Role of Fe(II) and phosphate in arsenic uptake by coprecipitation

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Abstract

Natural attenuation of arsenic by simple adsorption on oxyhydroxides may be limited due to competing oxyanions, but uptake by coprecipitation may locally sequester arsenic. We have systematically investigated the mechanism and mode (adsorption versus coprecipitation) of arsenic uptake in the presence of carbonate and phosphate, from solutions of inorganic composition similar to many groundwaters. Efficient arsenic removal, >95% As(V) and ~55% in initial As(III) systems, occurred over 24 h at pHs 5.5–6.5 when Fe(II) and hydroxylapatite (Ca₅(PO₄)₃OH, HAP) “seed” crystals were added to solutions that had been previously reacted with HAP, atmospheric CO₂(g) and O₂(g). Arsenic adsorption was insignificant (<10%) on HAP without Fe(II). Greater uptake in the As(III) system in the presence of Fe(II) was interpreted as due to faster As(III) to As(V) oxidation by molecular oxygen in a putative pathway involving Fe(IV) and As(IV) intermediate species. HAP acts as a pH buffer that allows faster Fe(II) oxidation.

Solution analyses coupled with high-resolution transmission electron microscopy (HRTEM), X-ray Energy-Dispersive Spectroscopy (EDS), and X-Ray Absorption Spectroscopy (XAS) indicated the precipitation of sub-spherical particles of an amorphous, chemically-mixed, nanophase, Fe₃[(OH)₃(PO₄)(AsVO₄)]ÀnH₂O or Fe₃[(OH)₃(PO₄)(AsIVO₄)₃]ÀnH₂O, where AsIVO₄ is a minor component.

The mode of As uptake was further investigated in binary coprecipitation (Fe(II) + As(III) or P), and ternary coprecipitation and adsorption experiments (Fe(II) + As(III) + P) at variable As/Fe, P/Fe and As/P/Fe ratios. Foil-like, poorly crystalline, nanoparticles of Fe₃[(OH)₃] and sub-spherical, amorphous, chemically-mixed, metastable nanoparticles of Fe₃[(OH)₃], PO₄nH₂O coexisted at lower P/Fe ratios than predicted by bulk solubilities of strengite (FePO₄•2H₂O) and goethite (FeOOH). Uptake of As and P in these systems decreased as binary coprecipitation > ternary coprecipitation > ternary adsorption.

Significantly, the chemically-mixed, ferric oxyhydroxide–phosphate–arsenate nanophases found here are very similar to those found in the natural environment at slightly acidic to circum-neutral pHs in sub-oxic to oxic systems, such phases may naturally attenuate As mobility in the environment, but it is important to recognize that our system and the natural environment are kinetically evolving, and the ultimate environmental fate of As will depend on the long-term stability and potential phase transformations of these mixed nanophases. Our results also underscore the importance of using sufficiently complex, yet systematically designed, model systems to accurately represent the natural environment.

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1. INTRODUCTION

Predicting arsenic uptake at mineral surfaces in natural environments for developing effective remediation strategies has been the focus of intense interest because arsenic, especially As(III), is extremely toxic and highly mobile (Hug et al., 2001; Goldberg, 2002; Harvey et al., 2002; Roberts et al., 2004). In oxic or sub-oxic environments and circum-neutral pHs, arsenite (As(III)) and arsenate (As(V)) are the most common oxidation states, existing as H3AsO3⁻, H2AsO4⁻ or HAsO4²⁻ (Sadiq, 1997; Smith et al., 1998; Yang et al., 2005). Several laboratory and field studies have shown that arsenic speciation and sorption are governed by factors such as solution composition, competition with other oxyacids and the type of sorbent phases, ultimately controlling arsenic mobility and bioavailability (Wilkie and Hering, 1996; Manning and Goldberg, 1997; Manning et al., 1998; Arai et al., 2001; Goldberg and Johnston, 2002; Harvey et al., 2002; Dixit and Hering, 2003; Amirbahman et al., 2006).

