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# Simultaneous dissolution of hydroxylapatite and precipitation of hydroxypyromorphite: Direct evidence of homogeneous nucleation

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**Abstract**—Results of in situ atomic force microscopy (AFM), ex situ AFM, optical microscopy, scanning electron microscopy, energy dispersive spectroscopy, and x-ray diffraction were combined with previous macroscopic investigations to characterize aqueous  $Pb(NO_3)_2$  reaction with hydroxylapatite ( $Ca_5(PO_4)_3OH$ ) (HAP). Experiments were conducted by immersing particulate HAP crystals in the AFM fluid cell in solutions with initial Pb concentrations = 100 mg L<sup>-1</sup>, at pH 6 and 22°C under static conditions. Experimental results showed that transport-controlled HAP dissolution provided phosphate for precipitation of hydroxypyromorphite ( $Pb_5(PO_4)_3OH$ ) (HPY), which in turn sequestered aqueous Pb. The combination of in situ and ex situ techniques provided direct evidence that HPY formed primarily by homogeneous nucleation in solution. Nevertheless, HPY needles were found in close association with HAP surfaces, most probably due to diffusional controls on phosphate concentrations. Diffusion of phosphate away from dissolving HAP appeared to be the rate-limiting step in the overall reaction sequence. *Copyright* © 1998 Elsevier Science Ltd

# 1. INTRODUCTION

Hydroxylapatite ( $Ca_5(PO_4)_3OH$ ) (HAP) has been shown to provide an effective means for removing dissolved Pb from aqueous solution at pH values ranging from 2 through 7 (Suzuki et al., 1981, 1982, 1984; Takeuchi et al., 1988; Takeuchi and Arai, 1990; Ma et al., 1993, 1994a,b 1995; Xu and Schwartz, 1994; Lower et al., 1998). Ma et al. (1993, 1994a,b, 1995) and Xu and Schwartz (1994) have shown that HAP dissolution provides phosphate, which quickly reacts with Pb to form highly insoluble hydroxypyromorphite (Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH) (HPY), according to the following equations:

$$Ca_5(PO_4)_3OH + 7H^+ \stackrel{dis}{\longleftrightarrow} 5Ca^{2+} + 3H_2PO_4^- + H_2O$$
 (1)

$$5Pb^{2+} + 3H_2PO_4^- + H_2O \xrightarrow{ppt} Pb_5(PO_4)_3OH + 7H^+$$
. (2)

The overall reaction is fast; Ma et al. (1993) and Xu and Schwartz (1994) have demonstrated that HAP can reduce an initial aqueous Pb concentration ([Pb]<sub>i</sub>) of 100 mg L<sup>-1</sup> to  $<1 \ \mu g \ L^{-1}$  in under 10 min. HAP also has been used effectively in soils to convert solid Pb phases into less reactive Pb-phosphates (Laperche et al., 1996). Laperche et al. (1996) observed formation of euhedral, doubly terminated needles of HPY when HAP was reacted with cerussite (PbCO<sub>3</sub>) crystals and with soil materials contaminated with cerussite. The removal of Pb from a dissolved or loosely sorbed state to a less reactive one via the formation of insoluble Pb-phosphates effectively limits Pb bioavailability (Nriagu, 1974; Ruby et al., 1992; Davis et al., 1993).

Maurice and Lower (1997) and Lower et al. (1998) combined macroscopic measurements with ex situ atomic force microscopy (AFM), transmission electron microscopy (TEM) scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), electron diffraction, and X-ray diffraction (XRD) to study the effects of initial saturation state on the formation of HPY from Pb(aq)-HAP interactions at pH 6, 22°C. At high supersaturation ([Pb]<sub>i</sub> = 500 mg L<sup>-1</sup>), multiple nuclei formed simultaneously in solution, resulting in an intergrown network of small HPY crystals (generally  $\ll 1 \ \mu m$  in size). At somewhat lesser values of supersaturation ( $[Pb]_i = 10$ to 100 mg  $L^{-1}$ ), nucleation again appeared to be largely homogeneous. Fewer nuclei formed and most Pb was consumed by crystal growth, leading to the formation of larger, euhedral needles of HPY (several  $\mu m$  in length) in solution. At the lowest initial saturation state ( $[Pb]_i = 0.5, 1.0 \text{ mg L}^{-1}$ ), HPY or some other Pb-phosphate phase appeared to nucleate primarily heterogeneously on the surfaces of HAP crystals. These studies were conducted ex situ, by comparing reactants and products prior to and following reaction. Hence, interpretations were necessarily based on indirect evidence of particle morphologies and associations.

