03
	50	6.85 ±0.01	6.15 ±0.01	6.03 ±0.01
Dissolved PO_4 (µM)	0.0	18.4 ±1.2	25.0 ±9.0	20.4 ±2.2
	0.1	135 ±4.7	135 ±2.3	143 ±6.1
	1.0	1288 ±61.3	1288 ±60.1	1343 ±76.1
	10	12404 ±44.2	12375 ±172	12476 ±365
	50	55760 ±293	55246 ±157	52286 ±1383
Dissolved Pb (µM)	0.0	2.58 ±0.26	2.28 ±0.16	1.44 ±1.03
	0.1	0.18 ±0.06	0.048 ±0.00	0.121 ±0.034
	1.0	0.17 ±0.10	0.20 ±0.13	0.05 ±0.02
	10	0.23 ±0.25	0.11 ±0.10	0.13 ± 0.10
	50	0.16 ±0.05	0.15 ±0.01	0.11 ± 0.06
- log (Pb^{2+})	0.0	6.61 ±0.09	6.23 ±0.09	6.48 ±0.22
	0.1	6.98 ±0.04	6.91 ±0.06	7.72 ±0.17
	1.0	8.66 ±0.04	8.59 ±0.06	8.60 ±0.14
	10	9.34 ±0.01	9.18 ±0.01	9.17 ±0.04
	50	9.3 ±0.04	9.05 ±0.03	9.13 ±0.07

Dissolved Pb at Equilibrium with OH-pyromorphite

Equilibration of the crystalline HPM in aqueous solutions containing a wide range of dissolved

phosphate (from 0.01 to 50 mM) had the effect of reducing dissolved Pb at higher phosphate levels,

as summarized in Table S1 and displayed in Figure 2. The relatively large variability in measured

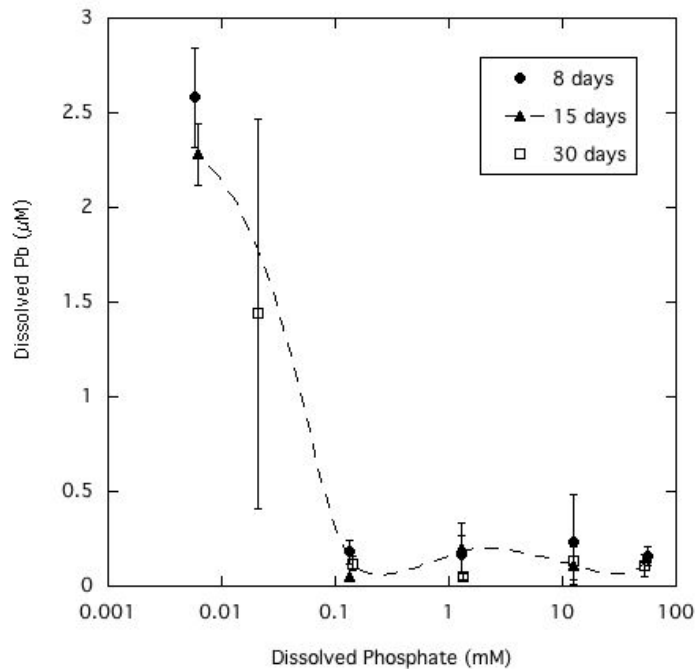dissolved Pb observed here is commonly seen in equilibrated aqueous media where Pb

Figure 2: Dissolved Pb concentration as a function of soluble phosphate in aqueous HPM suspensions equilibrated from 8 to 30 days.

precipitation is limiting solubility.[6,31] A possible reason for the variability which is seen only at the

lowest dissolved phosphate concentrations, is that the addition of phosphate may have changed the

surface charge of HPM by anion adsorption.[5] If the HPM suspension without added phosphate was

in a more dispersed colloidal state due to surface charge, some of the smaller HPM crystallites may

have passed through the paper filters and caused poorer reproducibility and an overestimate of

dissolved Pb. A recent study has shown that the aggregation of ultrafine Pb phosphate particles is

an important factor in allowing filtration of water to trap particles with much smaller diameters than

the nominal filter pore size.[32]

Equilibration times ranging from 8 to 30 days did not significantly affect average dissolved Pb,

indicating that the microcrystalline mineral had reached steady state with the solution phase. The

lowered dissolved Pb at higher phosphate is qualitatively consistent with expectation from the principle of mass action, as higher phosphate in solution inhibits dissolution of the Pb phosphate mineral phase. However, as Figure 2 shows, increasing dissolved phosphate above 0.1 mM (about 3 mg P L^{-1}) had no significant effect in reducing Pb solubility beyond the initial decrease. The pH of the aqueous suspensions of HPM were generally in the range of 5.7 to 6.8 (Table S1), approaching 7.0 at the higher phosphate levels as the added Na_2HPO_4 added alkalinity to the solutions. Longer reaction times (15 and 30 days) with sample agitation caused the pH in most cases to decrease to about 5.7-6.0 as slow equilibration with CO_2 in the atmosphere neutralized excess alkalinity.