A large number of studies have characterized As(V) uptake at different oxyhydroxide surfaces, but fewer have dealt with As(III). Uptake has been examined in terms of the acid–base behavior of aqueous arsenic species and of oxyhydroxide surface functional groups, over a range of solution conditions. For example, arsenate adsorption on ferrhydrite increases with decreasing pH, whereas sorption of arsenite is less pH-sensitive (Raven et al., 1998). On γ-Al2O3, As removal is strongly pH-dependent but insensitive to changes in ionic strength (Arai et al., 2001). X-Ray Absorption Spectroscopy (XAS) results show that As(III) forms inner- and outer-sphere surface complexes, whereas inner-sphere As(V) surface complexes dominate over a wide range of solution compositions (Arai et al., 2001).

The presence of co-occurring oxyanions may significantly influence sorption of arsenic at the solid–water interface (Wilkie and Hering, 1996; Meng et al., 2000, 2001; Gräfe et al., 2004). The affinities of phosphate and arsenate for iron oxyhydroxide surfaces are quite similar (Liu et al., 2001), but because phosphate (and silicate) are usually present in larger concentrations, they may significantly reduce As sorption. Carbonate also has high affinity for iron oxyhydroxide surfaces but its role in As uptake is less clear (e.g., Van Geen et al., 1994; McNeil and Edwards, 1997; Meng et al., 2002; Villalobos and Leckie, 2000; Appelo et al., 2002; Roberts et al., 2004; Ciardelli, 2006).

The effect of metal ions on As uptake has also been examined by XAS. Sorption of As(V) on goethite increases in the presence of Zn, forming predominantly binuclear, bidentate, inner-sphere complexes at concentrations below surface saturation; an adamite-like [Zn₃(AsO₄)OH] surface precipitate is more favorable at 1 mmol m⁻² of Zn which the authors interpreted as “surface saturation” (Gräfe et al., 2004). Improved As(III) uptake is observed in the presence of added aqueous iron, due to coprecipitation of ferric oxyhydroxides that sequester arsenic, and Fe(II) is more effective than Fe(III). These results are obtained even in complex solutions such as synthetic and natural Bangladeshi groundwaters that contain competing oxyacids such as bicarbonate, phosphate, and silicate (Huang and Vane, 1989; Hug and Leupin, 2003; Roberts et al., 2004; Ciardelli et al., 2006). The enhancing effect of Fe(II) was interpreted in terms of enhanced oxidation rates of As(III) to As(V) by molecular oxygen in a Fenton Reaction pathway promoted by putative Fe(IV) and As(IV) reactive intermediates (Hug and Leupin, 2003). The mode of As uptake in terms of adsorption versus coprecipitation in such systems has not been investigated in detail, and provides one of the main motivations of the present work.

Although arsenic uptake at oxyhydroxide surfaces has been investigated thoroughly, phosphate mineral surfaces have received much less attention as possible sorbents. Furthermore, the possibility of mixed phases such as ferric oxyhydroxide–phosphate/sulfate–arsenate/arsenite acting as potential sinks for contaminants has not been studied in detail, partly because of the complexity involved in systematic identification, characterization, and determination of the stability of such phases, even when it is becoming increasingly evident that mixed phases are formed in natural environments (Craw and Chappell, 2000; Perret et al., 2000; Webb et al., 2000; Harvey et al., 2002; Morin et al., 2003; Hyacinthe and Van Cappellen, 2004). In most of these environments, the solutions are initially anoxic or sub-oxic where Fe(II) is oxidized to Fe(III), but it is not known whether As is taken up by simple adsorption and/or coprecipitation. The motivation of the present study was to investigate the mechanism and modes of As uptake by adsorption and/or rapid coprecipitation of mixed ferric oxyhydroxide–phosphate phases from solutions that contain iron and are supersaturated with respect to hydroxyapatite (Ca₅(PO₄)₃OH, HAP) similar to many groundwaters.

2. EXPERIMENTAL PROCEDURES

2.1. Chemicals and preparation of solutions

All sorption samples were prepared at room temperature using solutions pre-reacted with air and HAP crystals to obtain steady-state values of total dissolved calcium, phosphate, and pH (Lee et al., 2005). We used precipitated, reagent-grade, tribasic calcium phosphate (Ca₅(PO₄)₃OH, HAP; J.T. Baker™) with an average particle size of 100 nm, and a specific surface area of 57 m² g⁻¹ determined by a multi-point N₂(g) B.E.T. isotherm. Oxygen and CO₂(g) were introduced into solution by bubbling air through an HAP 0.5 g L⁻¹ B.E.T. isotherm. Oxygen and CO₂(g) were introduced into solution by bubbling air through an HAP 0.5 g L⁻¹ (DI) water, till the final suspension pH remained steady at 7.3. The suspension was then centrifuged and filtered through 0.1 μm nylon membrane filters to remove suspended HAP particles. This solution is called “pre-equilibrated” (PE) solution.