In the study reported here, we expand upon the ex situ experiment at  $[Pb]_i = 100 \text{ mg L}^{-1}$  to further test the hypothesis that under these conditions, HPY formation is primarily through homogeneous precipitation in solution. This initial Pb concentration was chosen because Lower et al. (1998) results suggested that at  $[Pb]_i \gg 100 \text{ mg L}^{-1}$ , the reaction would be so rapid that the system would become unstable with respect to in situ AFM imaging, while at lower concentrations, reaction products might be too sparse to be detected by a high resolution microscopic technique. Although such high Pb conditions are not representative of most natural environments, they are in keeping with highly Pb-contaminated sites, where [Pb(aq)] can be  $\gg 100 \text{ mg L}^{-1}$  (e.g., Xintaras, 1992; Ma et al., 1993).

Although in nature, fluoroapatite  $(Ca_5(PO_4)_3F)$  is the most abundant apatite phase, we chose to use HAP because previous investigators (e.g., Suzuki et al., 1981, 1982, 1984; Takeuchi et

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al., 1988; Takeuchi and Arai, 1990; Ma et al., 1993, 1994a,b, 1995; Xu and Schwartz, 1994; Laperche et al., 1996; Lower et al., 1998) have used HAP, thereby forming a baseline for comparison. Moreover, although HAP of geologic origin is uncommon and synthetic HAP is costly, HAP reacts with Pb much more rapidly than does fluorapatite, and naturally occurring carbonated-HAP is available as inexpensive bone-meal. Thus, HAP may be more useful in actual Pb-remediation projects.

#### 2. MATERIALS AND METHODS

#### 2.1. Materials

Synthetic HAP manufactured by Bio-Rad laboratories (Hercules, California, USA) was used. Thorough descriptions are provided by Xu and Schwartz (1994) and Lower et al. (1998). Briefly, this HAP is hexagonal, poorly crystalline, nonstoichiometric, and consists of small crystalline particles  $<200 \ \mu m$  on a side (Tiselius et al., 1956; Lower et al., 1998). Individual crystals do not exhibit elongate or pinacoidal habits characteristic of apatite in rock thin sections, and the crystals are too small to determine crystallographic orientation with a polarizing microscope. The HAP was used as received from the manufacturer, with no grinding or washing.

Lead solutions at a concentration of 100 mg  $L^{-1}$  were prepared from Pb(NO<sub>3</sub>)<sub>2</sub> stock solution (Spex), using Milli-Q distilled, deionized water (DDIW) and reagent grade NaOH (Fisher Scientific) to adjust the pH to 6. Both DDIW and Pb solutions were injected into the AFM fluid cell at 22°C.

#### 2.2. In Situ Experiment

Double-sided cellophane tape was used to attach 5–10 HAP particles (approximately 0.1 mg) to stainless steel AFM sample stubs. Although at reaction times greater than 24 h, this tape appeared to be a source of Cl contamination (as evidenced by the formation of chloropyromorphite on a sample allowed to sit in the fluid cell for several days; Lower, 1997), it did not create imaging artifacts as did expoxies used during preliminary experiments. Samples were then placed in the AFM glass fluid cell, which holds ~100  $\mu$ L of solution (for description, see Johnsson et al., 1991; Dove and Chermak, 1994; Maurice and Lower, 1997). This set-up provided a Pb-to-HAP ratio of ~0.2 which is in keeping with ex situ experiments published by others (e.g., Ma et al., 1993; Lower et al., 1998).

