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Formation of Chloropyromorphite from Galena (PbS) in the Presence of Hydroxyapatite

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Abstract

Transformation of unstable lead [Pb(II)] forms into insoluble pyromorphite, [$Pb_5(PO_4)_3(OH, Cl, F...)$], by addition of phosphate to Pb contaminated soil has been proposed as a remediation technology which reduces the mobility and bioavailability of Pb. Under aerobic condition, oxidation of dissolved sulfide increases dissolution of galena (PbS), causing it to become a source of liable Pb forms in soils, sediments and wastes. Thus, a galena ore was reacted with synthetic hydroxyapatite [$Ca_5(PO_4)_3OH$] under various pH condition to determine the formation rate of pyromorphite and the solubility of galena under the ambient conditions. In a 6 day reaction period the dissolution rate of galena increased with pH due to the oxidation of dissolved sulfide. Correspondingly, formation of chloropyromorphite became apparent in the galena-apatite suspensions with increasing pH. The insignificant effect of mineral P/Pb molar ratio on the formation of chloropyromorphite implied that dissolution of galena was the rate limiting step.

DISCLAIMER

Introduction

In-situ immobilization of soil lead [Pb(II)] by addition of phosphate minerals has been considered a cost effective and environmental benign alternative remediation technology for Pb contaminated soils. This approach transforms the reactive and bioavailable soil Pb species, or labile Pb species, into the chemical forms that are stable and have reduced mobility and boiavailability under environmental conditions. It has been demonstrated that pyromorphite [$Pb_5(PO_4)_3(OH, Cl, F...)$] is one of the most stable Pb forms that can be formed under ordinary soil conditions and the bioaccessibility of soil Pb can be drastically reduced when unstable soil Pb forms, such as cerrusite ($PbCO_3$), are converted into pyromorphite (1). Soluble Pb concentrations in soil solutions have been reduced by addition of phosphate minerals (2-6), and the formation of pyromorphite in aqueous Pb solution, on exchange resin surface, and from geothite adsorbed Pb by reaction with hydroxyapatite (2, 7) have been reported. Additionally, formation of pyromorphite in contaminated soils and wastes which contained high levels of phosphate has been demonstrated (8-10), and direct evidences of formation of pyromorphite in contaminated soils amended with soluble phosphate and/or hydroxyapatite have been obtained (10-11, 6).

Although substitution of Pb for Ca in apatite may be possible (9), the dominant mechanism of pyromorphite formation in the Pb-P-H_2O system has been reported as precipitation of soluble lead and phosphate (12, 2, 5). The precipitation of pyromorphite from the soluble Pb and PO_4 is a rapid process, completed within seconds in solutions which are saturated with respect to pyromorphite (our unpublished data). Thus, the rate of pyromorphite formation in systems containing solid Pb-bearing forms and PO_4 minerals will be determined by the dissolution rate of the solid Pb and/or PO_4 forms. Accordingly, the soluble Pb concentration in aqueous system containing apatite and Pb-bearing solids will be determined by the dissolution rate of apatite and the overall Pb release rate (desorption, dissociation and dissolution) of the Pb species. As the forms of soil Pb vary and dependent upon the sources of Pb contamination and environmental conditions, knowledge of the reaction behavior of primary Pb forms with phosphate becomes important in assessing the efficiency of Pb immobilization by addition of phosphate.

Galena, an insoluble lead sulfide mineral (PbS) frequently found in mining wastes and under reducing environment, such as anaerobically digested sludge and anoxic aquatic sediments (13-16) become unstable upon exposure to oxidizing conditions and sulfide is oxidized to a higher oxidation state, eventually to sulfate ion, and Pb ion is released into the solution (17). Thus, galena becomes a potential bioavailable Pb species when it is in soils, wastes and sediments under ambient conditions. Therefore, a series of kinetic experiments were conducted in systems containing hydroxyapatite and galena to determine the effects of dissolution rates of apatite and galena on: 1) the rate of formation of pyromorphite, and 2) the soluble Pb level during the reaction. These experiments were conducted in the presence of oxygen allowing an evaluation of the formation of pyromorphite in aqueous solutions.

Materials and Methods

Minerals Galena, a lead sulfide ore, obtained from The Doe Run Company was used in this study. Prior to use, the mineral was passed through a 25 μm sieve. The specific surface area of the galena sample was 0.533 $m^2 g^{-1}$, determined by BET nitrogen absorption surface area analyzer (Gemini III, Micromeritics). The elemental composition of this mineral was 84.7 and 13.5% (w/w %) of Pb and S, respectively. Impurities in the mineral included Zn (0.01%), Fe (0.03%), MgO (0.03%) and Cr (0.05%). The mineral exhibited a characteristic X-ray diffraction (XRD) pattern of galena and no other minerals were detectable.

A synthetic hydroxyapatite [$Ca_5(PO_4)_3OH$] (obtained from Bio-Rad) was used as the phosphate source. The specific surface area of the mineral was 67.3 $m^2 g^{-1}$, determined by a BET nitrogen absorption. The molar ratio of P/Ca of the apatite was 1.62 which is close to the ideal ratio of 1.67.

Dissolution of Galena and Hydroxyapatite Dissolution of galena was conducted in a brown glass bottle containing 1.0 L of 0.10 M $NaNO_3$ and 0.001 M NaCl solution. Prior to addition of 0.120 g of galena (5.0×10^{-1} mmole), the solution was adjusted with 0.1 N HNO_3 to a pH of 2, 3, 4, 5, 6 or 7. The pH was maintained with an automatic titrator for 30 min after addition of galena. The bottles containing the suspensions were then capped and rotated on a parallel rotator. The suspension pH was monitored and adjusted as needed. Suspension samples were periodically taken with a syringe, filtered with a 0.2 µm membrane and were analyzed for soluble Pb and S on an inductively coupled plasma spectrophotometer (ICP). The dissolution of galena was determined by measuring the soluble Pb and S concentrations as a function of time.

The dissolution rates of hydroxyapatite was determined at the pHs of 4, 5, 6 and 7. Below pH 4, the dissolution was too fast to be accurately monitored. One to three (1.00-3.00) grams of apatite was used for dissolution rate determination. Dissolution was conducted in a 1.1 L glass beaker which contained a glass pH electrode and a stirring paddle. The beaker was placed in a water bath with a constant temperature of 25 °C. An automatic titrator was used to adjust and maintain the suspension pH with 0.1 N NaOH and 0.1 N HNO_3 solutions. One liter (1.0 L) solution of 0.100 M $NaNO_3$ and 0.001 M NaCl was adjusted to a desired pH. After apatite addition, the suspension was maintained at a constant pH and sampled periodically for 2-3 hours. The suspension samples were filtered with a 0.2 µm membrane and soluble PO_4 and Ca concentrations were analyzed on ICP. The dissolution of apatite was determined by measuring the soluble Ca and PO_4 concentrations as a function of time.