The mole ratio of dissolved Pb to phosphate was determined for the equilibrated OH-pyromorphite suspensions without added phosphate in aqueous $NaNO_3$ at 8,15 and 30 days equilibration and found to average 0.53 ± 0.26 , 0.28 ± 0.25 and 0.25 ± 0.36 , respectively, well below the ratio of 1.67 that would be expected for stoichiometric dissolution. There was no statistically significant effect of equilibration time on the average Pb/P ratio in solution, and the overall mean value of 0.355 ± 0.29 indicates a high degree of non-stoichiometric mineral dissolution favoring release of phosphate over Pb to solution. Zhu et al.[21] also observed the Pb/P mole ratio to be well below the stoichiometric value of 1.67 when HPM was equilibrated in pure water at pH 5.6. Incongruent dissolution is a well-known characteristic of pyromorphite and other minerals of the apatite group.[15] The systems studied here had pH close to neutral, but dissolution under more strongly acidic conditions has been shown to favor release of Pb relative to phosphate , with mole ratios indicative of stoichiometric dissolution at least in the early stages of mineral dissolution.[11]

Pb²⁺ Ion Activity at Equilibrium with OH-pyromorphite

The activity of free Pb^{2+} ions in aqueous solutions at equilibrium with HPM as measured by ion

selective electrode (ISE) was lowered with increasing dissolved phosphate concentrations, as shown

in Table 1 and Figure 3. As solution phosphate was increased from about 0.02 mM to more than 50

mM, free Pb^{2+} activity decreased progressively by approximately 2.7 log units. This observation is

qualitatively consistent with a shift in the solid-solution equilibrium in favor of greater precipitation of

Pb at higher dissolved phosphate activity. However, as shown in Figure 4, dissolved Pb did not

decrease in response to added phosphate to the extent that free Pb^{2+} activity did, reaching a near-

constant solubility at 0.1 mM dissolved phosphate and higher. At high dissolved phosphate, free

Pb^{2+} activity was more than 2 log units lower than dissolved Pb. a result that may be explained by

increased ion-pair formation between Pb^{2+} and the phosphate anion. This large difference between

free Pb^{2+} activity and Pb solubility was not predicted by the Visual MINTEQ program as shown in

Figure 4. This simulation predicted the difference between Pb activity and solubility to be much

smaller than was actually measured and virtually unaffected by dissolved phosphate concentrations.

As discussed below, underestimation of the stability constants of soluble Pb-orthophosphate ion

pairs could account for this discrepancy between model and measurement.

The dominant species of Pb expected to be in solution over the range of phosphate tested in the

experiment are shown in Figure 5 based on predictions of the Visual MINTEQ chemical equilibrium

model. At soluble phosphate concentrations of 1 mM and lower, Pb-phosphate ion pairs are

predicted to be minor soluble species, as the free Pb^{2+} ion (> 60%) and $PbNO_3^+$ ion pair (<30%) are

the prevalent species. The model indicates that very high phosphate concentrations (> 1 mM) result

in the $PbHPO_4^0$ ion pair becoming the dominant soluble form of Pb. The Pb-phosphate ion pairing

favored at high phosphate levels can at least qualitatively explains the large difference between
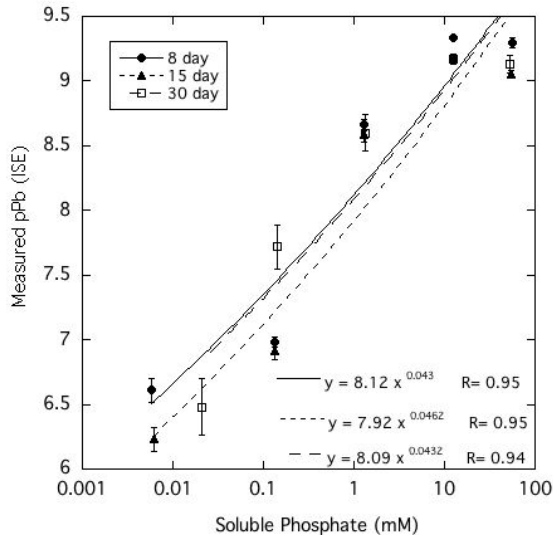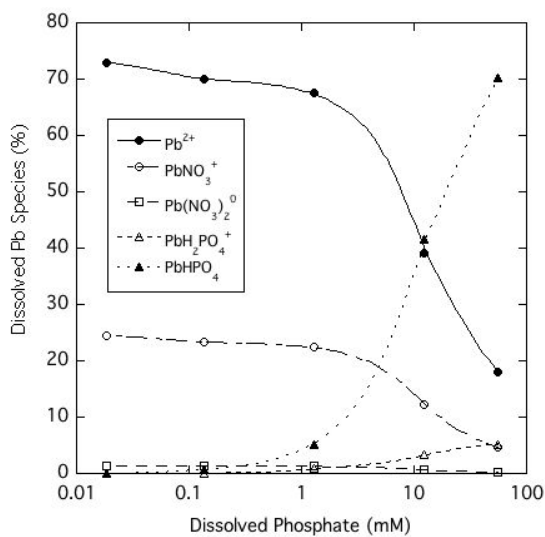
dissolved Pb and free Pb^{2+} concentrations.