Stock solutions containing total dissolved concentrations of 0.01 M [As(III)]ₗₒtotal, 0.01 M [As(V)]ₗₒtotal and 0.1 M [Fe]ₗₒtotal were prepared using NaAsO₂ (Sigma–Aldrich™), Na₂H₂AsO₄·7H₂O (J.T. Baker™) and FeCl₃·4H₂O (Fisher™), sealed and stored at 4°C. All batch and ambient room-oxidation experiments were conducted in the presence of light in low density polyethylene (LDPE) bottles and capped lightly for the duration of the experiment.
2.2. Batch uptake and desorption experiments in PE solution

The initial solution composition used is provided in Table 1. The As(III) or As(V) stock solution was added to 200 mL of PE solution at pH 7.3 to obtain a final solution of 6 μM As. In one experiment, Fe(II) stock solution was added to the PE solution to yield 250 μM total Fe(II) without any As. These are the As(III), As(V) and Fe control systems. As(III) or As(V) and Fe(II) were also combined together with PE solution (As + Fe system). Each experiment was prepared without and with 0.5 g L−1 HAP seed crystals. These are called the As + HAP, Fe + HAP, and As + Fe + HAP systems. All experiments were performed in duplicate and allowed to react for 24 h. Solution pH was measured by an Orion Ross® electrode. In Fe-bearing solutions pH dropped from 7.3 to ~5.5 in the absence of HAP seeds and to ~6.5 in the presence of HAP seeds. After 24 h reaction, each solution was centrifuged for 30 min at 15,000 rpm and the supernatant solution was filtered through 0.1 μm nylon membrane filters to remove HAP seed crystals (if present) and any newly precipitated solid phases. The filtered solutions were frozen and stored at −20 °C until analysis by inductively coupled plasma–optical emission spectroscopy (ICP-OES).

The As-sorbed HAP crystals (0.5 g HAP L−1) were re-suspended in 200 mL of pre-equilibrated solutions to initiate desorption. The suspensions were equilibrated on a reciprocal shaker table at 120 osc min−1 at room temperature for 7 days, centrifuged, filtered, and analyzed by ICP–OES for [As]tot. The pH of these suspensions remained constant throughout the duration of the desorption experiment.

2.3. Fe oxidation and As(III) uptake kinetic experiments in PE solution

Iron oxidation experiments were conducted for 24 h, with initial [Fe(II)]tot = 250 μM and initial [As]tot = 6 μM in PE solution (Table 1). Total solution volumes were 200 mL. The Fe(II) was added with stirring for the first 10 min in a N2-filled glove bag and allowed to sit without stirring in the glove bag for the remainder of 1 h. The bottles were then removed from the glove bag, lightly capped, and placed in air without stirring for 23 h. Aliquots of the suspensions were periodically collected and filtered through 0.1 μm nylon membrane filters. All experiments were performed in duplicate. At 24 h, solution pHs were ~5.5 and 6.5 in experiments without and with HAP seeds.

Fe(II) oxidation kinetics were determined as loss of Fe(II) over time. Aqueous [Fe(II)] was analyzed using a UV–Vis ferrozine assay (Stookey, 1970), where 0.5 mL of the filtered solution was mixed into 0.5 mL of a 0.1 HCl solution. Then, 100 μL aliquot of the mixed solution was added into 5 mL of the ferrozine reagent in a 10 mL test tube. The ferrozine reagent (monosodium salt hydrate of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-p,p'-disulfonic acid) reacts with Fe(II) to form a stable magenta-colored complex, absorbing at 562 nm with a molar absorption coefficient close to 30,000 L mol−1 cm−1 at 4 < pH < 9.