Reactions between Galena and Hydroxyapatite The reactions between galena and hydroxyapatite were carried out at three molar ratios of P/Pb; 3/5, 6/5 and 12/5, established by mixing 0.12 g (5.0×10^{-1} mmole) of galena with 0.05 g (1×10^{-1} mmole), 0.10 g (2×10^{-1} mmole), and 0.20 g (4×10^{-1} mmole) of hydroxyapatite, respectively. The amount of phosphate contained in the added hydroxyapatite were one, two and four times that needed to stoichiometrically react with the Pb contained in the 0.12 g of galena to form pyromorphite [$Pb_5(PO_4)_3Cl$]. For each of these three P/Pb ratio experiments, the reaction was conducted at a pH of 2, 3, 4, 5 and 6. After adding the galena-apatite mixture into 1.0 L of 0.10 M $NaNO_3$ and 0.001 M NaCl solution, the suspension was stirred for two hours while the pH was maintained with an automatic titrator. The suspension was then placed into a brown bottle, capped and rotated on a parallel rotator. The suspension pH was monitored and adjusted as needed. The suspensions were periodically sampled with decreasing frequency during the 6 day reaction period. Sampled suspensions were filtered through a 0.2 μm membrane and the filtrates were analyzed for PO_4, Ca, Pb and S using ICP. At the end of the experiment, the solids were collected and their mineral composition and surface chemical composition and morphology were determined using XRD and a scanning electronic microscope equipped with energy dispersive X-ray spectroscopy (SEM/EDS).

Analytical Procedures An inductively coupled plasma spectrophotometer (Tracer 61E, Therm Jerrel Ash) was used to quantify soluble Pb, PO_4, Ca, S. The detection limit for these 4 elements was 2 μg L^{-1}. The Water Supply Performance Evaluation Study solution (WS033) by US EPA was used to calibrate and verify the analytical standard solutions used for ICP analysis. Experimental blanks, standards and spiked samples were used for analytical quality control. Solution and suspension pH was measured by a glass pH electrode which was connected to the Mettler titrator. With this set-up, the variation of pH could be maintained within 0.01 pH unit.

The solid samples were examined with an X-ray diffractometer (Scintag, XDS 2000; Cu-Kα radiation at 35 kV filament current of 30 mA) and a step-scanning rate of

0.04 °2θ/sec was employed. A scanning electron microscope coupled with energy dispersive X-ray spectroscope (SEM/EDS, JEOL, JSM 5300) was used to obtain the solid images and surface elemental composition.

Results

Dissolution of Galena and Hydroxyapatite

Dissolution of Galena As measured by soluble Pb concentration, dissolution of galena increased as pH decreased during the initial 180 min reaction time (Figure 1, insert). Soluble S concentrations (not shown) were similar to soluble Pb, thus dissolution of galena was stoichiometric.

In contrast, after longer reaction times the dissolution rate of galena was positively related to suspension pH (Figure 1). After 144 h reaction the soluble Pb was 8.0×10^{-2} mmol L^{-1} at pH 2 and 3 and increased to 1.2, 1.6 and 2.0×10^{-1} mmol L^{-1} at pH 4, 5, and 6, respectively (Figure 1).

Dissolution of Hydroxyapatite The results from this study confirms the dissolution of apatite is inversely related to pH (Figure 2). Below pH 4, the dissolution was too rapid to be accurately determined under the experimental conditions. At pH 4, 1.2 (±0.2) g of apatite dissolved within 80 min, resulting in a solution of $1.2(\pm0.2) \times 10^{-2}$ M Ca and $7.2(\pm1.1) \times 10^{-3}$ M PO_4. These concentrations gave an activity product of $10^{14(\pm1.2)}$ which is close to the published solubility product (K_{sp}) of $10^{15.8(\pm1.7)}$ (18). Thus, the solution was saturated with respect to apatite. At the relatively high pHs, e.g., pH 6 and 7, the dissolved Ca and PO_4 concentrations reached steady state in a shorter time period (Figure 2). This might be attributed to the effect of the total surface area of the solid apatite on dissolution rate. At pH 6 and 7 only 4 and 1% of the total added mineral were dissolved, respectively, compared to 40 and 20% of apatite dissolution at pH 4 and 5 within 25 min. The soluble species compositions at pH 4, 5 and even 6 were stoichiometric to the elemental composition of apatite with a P/Ca molar ratio of 3/5 (Figure 2). However, the soluble PO_4 and Ca concentrations at pH 7 were essentially equal. This can be attributed to surface adsorption of Ca^{2+} because the greater amount of undissolved apatite provided a high surface area and high solution pH favor surface adsorption.

Reactions of Galena and Hydroxyapatite Formation of pyromorphite is the dominant process in the systems containing soluble Pb and phosphate (19, 2, 5) or solid Pb-bearing forms such as cerrusite and anglesite and apatite (11, and our unpublished data). If chloride ions, Cl^-, are present, the reaction product will be chloropyromorphite [$Pb_5(PO_4)_3Cl$], the least soluble form in the pyromorphite mineral group. Accordingly, the removal of soluble Pb and PO_4 from solution in these galena-apatite suspensions was attributed to precipitation of chloropyromorphite. This assumption is ultimately verified with XRD and EDS analysis. In suspensions involving dissolution of apatite and galena, there were no processes such as adsorption and precipitation to remove soluble Ca and S from solutions. Thus, soluble Ca and S concentrations were used to determine the quantities of apatite and galena dissolution. Considering the oxidation of dissolved sulfide, calcium sulfate ($CaSO_4$, gypsum) was the most probable mineral formed from Ca^{2+} and SO_4^{2-}, however, gypsum has a relatively high solubility product (4.5×10^{-5}) that apparently, as demonstrated later, precluded precipitated in these suspensions.

Soluble Species Soluble S concentrations as a function of reaction time for the three P/Pb ratios of 3/5, 6/5 and 12/5 are presented in Figure 3a, b and c, respectively. At pH 2 and 3, the soluble S levels were equal at 1.2 (±0.2) $\times 10^{-2}$ mmol L^{-1} for the three

P/Pb ratios after 144 hrs reaction (Figure 3a, b and c). As pH increased, soluble S concentrations increased. This increase was more apparent at the longer reaction times, (Figure 3a, b and c). There was no significant effect of the P/Pb ratio on galena dissolution and the average concentrations of soluble S in the three solutions were 2.5 (±0.5), 3.0 (±0.6) and 4.0 (±0.5) $x10^{-2}$ mmol L^{-1} at pH 4, 5 and 6, respectively. However, there was a greater S concentration in the systems which contain apatite (Figure 1 vs. Figure 3), indicating a greater dissolution of galena in the present of apatite.