HAP particles were imaged initially in air, after which the fluid cell was filled with DDIW. Using the AFM's binocular microscope attachment, the integrated cantilever/tip was positioned over a single crystal of HAP, and imaging commenced. Resulting images were compared to images of the same particles collected in air to ensure that the instrument was functioning properly. Additionally, these images served as a catalog of reaction blanks. The tip was then withdrawn from the surface, a solution of 100 mg L<sup>-1</sup> Pb, pH = 6, and temperature = 22°C, was flushed through the system. In situ AFM was initiated again on the surface of the same HAP particle. HAP particles were often close enough that we were able to image the surfaces of adjacent particles. The AFM's binocular microscope was used to monitor the reaction on a larger scale.

Lead contamination is of primary concern in soils and aqueous environments associated with soils (Xintaras, 1992). Therefore, in order to simulate the flow dynamics of porewater (i.e., stagnant conditions where diffusional gradients may exist), we used a pulsed flow approach (Fig. 1). Moreover, this pulsed flow approach allowed accumulation of phosphate upon HAP dissolution, allowed aqueous Pb to be regenerated, and permitted filtration of reaction products from reaction effluent. At approximately 2 h time intervals, the fluid cell was flushed with a pulse of  $\sim$ 20 mL of Pb solution, after which the outlet line was clamped shut. Based on previous experiments (Ma et al., 1993; Xu and Schwartz, 1994; Lower et al., 1998) this time frame should have allowed virtually all Pb to be removed from solution and the system to equilibrate. During these injections, the tip was withdrawn from the surface. A disadvantage of this approach vs. a continuously flowing



Fig. 1. Schematic diagram of the in situ experiment. Pulses of solution were injected by using a gravity flow-through set-up. A clamp on the outlet tube was used to regulate flow. TMAFM and a binocular-optical microscope were used for in situ observations. The effluent was filtered through 0.1  $\mu$ m pc membrane and imaged with TMAFM in air. The reacted sample was removed from the fluid cell and analyzed ex situ with SEM/EDS and XRD. The cantilever/tip also was removed from the fluid cell and imaged with SEM/EDS.

regime was that effluent solution chemistry could not be monitored. However, we were able to rely on previously reported macroscopic solution data (Ma et al., 1993, 1994a,b; Xu and Schwartz, 1994) to address this shortcoming.

In situ experiments were run in quadruplicate for time periods ranging from 3 to 12 h, depending upon the stability of the system. During each experiment, the tip was periodically withdrawn from the HAP surface for 15 min to 2 h and then reengaged. This procedure ensured that the results were not artifacts of the imaging procedure (i.e., that the tip did not prevent heterogeneous nucleation of HPY as the HAP surface was scanned beneath the tip). Using a similar approach, Junta and Hochella (1994) found that AFM did not affect heterogeneous nucleation on mineral surfaces. The AFM laser also was shut down during these time periods, to prevent heating of the fluid-cell sample.

The effluent from each pulse of Pb solution was collected and filtered immediately through a 0.1  $\mu$ m Nucleopore polycarbonate (pc) membrane. The pc membranes were rinsed immediately with deionized water (Maurice and Lower, 1997) to avoid drying-induced artifacts and imaged by ex situ AFM within 2 days.

Subsequent to reaction, the sample and cantilever/tip were removed from the fluid cell, moisture was wicked away with lens tissue, and the materials were allowed to air dry under protective cover. The reacted fluid cell sample was analyzed by ex situ AFM and XRD within 2 days and by SEM/EDS within 5 days. The cantilever/tip was analyzed by SEM/EDS within 2 days.