Uptake of As in the As(III) + Fe(II) + HAP system was determined by periodically measuring [As]tot in the centrifuged, filtered solutions by ICP-OES, and is designated [As]tot,pre-cartridge. An aliquot of the filtered solution was passed through an arsenic speciation cartridge (MetalSoft™, Inc.) that selectively retains As(V) (Meng and Wang, 1998; Meng et al., 2002). The eluent was analyzed for remaining [As]tot, post-cartridge = [As(III)]tot,unbound by ICP–OES. The unbound amount of As(V), not taken up by adsorption or coprecipitation is:

\[
[\text{As(V)}]_{\text{tot,unbound}} = [\text{As}]_{\text{tot,pre-cartridge}} - [\text{As(III)}]_{\text{tot,unbound}}
\]

These cartridges are reported to have an As(V) retention efficiency of 91–95% (Meng and Wang, 1998; Dr. Linda Roberts, EAWAG, Switzerland, pers. commun.).

Dissolved oxygen (DO) levels were monitored periodically using a Diamond General™ polarographic needle.

Table 1

<table>
<thead>
<tr>
<th>Species</th>
<th>PE solutiona</th>
<th>0.1 M NaCl solution</th>
<th>SBGW</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8H5Cl</td>
<td>75</td>
<td>—</td>
<td>2500</td>
</tr>
<tr>
<td>NaCl</td>
<td>0</td>
<td>—</td>
<td>1600</td>
</tr>
<tr>
<td>Na2AsO3 or Na2HAsO4·7H2O</td>
<td>6 or 12</td>
<td>0.1 M (+10, 50, 100 μM)</td>
<td>6.67 or 13.34</td>
</tr>
<tr>
<td>Fe(II)Cl2</td>
<td>250</td>
<td>250</td>
<td>68–895</td>
</tr>
<tr>
<td>CH3COOH</td>
<td>500</td>
<td>0.1005 M</td>
<td>6.67</td>
</tr>
<tr>
<td>As(III) or As(V)</td>
<td>6</td>
<td>0, 1, 10, 50, 100</td>
<td>68–895</td>
</tr>
<tr>
<td>HCO3−</td>
<td>Not measured (83.47, calculatedc)</td>
<td>Not measured</td>
<td>8000</td>
</tr>
<tr>
<td>PO43−</td>
<td>43</td>
<td>0, 1, 10, 50, 100</td>
<td>96.8</td>
</tr>
<tr>
<td>SO42−</td>
<td>0</td>
<td>—</td>
<td>68–895</td>
</tr>
<tr>
<td>pHd</td>
<td>7.3</td>
<td>7.0 ± 0.1</td>
<td>6.5–8.5</td>
</tr>
<tr>
<td>pHf (− HAP seeds)</td>
<td>5.6–5.7</td>
<td>5.5–5.8</td>
<td>—</td>
</tr>
<tr>
<td>pHe (HAP seeds)</td>
<td>6.2–6.4</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

a All concentrations reported in μM units unless otherwise specified.
b Metastable, supersaturated with respect to HAP.
c Calculated using Geochemist’s Workbench® aqueous speciation software (Bethke, 1996).
d Initial pH.
e Final pH.
oxygen electrode connected to a pico-ammeter that was calibrated at room temperature by using a solution devoid of oxygen by purging with N\textsubscript{2} (g) and a second solution saturated with O\textsubscript{2} (g) by bubbling air through it.

2.4. Binary and ternary coprecipitation and adsorption batch experiments in 0.1 M NaCl solutions

For each batch experiment, 200 mL of deionized water (18.2 M\textsubscript{2} cm) was dispensed into acid-washed LDPE bottles. The ionic strength was controlled by adding 0.1 M NaCl (Fisher\textsuperscript{TM}). Depending on the experiment, As and/or P were added from stock solutions of 0.01 M Na\textsubscript{2}AsO\textsubscript{3} and 0.02 M Na\textsubscript{3}HPO\textsubscript{4} (Fisher\textsuperscript{TM}) at total concentrations of 1, 10, 50, and 100 \mu M (Table 1). Following the addition of As and/or P, 0.1 M HCl (Fisher\textsuperscript{TM}) or 0.1 M NaOH (Fisher\textsuperscript{TM}) was added to adjust the pH back up to 7.00 ± 0.1; the volume of acid and base added was less than 200 \mu L in all cases. Subsequently, 250 \mu M of Fe(II) from a stock solution of 0.1 M FeCl\textsubscript{2}·4H\textsubscript{2}O was added (Table 1). For the ternary adsorption experiment, As was added after 12 h of equilibration instead of at the start. In one experiment, only 250 \mu M Fe(II) was added to DI water (no NaCl or any other ions).