At low pH's of 2 and 3, the soluble Pb concentrations, 1.0 - 1.4 x 10^{-3} mmol L^{-1} (Figure 4), were approximately equalvent to that of soluble S, 1.2 (±0.2) x 10^{-3} mmol L^{-1} (Figure 3a, b and c) when the reactions reached an apparent steady state, about 48 hrs. This stoichiometric composition with respect to galena indicates limited removal of S or Pb from the solutions at pH 2 and 3. Thus, the formation of lead phosphate(s) or chloropyromorphite at these pHs was limit. At pH 4, the soluble Pb concentrations were 2.0, 1.0 and 0.2 x 10^{-3} mmol L^{-1} in the suspensions with P/Pb ratios of 3/5, 6/5 and 12/5, respectively, after 48 hrs reaction time (Figure 4a, b and c). The soluble Pb levels at pH 4 were 1 to 2 order of magnitude lower than that of soluble S and thus, lacked stoichiometry with respect to dissolution of galena. The disappearance of dissolved Pb can be attributed to formation of chloropyromorphite. At pH 5 and 6 the soluble Pb concentrations were below 2 µg L^{-1} (1 x 10^{-5} mmol L^{-1}), which was the analytical detection limit, in all of the suspensions after the first 60 min reaction (Figure 4a, b and c). The dissolved Pb from galena in these suspensions was readily precipitated as chloropyromorphite because of the high availability of soluble PO_4 from the dissolution of apatite. At pH 5 and 6, the soluble PO_4 levels ranged from 2 x 10^{-1} - 10^{0} mmol L^{-1} (Figure 5), the soluble Pb concentrations were at levels of 10^{-6} and 10^{-7} mmol L^{-1} (Figure

4) which agreed with the results calculated from the solubility of chloropyromorphite at these pHs (12). Thus, the formation of chloropyromorphite can be assumed to have occurred.

The mass balance calculation from the soluble S or Pb concentration indicated that only a small portion of the added galena was involved in the reactions during the 144 hrs reaction. At pH 2 and 3, 2-3% of the added galena was dissolved. At pH 4, 5 and 6, 5 (±1), 6 (±1.2) and 8 (±1)%, respectively, of the added galena was dissolved.

At the low pHs (2 and 3), the added hydroxyapatite was completely dissolved within 120 min (Figure 5). Above pH 3, the amount of apatite dissolution decreased with increasing pH as indicated by the soluble PO_4 (Figure 5) and Ca (not shown), resulting in a soluble PO_4 in the range of 1.5 - 6 x 10^{-1} mmol L^{-1} in the P/Pb ratios of 3/5 and 6/5 and 0.5 - 1.5 x 10^{-3} mol L^{-1} in the P/Pb ratio of 12/5 (Figure 5a, b and c). This greater dissolution of apatite as compared to galena, assured the availability of soluble PO_4. Thus, it was not limiting precipitation of the soluble Pb.

Mineralogical Analysis A series of SEM images were taken of the solids collected after 144 hrs reaction. As the solids from the three P/Pb ratio experiments were similar, the images from P/Pb = 6/5 were presented as an example (Figure 6). There was no new phase formed in the solid collected at pH 2, the cubic-shaped galena was the only mineral in the suspension (Figure 6a). At pH 3, there were a few tiny, needle-shaped particles observed in addition the dominant galena particles (Figure 6b). The chemical composition analysis on this needle-shaped solid surface, as illustrated by the EDS spectrum of Figure 7a, indicates an elemental ratio of Pb, P and Cl similar to a synthetic chloropyromorphite (Figure 7c). The needle-shaped particles became more apparent in the solids collected at pH 4 (Figure 6c) which also shows the chloropyromorphite-like chemical composition (not shown). At pH 5 and 6, the newly precipitated particles developed on the surface of apatite which was not completely dissolved at these pHs (Figure 6d and e). The EDS spectrum includes Ca in addition to Pb, P and Cl (Figure 7b). This observation implies that the spectra reflect the elements consisting of chloropyromorphite [$Pb_5(PO_4)_3Cl$] and hydroxyapatite [$Ca_5(PO_4)_3OH$]. Calcium was not found in spectra of solids at pH 3 (Figure 7a) and 4 (not shown) because the newly precipitated crystals were formed in solution rather than on the apatite surface. This observation is consistent with the results from solution analysis in which complete dissolution of the added apatite was achieved at pH 3 and 4. Therefore, the crystallization of chloropyromorphite occurred in the solution. In contrast, incomplete dissolution of apatite at pH 5 and 6 provided a surface for chloropyromorphite precipitation.

As indicated by the results from the solution analysis, only a small portion of added galena was dissolved, therefore, the amount of dissolved Pb involved in precipitation with phosphate to form chloropyromorphite was limited. This low content of chloropyromorphite in the mixture of galena and apatite was insufficient to generate a visible XRD pattern for chloropyromorphite. Therefore, powder X-ray diffraction analysis did not demonstrate the characteristic patterns for chloropyromorphite in the solids collected at pH 3, 4 and 5. However, the characteristic chloropyromorphite peaks were obtained in the solid collected at pH 6 for the P/Pb of 12/5 (Figure 8a). In this treatment, about 9% of the added galena-Pb was converted to chloropyromorphite-Pb. As shown in Figure 8a, one of the chloropyromorphite peaks at the 30.08 $^{\circ}2\theta$ is overlapped by a galena peak at 30.19 $^{\circ}2\theta$. However, another characteristic peak of chloropyromorphite at 30.94 $^{\circ}2\theta$ was apparent (Figure 8a). To confirm the formation of chloropyromorphite in the galena-apatite suspension, the XRD patterns for the galena used in this study and a synthetic chloropyromorphite were also presented in Figure 8b and c.

Discussion

The quantities of galena dissolved in the first 180 min reaction obtained in this study were in general agreement with that reported (17). Apparently, surface protonation, adsorption of H^+ on the mineral surface is the first step for most mineral dissolution processes, and was the driving force in the galena dissolution. At low pH, the high proton concentration enhanced the surface protonation and thus increased dissolution rate:

$$PbS(s) + 2\,H^+ = PbSH_2^{2+}(s) \rightarrow Pb^{2+} + H_2S \qquad (1)$$

The pH_{zpc} (the pH at zero point of charge of a surface) of galena is between 2 to 4, depending upon the galena sources (17). At pH < 4, the surface is positively charged $[PbSH_2^{2+}{}_{(s)}]$ because of the adsorption of protons, and a higher dissolution of galena can be expected. This was confirmed by the results obtained in the initial 180 min reaction (Figure 1). Between pH 4 and 8, the net charge of the surface is either neutral or negative, thus dissolution of galena can be limited by the low surface protonation (17).

Soluble sulfide is not stable and will be transformed into the species with higher oxidation state such as S^0, S_2O_3, SO_3 and SO_4 in the present of oxygen (17, 20-21). Dissolution of galena was carried out under aerobic condition. Therefore, oxidation of dissolved sulfide would lower the activity of soluble sulfides (H_2S and HS^-) and decreased the degree of saturation with respect to galena, resulting in increasing dissolution. The oxidation of galena dissolved sulfide to SO_4, the final oxidation product, was demonstrated to be completed within 6 hrs (17). However, the effect of pH on sulfide oxidation under constant oxygen partial pressure condition suggested an increase oxidation rate constants with increasing pH, especially in the pH range of 4 to 8 (21). The rate of oxidation of soluble sulfide to element sulfur was extremely slow when the pH was lower than 6, but sharply increased from pH 6 to 7 (20). The measured oxidation rate constant (log k) increased from 1.85 at pH 1.95 to 2.33 at pH 6.17, with the greater increase occurring from pH 4 to 6 (21). This appears to agree with the results from galena dissolution in this study in which the dissolution rates at pH 2 and 3 were approximately equivalent and the rate increased significantly from pH 4 to 6 within the 144 hrs reaction time (Figure 1). The higher oxidation of dissolved sulfide, observed at higher pH, removed soluble sulfide making the solution undersaturation with respect to galena and resulted in an increase in galena dissolution (Figure 1). The estimated half time ($t_{1/2}$) of oxidation ranged from 20 - 50 hours (21). The difference in galena dissolution became apparent in a relatively long reaction time (Figure 1), which is consistent with the results obtained the latter study (21). The higher dissolution of galena at higher pHs may imply that the higher transformation of Pb from galena to pyromorphite can be observed.