#### 2.3. Sample Analyses

A Digital Instruments Nanoscope III AFM with tapping-mode (TMAFM<sup>TM</sup>, Digital Instruments, Inc.) capability was used. TMAFM reduces lateral frictional forces during scanning which is of great importance when imaging particles. Force modulation (fesp) integrated cantilever/tip probes (225  $\mu$ m in length) were used in solution because these were found to work better than the shorter etched Si probes (125  $\mu$ m in length). However, etched Si probes were used for all ex situ TMAFM imaging. Specifics on tip properties can be obtained from the Digital Instruments, Inc. web site (http://www.di.com) and from Lower (1997). So-called amplitude images were collected simultaneously with more traditional height data. Amplitude images (presented in this study) provide essentially the first-derivative of height data and therefore highlight changes in relief. Such images produce accurate lateral dimensions, but height data are distorted. Amplitude images are best



Fig. 2. Schematic diagram of in situ observations made via the binocular microscope. (a) Before injecting the Pb solution, the cantilever/tip was positioned over a HAP particle immersed in DDIW. The resulting in situ AFM images of this reaction blank were used as a baseline for comparison. (b) Shortly after injecting the Pb solution, a dark-colored precipitate was observed around HAP particles in the fluid cell. The HAP sample moved relative to this precipitate, upon scanning. However, in situ AFM images of the HAP surface were still similar to the reaction blank. (c) By moving the cantilever/tip, we were able to see that the HAP surface below the cantilever/tip was noticeably void of precipitate.

for rough surfaces such as the HAP imaged here, when precise height data are not required (Maurice and Lower, 1997).

The AFM had a Nikon binocular-optical microscope attachment with 10x magnification. This binocular microscope attachment allowed us to select particles for imaging, ensured that the tip was over a HAP particle during imaging, and enabled us to obtain a general sense of reaction progress.

XRD analysis was performed using an automated Rigaku Theta-Theta goniometer equipped with a monochromator. All diffraction patterns were conducted using CuK $\alpha$  radiation at 45 kV and 35 mA. Measurements were made from 3 to 70° 2 $\Theta$  using a scan-speed of 0.5–1.0° 2 $\Theta$  per minute. By overlaying the diffractogram from the reacted fluid cell sample (i.e., particles + metal stub + tape), with that from a blank AFM sample stub (i.e., metal stub + tape), we were able to identify the reflections unique to the product(s) in the reacted sample. SEM analysis was conducted on a Princeton Gamma Tech ISIABT (model SX-40A) equipped with EDS capabilities. The reacted fluid cell sample was coated with gold and/or carbon prior to analysis with SEM/EDS.

#### 3. RESULTS

# 3.1. In Situ Binocular Microscope Observations and XRD Results

As shown schematically in Fig. 2, within 1 h after injecting the Pb solution, binocular optical microscope observations revealed a dark precipitate forming in the vicinity of HAP particles. As a HAP surface was scanned under the tip, the precipitate remained in association with the tip rather than moving with the underlying HAP particle. In fact, precipitate in the immediate vicinity of the cantilever appeared to oscillate back and forth as the cantilever/tip caused perturbations to the otherwise stagnant solution. The scan area, itself, remained free of precipitate, which apparently was swept away by the scan procedure. This provided large scale evidence that a precipitate formed in solution over the HAP particles. Ex situ XRD analysis of the sample following reaction (Fig. 3) revealed the presence of HPY and the absence of HAP. The precipitate, therefore, consisted of HPY needles, in agreement with previ-



Fig. 3. XRD of the reacted fluid cell sample (bottom line). By overlaying this diffractogram with that from a metal stub with tape (top line), we were able to identify the precipitate in the fluid cell as HPY. The dissolution of HAP must have supplied phosphate which combined with Pb to form HPY.

ous research (e.g., Ma et al., 1993, 1994a,b; Xu and Schwartz, 1994; Lower et al., 1998). HAP was probably present in quantities below the detection limit of our diffractometer. Because HAP was the only source of phosphorous, HAP must have dissolved.