All experimental bottles were lightly capped and allowed to react for 24 h. The solution pH decreased to ~5.5–5.8 at 24 h. At the end of each reaction time, the suspensions were centrifuged for 30 min at 15,000 rpm and filtered through a 0.1 \mu m nylon filter. The solutions were then acidified (2\% HNO\textsubscript{3}, ultra high purity Fisher\textsuperscript{TM}), and stored at 4 \degree C until ICP–OES analysis, and the solids collected were analyzed by HRTEM/EDS.

2.5. ICP–OES solution analyses

Aliquots (7 mL) of the centrifuged and filtered solutions were analyzed by ICP–OES on a Perkin-Elmer Optima 4300 DV instrument for [Ca\textsubscript{tot}], [P\textsubscript{tot}], [As\textsubscript{tot}], and [Fe\textsubscript{tot}], as appropriate, from the batch uptake experiments in PE solution, binary and ternary coprecipitation and adsorption experiments in 0.1 M NaCl experiments and in the desorption experiments.

2.6. HRTEM–EDS analysis of precipitated solids

The HAP seed crystals were confirmed to be HAP before and after reaction by powder X-ray diffraction (XRD) (Scintag Pad V with a Ge solid-state detector; Cu K\alpha radiation) with the solid mounted on a low-background specimen-holder. Any solid phases formed during the 24-h batch uptake experiments and HAP seed crystals (if present) were collected from the filter paper, dried in air, and characterized by XRD but only “amorphous” phases were detected.

For high-resolution transmission electron microscopy (HRTEM) analysis, solid phases were prepared by centrifuging the 24-h batch uptake suspensions, decanting the supernatant solution, re-suspending the solids in DI water, depositing a drop of the suspension onto holey carbon-coated Cu grids and drying in air. In addition to the batch uptake experiments, HRTEM analyses were also performed for solids formed in one experiment where 250 \mu M FeCl\textsubscript{2} was added to 200 mL of deionized water (18 M\textsubscript{2} cm), and for solids from the binary experiments in 0.1 M NaCl solution. All samples were analyzed on a Tecnai F30 field emission gun scanning transmission electron microscope equipped with an X-ray Energy-Dispersive Spectroscopy (EDS) system (EM Vision 4.0), at the University of Chicago or on a JEOL 2010 FASTEM equipped with EDS at the University of New Mexico, Albuquerque. Point-to-point resolution of the HRTEM is 0.19 nm.

2.7. EXAFS and XANES analysis of precipitated solids

For XAS analysis, aqueous and solid-phase standards for As\textsuperscript{III} \textsubscript{aq}, As\textsuperscript{V} \textsubscript{aq}, As\textsubscript{5}O\textsubscript{5}(s), and solids from the As\textsuperscript{III} or As\textsuperscript{V} + Fe\textsuperscript{II} + HAP systems were prepared fresh before each run and preserved under N\textsubscript{2}(g) atmosphere to avoid further oxidation. Wet samples retained by filtration were placed between pieces of Kapton tape. XAS measurements were performed at the Advanced Photon Source, Argonne National Laboratory on the bending magnet beam-line of the DUPONT-Northwestern-Dow Collaborative Access Team (DND-CAT, Sector 5). The storage ring was operating at 7.0 GeV with a beam current maintained at 100 mA. The beamline was equipped with a Si(111) double crystal monochromator that was used to vary the X-ray energy from 200 eV below to 900 eV above the absorption K edge of As at 11,868 eV. Higher harmonics were rejected using a flat Rh-coated mirror with a cutoff energy of 20 keV at 3 mrad, and detuning slightly the second crystal of the monochromator. For edge energy calibration, the X-ray absorption spectrum of a reference foil was collected with each sample. The incident intensity, \textit{I}_0, and transmitted intensity, \textit{I}_T, were measured using Oxford ionization chambers with a path length of 29.6 cm. The fluorescence signal was measured with a Stern-Heald “Lytte” detector equipped with a Z-1 filter for continuous scan experiments (CS-XAS), and with a 13 element Canberra solid-state detector for step scans. For CS-XAS experiments, the detectors were connected to Stanford Research System SRS 570 current amplifiers, and the signals were continuously recorded at 12.5 kHz using a sixteen-bit analog to digital converter. In general, 9 successive scans, of 90 s each, were recorded for every sample (Webb et al., 2003). The data were then binned and averaged over 1 eV for the pre-edge and the near edge regions, and over \textit{k} = 0.05 \AA\textsuperscript{–1} in the EXAFS (Gaillard et al., 2001). The analysis of the spectra was performed using the package SIXPack (Webb, 2005).