In the suspensions containing galena and hydroxyapatite, chloropyromorphite can not be formed directly as the overall reaction:

$$Ca_5(PO_4)_3OH_{(s)} + 5PbS_{(s)} + Cl^- + H^+ = Pb_5(PO_4)_3Cl_{(s)} + 5S^{2-} + 5Ca^{2+} + H_2O \qquad [2]$$

can not be carried out spontaneously, ($\Delta G_f = +345.7$ kJ mol^{-1}). In the presence of oxygen the dissolved sulfide is oxidized and the sulfur species with higher oxidation states such as S^0, S_2O_3, and SO_4 will be formed. Considering sulfide oxidation, the possible reactions, depending upon the oxidation products, in the galena and apatite suspensions can be expressed as:

$$Ca_5(PO_4)_3OH_{(s)} + 5PbS_{(s)} + Cl^- + 11H^+ + 5/2O_2 = Pb_5(PO_4)_3Cl_{(s)} + 5S^0 + 5Ca^{2+} + 6H_2O \qquad [3]$$

ΔG_f = -960.0 kJ mol^{-1}

and/or

$$Ca_5(PO_4)_3OH_{(s)} + 5PbS_{(s)} + Cl^- + H^+ + 10O_2 = Pb_5(PO_4)_3Cl_{(s)} + 5SO_4^{2-} + 5Ca^{2+} + H_2O \quad [4]$$

ΔG_f = -2426.6 kJ mol^{-1}

Reactions 3 and 4 will take place spontaneously and formation of chloropyromorphite can be expected under aerobic conditions as used in this study. Although various oxidation products can be formed, the sulfur-oxygen anions such as S_2O_3, SO_3 and SO_4 are the more likely oxidation products of dissolved sulfide (17, 21).

At the low pHs, e.g., pH 2 and 3, the oxidation rate of dissolved sulfide was slow, thus the amount of dissolved galena, about 1 x 10^{-2} mmoles (Figure 3), was equal for the solutions without and with apatite addition (Figure 1 vs. Figure 3). The soluble Pb concentrations (Figure 4) were approximately equivalent to the soluble S (Figure 3) at pH 2 and 3, indicating a lack of removal of soluble Pb from the solution. Formation of chloropyromorphite at these pHs was limited. In contrast, the amount of galena dissolution in the apatite added suspensions was nearly doubled at pH 4 and above (Figure 3) compared to that of galena alone (Figure 1). This implies that the formation of chloropyromorphite in the suspension depleted the soluble Pb from the solutions (Figure 4) and enhanced dissolution of galena and oxidation of dissolved sulfide. The SEM analysis (Figure 6) in which chloropyromorphite was not found in pH 2 but become more apparent with increasing pH confirms this conclusion. Accordingly, both dissolution of galena and formation of chloropyromorphite were determined by the rate of dissolved sulfide oxidation.

At pH 4 and above, the measured soluble Pb concentrations in the three P/Pb ratio suspensions were in the range determined by the solubility of chloropyromorphite, similar results were determined by the geochemical model simulation, EQ3, (22). This further confirmed the formation of chloropyromorphite in the suspensions and also implied the oxidation occurrence in the suspension. If the dissolved sulfide was not oxidized, the solutions would be supersaturated with respect to galena as indicated by the soluble S concentration in Figure 3, and further dissolution of galena would be prohibited. Assuming the predominant final oxidation product of the sulfide was SO_4 (17), lead sulfate ($PbSO_4$, or anglesite) could remove the soluble Pb from solution. However, at pH 4 the solubility of chloropyromorphite was several orders of magnitude lower than that of anglesite (23), thus solutions were saturated with respect to chloropyromorphite and the formation of anglesite was not possible. This was further confirmed by the XRD analysis (Figure 8) and the simulated species distribution by EQ 3. These results suggested that in an aerobic aqueous suspension of galena, the formation of chloropyromorphite was determined by the oxidation rate of sulfide and the soluble Pb concentration were determined by the solubility of the newly formed chloropyromorphite in the presence of apatite.

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Figure Captions

Figure 1. Effect of pH on galena dissolution. Soluble Pb is used to present the dissolution of galena. The insert is the dissolution in the initial 180 minutes.

Figure 2. Dissolution of hydroxyapatite as a function of time and pH. The solid black and unfilled symbols represent the phosphate and calcium concentrations, respectively.

Figure 3. Soluble sulfur concentrations in the galena-hydroxyapatite suspensions under various pHs and P/Pb molar ratios.

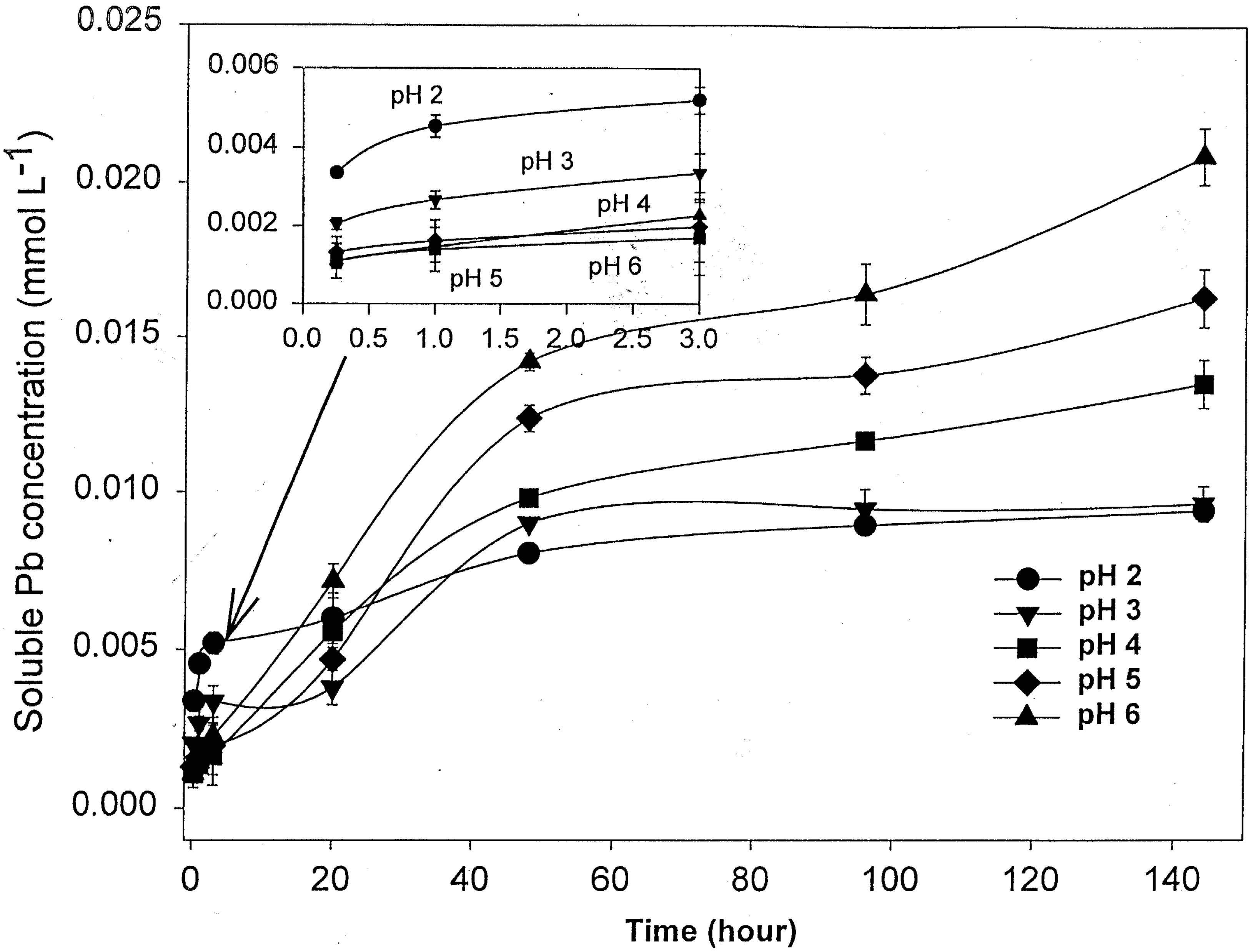
Figure 4. Soluble lead concentrations in the galena-hydroxyapatite suspensions under various pHs and P/Pb molar ratios.