# 3.2. In Situ TMAFM of HAP surfaces

TMAFM images of HAP surfaces immersed in DDIW showed relatively nondescript, rounded microtopography (Fig. 4a). Upon introduction of Pb containing solution, in situ imaging became difficult because the solution precipitate interfered with the cantilever/tip and potentially the laser detection system (see below). In all cases in which we were able to collect stable images, the surfaces of HAP particles revealed crystallographically indistinct features (Fig. 4b), similar to the reaction blank. In one experiment, the surface of a HAP particle immersed in a Pb solution was imaged at least once an h for a period of 12 consecutive h. At no time did the HAP surface appear to be anything but HAP. Needle-like features were never observed, nor were tip-sample shape interaction artifacts (see Maurice and Lower, 1997) observed. These results suggested that HPY either was not nucleating on the surface of HAP, or that any HPY nucleation was occurring only at scattered, unobserved locations on the HAP surface.

#### 3.3. Ex Situ SEM and EDS of Reacted Fluid Cell Sample

SEM/EDS analysis of the reacted fluid cell sample revealed that the precipitate detected with the binocular microscope consisted of HPY needles preferentially associated with HAP particles (Fig. 5a). By tilting the sample, we were able to determine that the needles' long axes (i.e., c axes) were oriented more-or-less perpendicular to the surfaces of the underlying HAP particles (Fig. 5b). These needles were comprised of hexagonal prism faces (e.g.,  $\{10\overline{1}0\}$ ) and dipyramidal faces (e.g.,  $\{10\overline{1}1\}$ ). Few needles were detected in regions of the substrate which were devoid of HAP. EDS analysis of the



Fig. 4. In situ TMAFM images of the surface of HAP. (a) Image of the HAP surface in DDIW. Scan size = 5.0 mm on a side. (b) Image of the same HAP particle 12 h after injecting the Pb solution. (Scan size = 3.73 mm on a side) No etch pits were observed on the dissolving HAP. Despite the fact that an HPY precipitate was observed with the binocular microscope, the surface of HAP did not support a precipitate.

needles revealed that they were relatively pure, consisting of Pb and P with no detectable Ca.

### 3.4. Ex Situ TMAFM of Fluid Cell Effluent

Ex situ TMAFM images of the fluid cell's effluent showed elongate needles with six-fold axes of symmetry (Fig. 6). The length-to-width ratio of these needles was similar to the HPY needles imaged on the reacted fluid cell sample, with SEM (Fig. 5). Furthermore, no such needles were detected in the effluent from the reaction blank. This provided direct evidence that needles of HPY precipitated homogeneously in solution. It is unlikely that the needles formed on the filter membranes upon drying because effluent solution was removed from the filter membrane by rinsing immediately with deionized water. The needles imaged in the effluent appeared to have rounded





Fig. 5. SEM/EDS of the reacted fluid cell sample. (a) SEM images revealed needles preferentially associated with HAP particles. (b) By tilting the sample we could see that the needles were oriented vertically with respect to the HAP. EDS of the needles (data not shown) revealed that they were dominated by Pb and P. The relatively slow rate of HAP dissolution apparently caused HPY needles to nucleate in the solution adjacent to HAP particles. Subsequent growth of HPY occurred such that the needles grew upward into the solution. Scale bar on both images =  $10.0 \ \mu$ m.

ends, most probably because of geometric limitations related to the AFM tip shape (see Maurice and Lower, 1997).

### 3.5. Ex Situ SEM of the Cantilever/Tip

Further evidence that HPY did not require an HAP surface for nucleation came from ex situ SEM images showing needles of HPY on the cantilever/tip (Fig. 7). More needles were observed on the top surface of the cantilever than on the bottom. These needles were similar in size and dimensions to those imaged on the reacted fluid cell sample (Fig. 5). The presence of HPY on the surface of the cantilever indicates that the surface of HAP is not a prerequisite for nucleation. The needles either nucleated on the cantilever, or they nucleated in solution and simply fell onto the cantilever. More than likely, the needles nucleated in solution and simply fell onto the cantilever. This would help to explain why the top of the cantilever was covered with more needles than the bottom.