Figure 3: Pb^{2+} activity measured by ion-selective electrode as a function of soluble phosphate in aqueous HPM suspensions equilibrated from 8 to 30 days.

In order to determine whether the Pb speciation in solution predicted by Visual MINTEQ quantitatively accounts for the large effect of high dissolved phosphate in lowering free Pb^{2+} activity as measured by the ISE, Pb^{2+} activity was estimated separately by entering the measured dissolved Pb, phosphate, nitrate, and pH into the Visual MINTEQ speciation program. Figure 6 compares these two independent determinations of Pb^{2+} ion activity, revealing a large discrepancy at the highest phosphate levels, with the ISE-determined Pb^{2+} activity being smaller than the Visual MINTEQ-calculated estimates by as much as 2 orders of magnitude. One reasonable explanation for the discrepancy in these estimates of free Pb^{2+} (Figure 6), which becomes greater as soluble phosphate increases, is that the stability constants of the Pb-phosphate ion pairs in the database of the Visual MINTEQ speciation program underestimate the true values. Although no direct measurement of formation constants for Pb-orthophosphate ion pairs have been reported to the

knowledge of the authors, research has shown that Pb^{2+} ions bond selectively and strongly with

phosphate groups of phosphate monoesters and nucleic acids.[23,33,34] It therefore is reasonable to

conclude that Pb^{2+} bonds much more strongly than alkaline earth metal ions with orthophosphate.
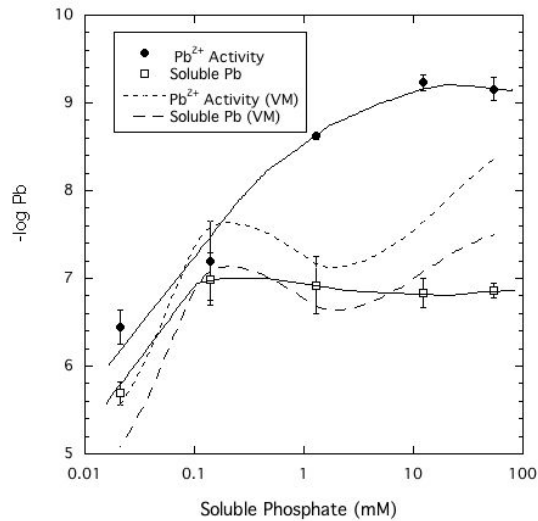
Figure 4 : Pb^{2+} ion activity and soluble Pb measured and modeled (by Visual MINTEQ, VM) as a function of soluble phosphate at equilibrium with crystalline HPM.

Figure 5: Estimated distribution of dissolved Pb species as a function of soluble phosphate for aqueous HPM suspensions (calculated using Visual MINTEQ).
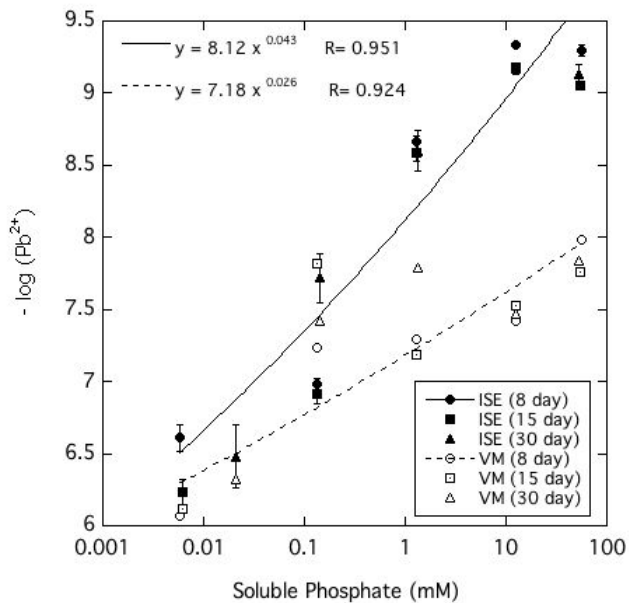
Figure 6:   Comparison of Pb^{2+} activities measured by ion-selective electrode (ISE) and calculated using Visual MINTEQ (VM) as a function of soluble phosphate in aqueous HPM suspensions equilibrated from 8 to 30 days.