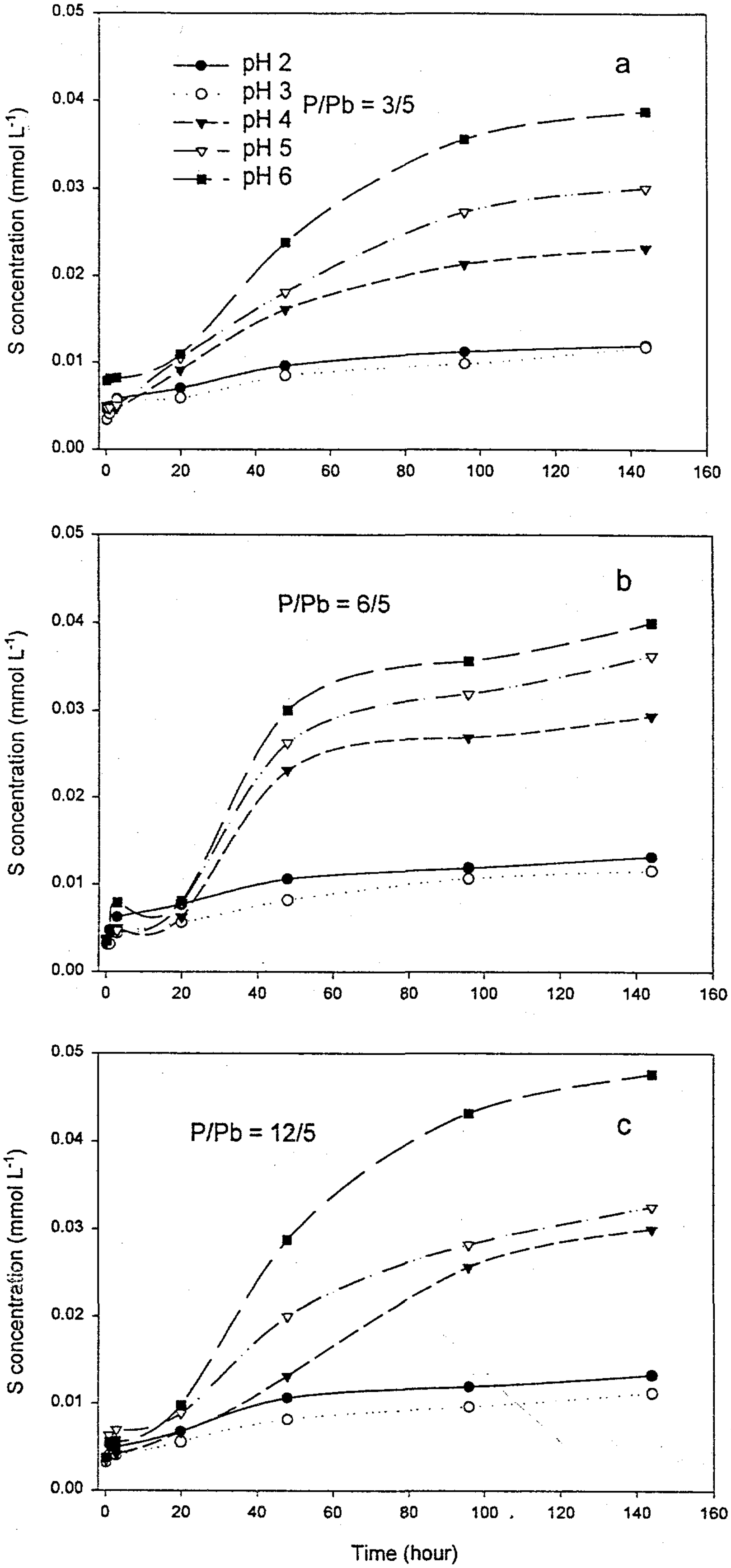
Figure 5. Soluble phosphate concentrations in the galena-hydroxyapatite suspensions under various pHs and P/Pb molar ratios.

Figure 6. SEM images for the solids collected from galena-hydroxyapatite suspensions from pH 2 to 6 after 144 hours reaction.