Fig. 6. Ex situ TMAFM image of products in the fluid cell effluent filtered onto pc membrane. Needles with hexagonal symmetry as well as prism and dipyramidal faces were observed. This provided direct evidence of homogeneous precipitation of HPY in solution. Scan size = 661 nm on a side.

#### 4. DISCUSSION

# 4.1. Simultaneous Dissolution of HAP and Precipitation of HPY

In agreement with the results of other studies (Ma et al., 1993, 1994a,b; Xu and Schwartz, 1994; Lower et al., 1998), our results show that HAP dissolution provides phosphate which combines with Pb to form HPY. At least three processes (see Fig. 8) are involved in the sequestration of Pb from solution: (1) HAP dissolution, (2) HPY nucleation, and (3) HPY growth. Comparison of solubility products (K<sub>sp</sub>) of HAP and HPY shows that HPY formation is thermodynamically favorable, in our study system. The  $K_{sp}$  of HPY at 25°C is  $10^{-77}$  (Nriagu, 1972, 1973). From the  $K_{sp}$  value for HPY and standard state chemical potentials for  $PO_4^{3-}$ ,  $OH^-$ , (Anderson and Crerar, 1993) and Pb<sup>2+</sup> (Wolery and Daveler, 1992) we calculated a standard state chemical potential of -3761.38 kJ mol<sup>-1</sup> for HPY. This value was then used with the standard state chemical potentials of Ca2+ (Anderson and Crerar, 1993) and HAP (Wolery and Daveler, 1992) along with the overall reaction:

$$Ca_{5}(PO_{4})_{3}OH + 5Pb^{2+} \longleftrightarrow Pb_{5}(PO_{4})_{3}OH + 5Ca^{2+}$$
(3)

to calculate a standard state Gibbs energy change ( $G_r$ ) of -137.08 kJ mol<sup>-1</sup> for stoichiometric conversion of HAP to HPY. Clearly, in the presence of dissolved Pb<sup>2+</sup>, conversion of HAP to HPY is thermodynamically favorable.

## 4.2. Hydroxylapatite Dissolution

Under our experimental conditions, HAP dissolution was transport controlled. Etch pits were not observed on dissolving HAP surfaces; instead rounded features indicative of transportcontrolled dissolution were present (Fig. 4). Fox et al. (1978) attributed rounded morphology to transport-controlled processes. Previous ex situ SEM, TEM, and AFM imaging of HAP particles reacted in batch studies (Ma et al., 1993; Xu and





Fig. 7. SEM image of the cantilever/tip used in a fluid cell experiment. (a) The top of the cantilever was covered with HPY needles. (b) The bottom of the cantilever, which supports the tip (sharp pyramidal feature at the end of the cantilever), showed considerably fewer needles. Apparently, HPY needles precipitated in solution and fell onto the cantilever/tip. Scale bar on both images = 6.7  $\mu$ m.

Schwartz, 1994; Lower et al., 1998) also showed rounded topography and an absence of etch pits.

Transport-controlled dissolution is supported by several other lines of evidence. First, Christoffersen et al. (1978) observed that dissolution of poorly crystalline HAP, in static unstirred systems is transport controlled. Our HAP was poorly crystalline (Lower et al., 1998) and was reacted in the unstirred environment of the AFM fluid cell. Second, the solubility of the HAP used in this study was greater than  $10^{-3}$  (Xu and Schwartz, 1994), suggesting transport controlled processes (Berner, 1978, 1980, 1981). Third, the surfaces of HAP particles were immersed in DDIW and Pb solutions which initially contained no detectable Ca or phosphate. Hence, the fluid cell solution was, at least initially, extremely undersaturated with respect to HAP. Christoffersen (1980) reported that at very low saturation, the stable size of etch pits becomes so small that nucleation is no longer rate determining. In our study, the significantly lower solubility of HPY as well as the more rapid precipitation of HPY, relative to HAP dissolution (see below) likely maintained a state of substantial undersaturation throughout the reaction periods. Finally, dissolution of HAP and pre-