Ion Activity Products (IAPs) of Solution Phases at Equilibrium with OH-pyromorphite

The ion activity products of HPM, given in Equation (4), were calculated by two approaches based on direct and indirect estimation of the free Pb^{2+} ion activities as described in the methods section. These are plotted in Figure 7 as a function of solution pH for all of the equilibration times and phosphate concentrations tested. Despite the considerable variability of estimated log IAP values over the range of pH, phosphate concentrations and reaction times, it is clear from Figure 7 that the IAPs estimated using the ISE to determine Pb^{2+} ion activity were generally lower than those estimated using an indirect determination of Pb^{2+} ion activity. This suggests that the indirect determination using Visual MINTEQ to speciate dissolved Pb may have underestimated ion pair formation of Pb with phosphate as explained earlier, and therefore overestimated free Pb^{2+} activity.

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Both estimates of log IAP trended toward less negative values at higher pH, implying a

shift in mineral solubility depending on pH. Most of the measured log IAPs deviated by several log

units from the widely reported K_{SP} of -4.14. The results strongly suggest that crystalline HPM does

not display reversible dissolution-precipitation behavior expected for minerals that dissolve

congruently. Furthermore, the assumption that the solubility behavior of this mineral can be

described by a single invariant solubility product applicable over a range of solution conditions

including variable pH and dissolved phosphate concentrations must be questioned. Nevertheless, as

little as 3 mg L^{-1} of P in the form of soluble phosphate added to aqueous solutions equilibrated with

excess HPM effectively reduced free Pb^{2+} ion activity and lowered dissolved Pb below 60 µg L^{-1}.
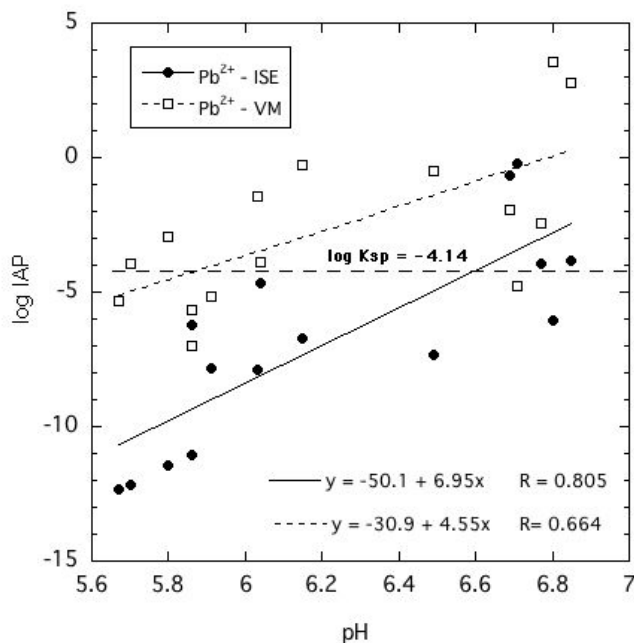

Figure 7:   Comparison of ion activity products (IAP) of all solutions in equilibrium with HPM suspensions over a wide range of soluble phosphate concentrations, calculated from ion-selective electrode (ISE) measurement of Pb^{2+} activities, pH and dissolved phosphate.

Conclusions

The solubility of Pb in aqueous solutions equilibrated with microcrystalline HPM was decreased by the addition of 0.1 mM phosphate. Higher added phosphate concentrations up to 50 mM had no significant further effect in lowering solubility, but free Pb^{2+} ion activity decreased from about $10^{-6.5}$ to 10^{-9} as soluble phosphate was increased in this range. The lowered Pb^{2+} activity is accounted for by inhibited dissolution of HPM and increased Pb^{2+}-phosphate ion pair formation in solution at higher solution concentrations of phosphate. The much greater Pb solubilities compared to free Pb^{2+} ion concentrations at high phosphate concentrations are attributed largely to $PbHPO_4^0$ and $PbH_2PO_4^+$ ion pair formation. Measurement of the ion activity products (IAP) of the solutions at equilibrium with HPM gave highly variable results that were sensitive to pH and generally not consistent with the reported solubility product of this mineral. It is concluded that a meaningful and constant solubility product of HPM cannot be established because of the incongruent dissolution behavior of this mineral in the near-neutral pH range.

Acknowledgments

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