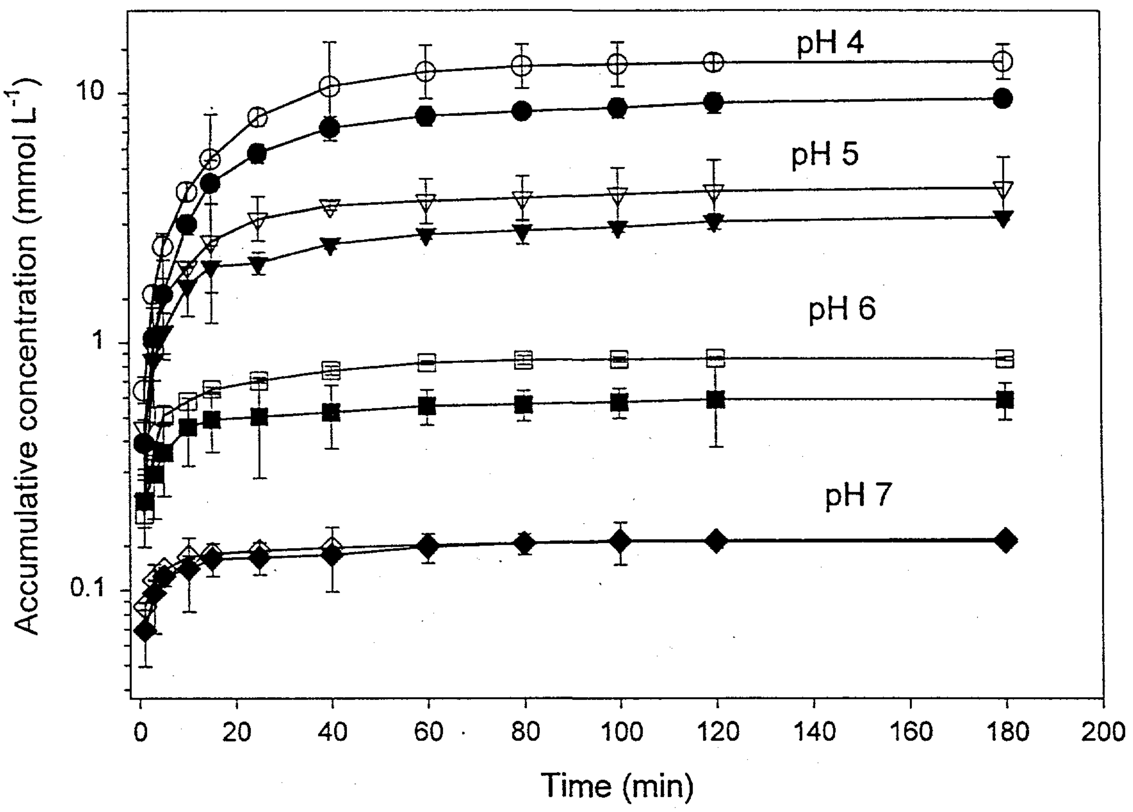
Figure 7. EDS spectra for the new solid phase in the galena-hydroxyapatite suspension at pH 3 (a), pH 6 (b) after 144 hours reaction and a synthetic chloropyromorphite (c).

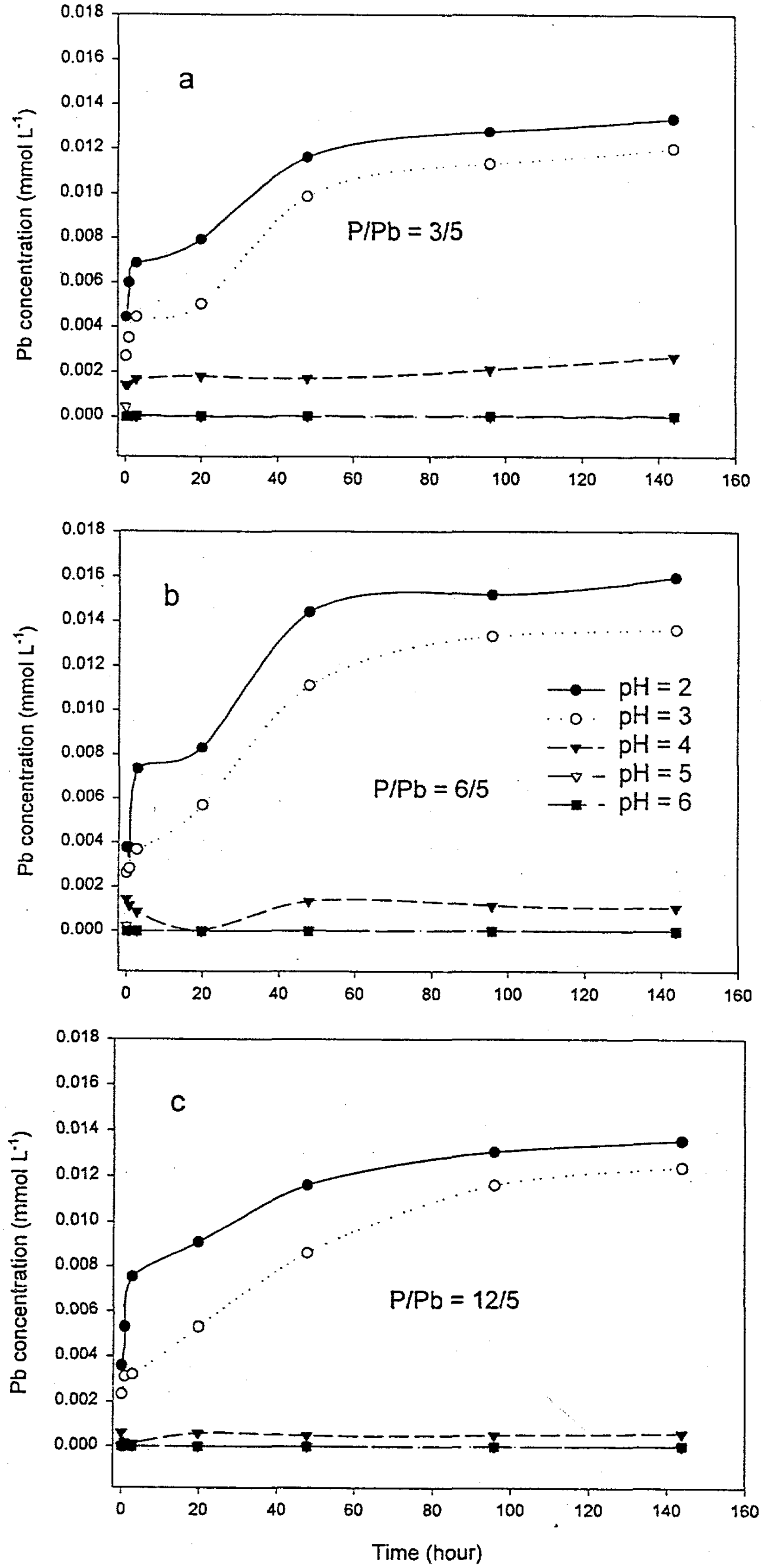
Figure 8. XRD pattern for the solid collected in the galena-hydroxyapatite suspension reacting at pH 6 for 144 hours (a), the galena mineral used in this study (b) and the synthetic chloropyromorphite (c).