Fig. 8. Schematic diagram of processes involved in the sequestration of Pb from solution. (a) The dissolution of HAP in a static environment resulted in a diffusional gradient of phosphate ions away from the HAP surface; whereas initially, Pb was uniformly distributed throughout the solution. (b) Nuclei of HPY form homogeneously near the surface of HAP, resulting in a depletion of ions within this nucleation zone. (c) Subsequent sequestration of aqueous Pb occurred via the growth or elongation of HPY needles. We hypothesize that phosphate ions diffuse along the prism faces (parallel to the c axis) of HPY needles to combine with Pb at the needles' terminal dipyramidal faces. This consumption of phosphate enhanced the continued dissolution of HAP until all available Pb was removed from solution.

cipitation of HPY occur very rapidly, often going to completion in <10 min (Ma et al., 1993, 1994a,b; Xu and Schwartz, 1994). Because transport controlled dissolution is the fastest means of dissolution (Berner, 1978), it is unlikely that surface reaction controlled dissolution could have supplied enough phosphate in such a short time period to sequester Pb via HPY precipitation.

#### 4.3. Hydroxypyromorphite Precipitation

Precipitation or crystallization of HPY can be divided into nucleation and growth processes. These processes compete for dissolved constituents such that, under different conditions, different processes may dominate (Berner, 1980, 1981). Lower et al. (1998) have discussed nucleation and growth processes related to HPY precipitation at different initial Pb concentrations.

### 4.4. Hydroxypyromorphite Nucleation

As presented above, nucleation of HPY appeared to occur primarily homogeneously, in solution, although we cannot rule out some potential heterogeneous nucleation at unobserved reactive sites. Homogeneous nuclei result from the collision of appropriate ions, the success of which is dependent upon collisional frequency (Nielsen, 1964). Upon injection of Pb solution into the fluid cell, Pb ions probably were distributed uniformly throughout the cell (Fig. 8a), except for short-range effects of surface charge. In this study, the only source of phosphate was HAP, and HAP dissolution resulted in a diffusional gradient of phosphate ions away from the HAP surface. Hence, nuclei of HPY would likely form near the HAP surface, where there was increased probability of successful collisions of Pb with phosphate (Fig 8b).

This reasoning is in agreement with both in situ binocular microscope observations (Fig. 2) and ex situ observations of the reacted fluid cell sample (Fig. 5), showing that HPY was preferentially associated with HAP. As the system was static, phosphate released by HAP dissolution was probably limited by diffusion to the environs of HAP particles, and quickly consumed by HPY precipitation. Upon HPY nucleation, the solution directly surrounding HAP particles would become at least temporarily depleted in Pb and phosphate (Fig. 8b).

The rates of these processes can be understood by considering Pb sequestration as a sequential reaction involving diffusion of phosphate ions away from dissolving HAP, followed by combination of phosphate with Pb to form HPY. In a sequential reaction, the slowest step controls the overall rate of reaction (Drever, 1988). Given that HPY is found almost exclusively in association with HAP, HPY formation must be occurring faster than phosphate diffusion rates, which would otherwise carry reactants further afield. Therefore, it is likely that diffusion of phosphate into solution is the limiting step to HPY crystallization, as shown in the following reaction sequence:

$$\operatorname{HAP}_{\longrightarrow}^{k_1}(\operatorname{PO}_4)_{aq} + \operatorname{Pb}_{aq}_{\longrightarrow}^{k_2}\operatorname{HPY}$$
(4)

where  $k_1 \ll k_2$ .

Previous researchers have hypothesized that close association of HPY with HAP indicated that the HPY formed heterogeneously on the surface of HAP. For example, after allowing a Pb solution to flow through a column of HAP, HPY was detected as an apparent coating on the HAP particles (Ma et al., 1993). However, we believe that the close association between HPY and HAP is a function of nucleation processes and relative rates of HAP dissolution and HPY precipitation. This hypothesis is supported by macroscopic observations reported in Xu and Schwartz (1994) suggesting that precipitation of HPY is faster than dissolution of HAP.