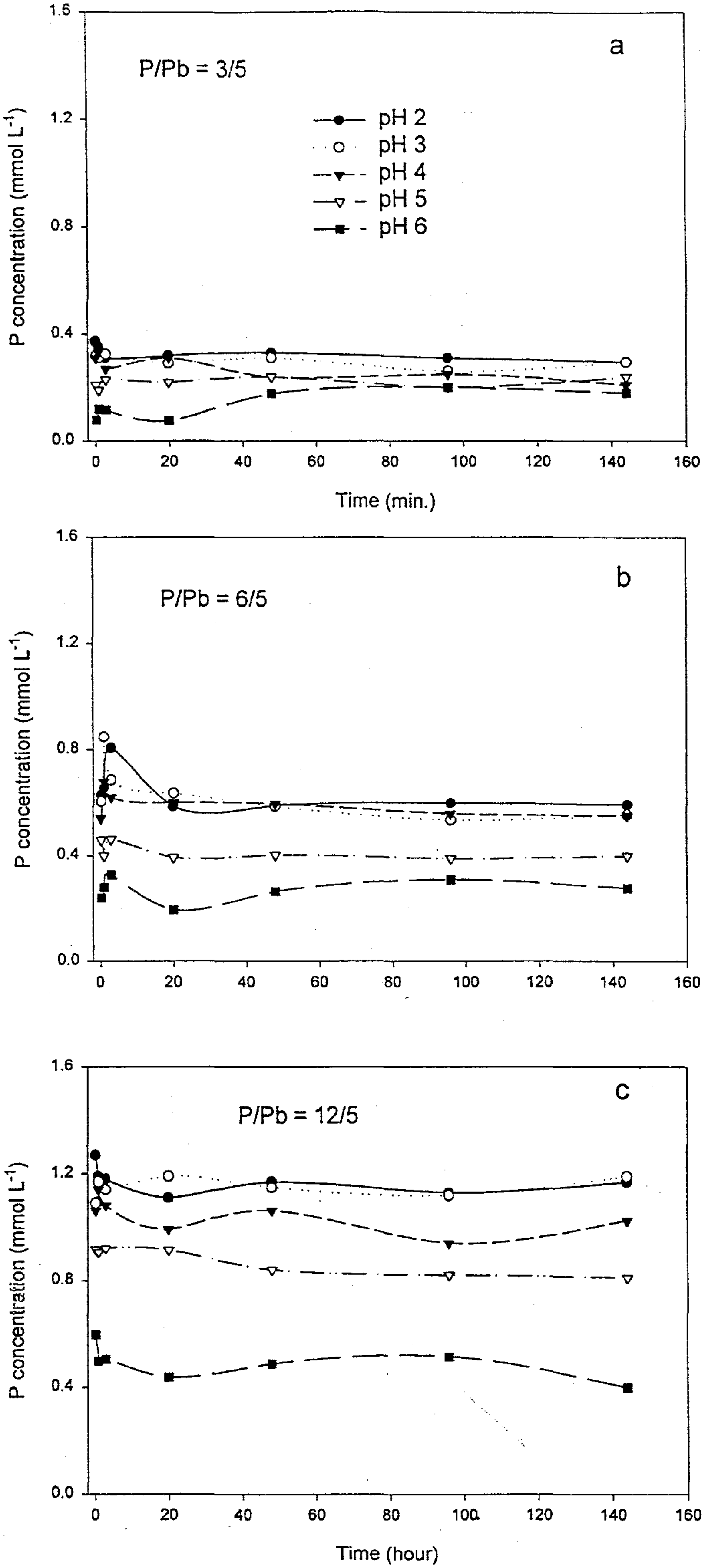

Soluble Pb concentration (mmol L^{-1})
0.025
0.020
0.015
0.010
0.005
0.000
0
20
40
60
80
100
120
140
Time (hour)
pH 2
pH 3
pH 4
pH 5
pH 6
0.006
0.004
0.002
0.000
0.0
0.5
1.0
1.5
2.0
2.5
3.0
pH 2
pH 3
pH 4
pH 5
pH 6