#### 4.5. Hydroxypyromorphite Growth

HPY needles were relatively large and had a homogeneous size distribution (Fig. 5), suggesting that once crystals nucleated, further Pb sequestration from solution was due to growth of these embryonic crystals, rather than continued nucleation of additional crystals. Nucleation creates an interface, resulting in increased Gibbs energy of reaction, whereas growth is a spontaneous process resulting in decreased Gibbs energy (Berner, 1981). The in situ study reported here revealed HPY needles with virtually identical attributes to those reported in the analogous experiment conducted by Lower et al. (1998), in which it was determined that HPY growth was the dominant means by which Pb was removed from solution. We calculate that the amount of HAP in the fluid cell would produce more than enough phosphate to remove all Pb from solution. Hence, much of the aqueous Pb apparently was removed via growth rather than continuous nucleation of HPY. Moreover, the elongate habit of HPY needles indicates that growth perpendicular to the c axis was much greater than that parallel to the c axis. As shown in the SEM and AFM images (Figs. 5 and 6), the prism faces (e.g., {1010}) were the largest faces on the HPY crystals and thus grew more slowly than the dipyramidal faces (e.g., {1011}). In other words, Pb sequestration was dominated by growth of dipyramidal faces resulting in elongation of HPY needles.

Electron Diffraction analyses of HPY needles formed in the analogous ex situ experiment described by Lower et al. (1998) indicated that the HPY needles may contain structural defects along their c axis. Such defects are to be expected in a solid phase which forms very rapidly, as did HPY in our experiments. Furthermore, these defects provide an infinite supply of kink sites (Burton et al., 1951; O'hara and Reid, 1973) and, therefore, may have caused HPY to grow as needles rather than as equant crystals.

SEM observations (Fig. 5) showed HPY needles oriented more-or-less radially around the surfaces of HAP particles, suggesting that HPY needles were growing outward toward the source of Pb (i.e., the Pb containing solution) as phosphate anions were consumed from within the diffusion field of the HAP particles. Most probably, phosphate ions diffused along the prism faces, parallel to the c axis of HPY needles and combined with Pb and OH to form growth layers more-or-less perpendicular to the c axis of the needles (Fig. 8c). Hence, the growth of HPY would control the activity of phosphate ions adjacent to the HAP particles. This would lead to an undersaturated state with respect to HAP, and enhanced dissolution, until all of the Pb was removed from solution.

Our results, which suggest increased dissolution of HAP in the presence of Pb, are in agreement with results of previous research. Macroscopic results of solution chemistry reported by Xu and Schwartz (1994), indicate a three-fold increase in the dissolution rate of HAP, in the presence of Pb. While it may be possible that Pb directly catalyzes HAP dissolution by removing phosphate ions directly from the HAP surface, the present data suggest that Pb plays a more indirect role by reducing the saturation state surrounding dissolved HAP particles.

### 5. CONCLUSIONS

Our results reveal that typical stirred, batch experiments may not be representative of soil environments when diffusion processes are limiting. The in situ results show that although HPY does not nucleate on the surfaces of HAP under the experimental conditions, the HPY needles are closely associated with the HAP surface due to diffusional limitations. These results are consistent with ex situ SEM, TEM, and AFM imaging of the same HAP particles reacted in batch studies (Ma et al., 1993; Xu and Schwartz, 1994; Lower et al., 1998). Thus, some extrapolation to a broader range of experimental conditions seems warranted.

While this study shows that at least some Pb is sequestered by the homogeneous nucleation and precipitation of a solid phase, there are some inherent limitations to the methods used in this study. For example, TMAFM was not capable of atomicscale resolution; hence, we could not rule out adsorption of Pb to the surfaces of HAP. Likewise, AFM is a surface-sensitive instrument, so that we could not rule out the possibility of diffusion of Pb into the HAP structure. Structure-sensitive and depth-sensitive measurements (i.e., X-ray absorption spectroscopy, Infra-red spectroscopy, and X-ray photoelectron spectroscopy) are presently being obtained and will be presented in a future publication to address these issues

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