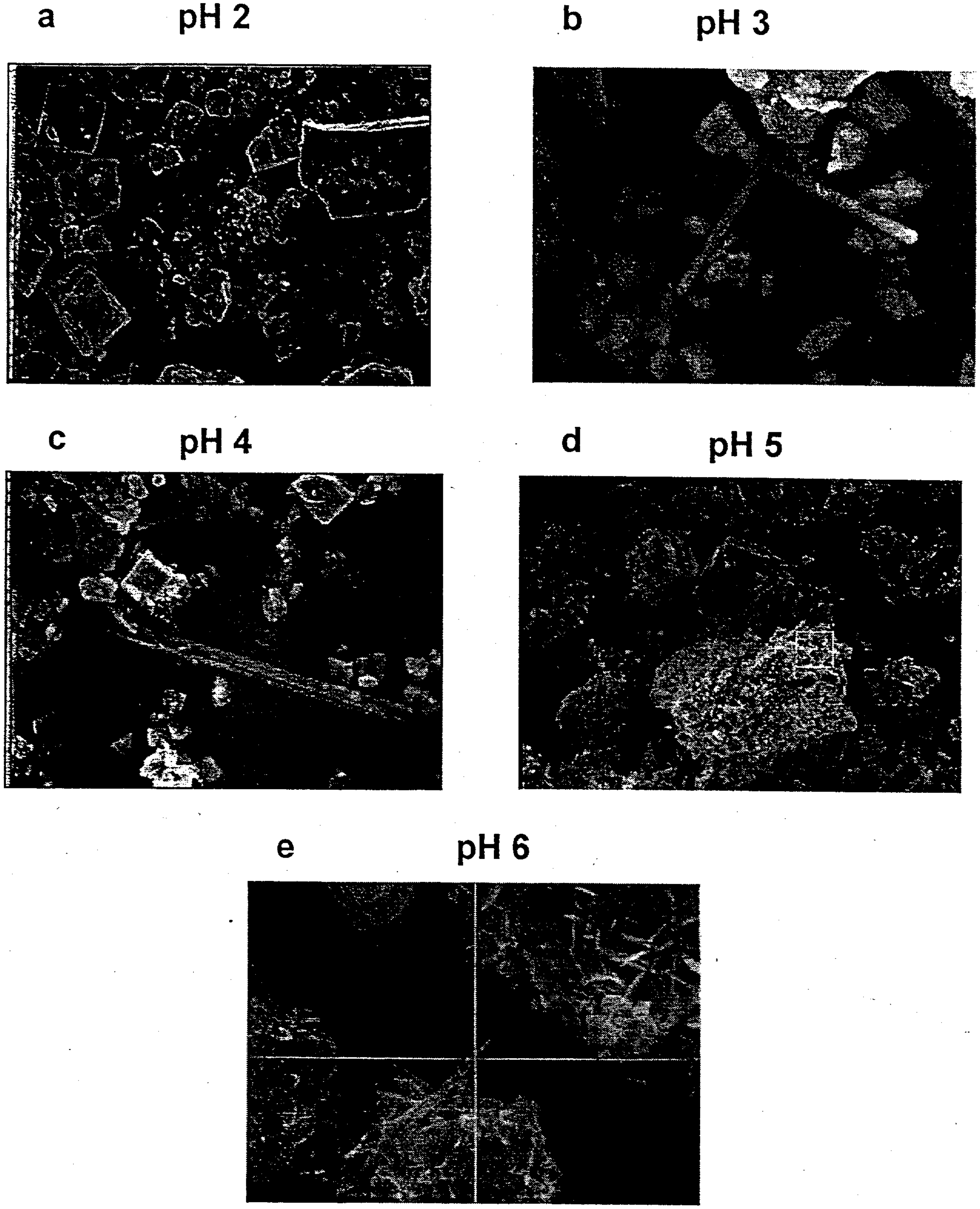


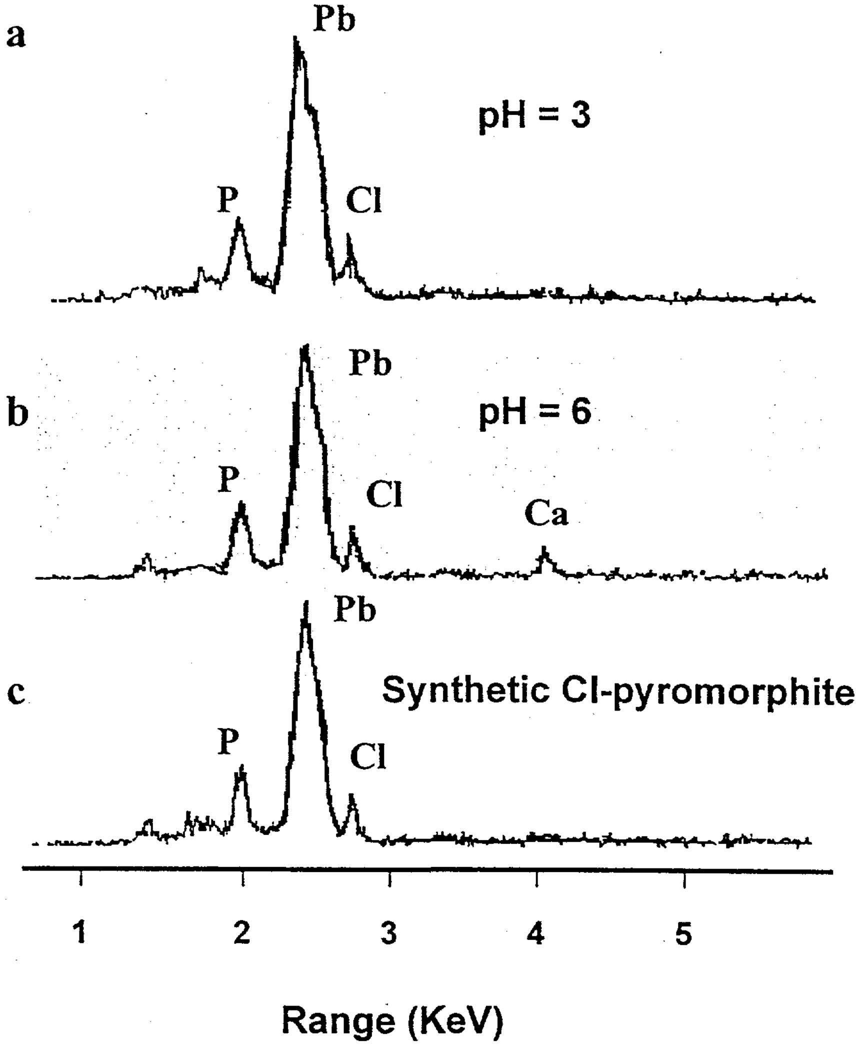
a
P/Pb = 3/5
b
P/Pb = 6/5
c
P/Pb = 12/5
pH 2
pH 3
pH 4
pH 5
pH 6
S concentration (mmol L^{-1})
0.00
0.01
0.02
0.03
0.04
0.05
0
20
40
60
80
100
120
140
160
Time (hour)

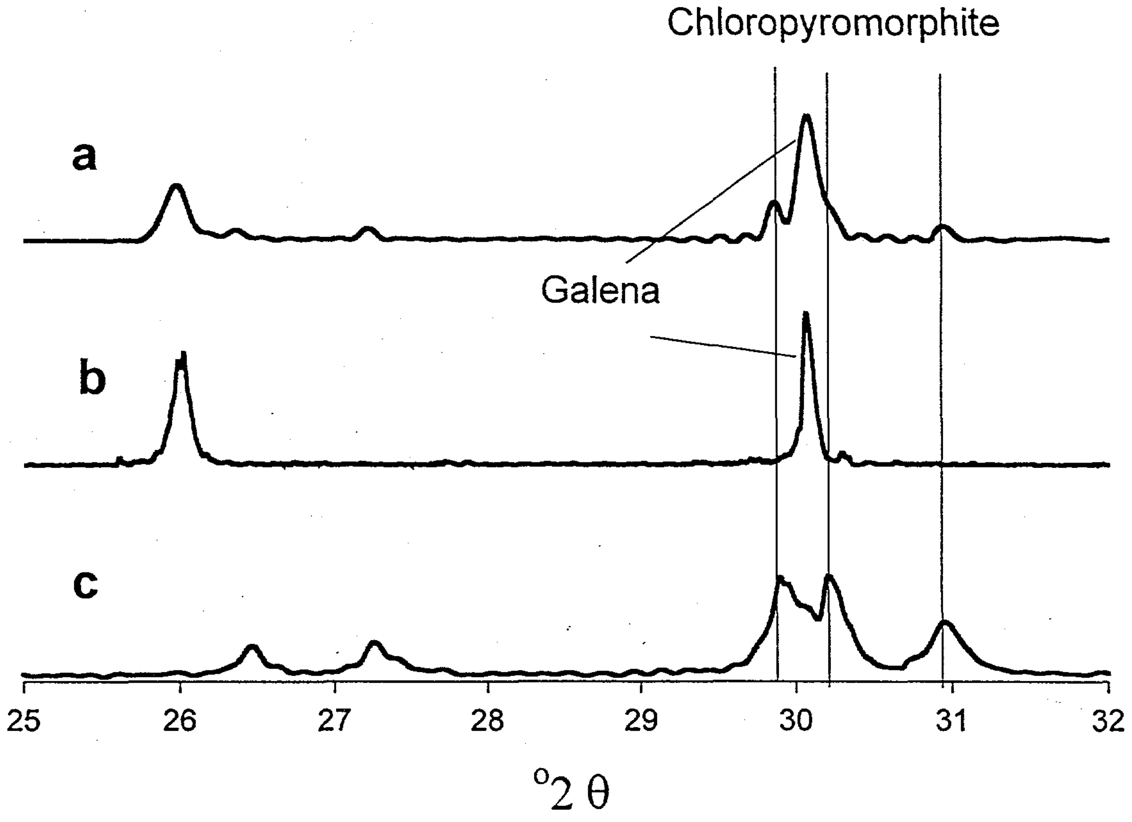

pH 4
pH 5
pH 6
pH 7
Accumulative concentration (mmol L^{-1})
0.1
1
10
Time (min)
0
20
40
60
80
100
120
140
160
180
200


a
P/Pb = 3/5
b
P/Pb = 6/5
pH = 2
pH = 3
pH = 4
pH = 5
pH = 6
c
P/Pb = 12/5
Pb concentration (mmol L-1)
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
0
20
40
60
80
100
120
140
160
Time (hour)


a
P/Pb = 3/5
pH 2
pH 3
pH 4
pH 5
pH 6
P concentration (mmol L^{-1})
1.6
1.2
0.8
0.4
0.0
0
20
40
60
80
100
120
140
160
Time (min.)
b
P/Pb = 6/5
P concentration (mmol L^{-1})
1.6
1.2
0.8
0.4
0.0
0
20
40
60
80
100
120
140
160
c
P/Pb = 12/5
P concentration (mmol L^{-1})
1.6
1.2
0.8
0.4
0.0
0
20
40
60
80
100
120
140
160
Time (hour)


a
pH 2
b
pH 3
c
pH 4
d
pH 5
e
pH 6


a
Pb
pH = 3
P
Cl
b
Pb
pH = 6
P
Cl
Ca
c
Pb
Synthetic Cl-pyromorphite
P
Cl
1
2
3
4
5
Range (KeV)


Chloropyromorphite
a
Galena
b
c
25
26
27
28
29
30
31
32
°2 θ