2.8. Thermodynamic speciation calculations

Thermodynamic speciation calculations were performed for solutions of compositions corresponding to the batch uptake experiments and the 0.1 M NaCl solutions. We used the software package Geochemist’s Workbench 3.0\textsuperscript{TM} (Bethke, 1996), based on the DATA0 thermodynamic database that is also used in SUPCRT and EQ3NR/EQ6NR (Johnson et al., 1992; Wolery, 1992a,b).
3. RESULTS

3.1. Speciation calculations

Thermodynamic speciation calculation on a solution of initial composition as shown in Table 1 was predicted to precipitate a small amount of HAP (6.09 μM or 3.06 mg), bringing the predicted solution pH to 6.6. \( [\text{Ca}]_{\text{tot}} = 19.68 \mu \text{M}, [\text{PO}_4]_{\text{tot}} = 24.6 \mu \text{M}, \text{HCO}_3^- = 59.47 \mu \text{M} \) and \( \text{CO}_2_{\text{aq}} = 3.53 \mu \text{M} \). The measured composition of the PE solution differed from this (see Table 1) suggesting that the solution was slightly supersaturated and at metastable equilibrium. Additional speciation calculations for PE solutions also containing Fe(II) and As(III) or As(V) were conducted. When Fe(II) is added to the PE solution without HAP seed crystals, at equilibrium, the calculations indicate precipitation of 147 μM strengite and 102 μM amorphous Fe(III)(OH)₃ accounting for almost 100% oxidation of the initial 250 μM Fe(II), and pH drops to 3.4 because buffering by atmospheric CO₂(g) is not sufficient to overcome the acid released by Fe(II) oxidation. In the presence of HAP seed crystals, dissolution of only 0.03 gL⁻¹ of HAP seed crystals is sufficient to buffer the pH at 6.3–6.5.

3.2. Batch uptake experiments

The fractional uptake of As(III) or As(V) and Fe from the various solutions is shown in Fig. 1(a). Almost no As was removed from the As control solution. In the As + Fe(II) system, As(III) and As(V) removals were 13% and 23%, and 40–50% Fe uptake was obtained comparable to the Fe control solution. The Fe uptake measured was less than the 100% uptake predicted by the thermodynamic calculations indicating that our system has not achieved equilibrium at 24 h. In the As + HAP systems, less than 10% As(III) and 20% As(V) uptake was achieved. Fe uptake increased to 96% in the Fe(II) + HAP system. Finally, in the As + Fe(II) + HAP solutions, uptake increased dramatically up to ~53% for As(III), 95% for As(V), and 85–96% for Fe.

In the Fe-bearing systems, solution pHs dropped rapidly from an initial value of 7.3 to 6.0 within 30 min, then stabilized over 3 h at pH 5.6–5.7 without HAP seed crystals and at 6.2–6.4 with HAP seeds. A yellowish color was seen visually for all Fe-bearing PE solutions.

Initial values of \( [\text{Ca}]_{\text{total},i} = 75 \mu \text{M} \) and \( [\text{P}]_{\text{total},i} = 43 \mu \text{M} \) were measured in the PE solution. The final amounts of Ca and P remaining in solution are shown in Fig. 1(b) for the As(III) and As(V) systems. Compared to the As and Fe control solutions, final \( [\text{Ca}]_{\text{tot}} \) was almost unchanged in the As(III) and As(V) systems. In contrast, final \( [\text{Ca}]_{\text{tot}} \) significantly increased in the Fe(II) + HAP and As + Fe(II) + HAP systems. Significantly greater removal of \( [\text{P}]_{\text{total}} \) was observed for all the experiments containing Fe relative to the As control, and limited P removal was seen in the As + HAP system similar to As controls. The \( [\text{P}]_{\text{tot}} \) trends were, thus, exactly opposite to the \( [\text{Ca}]_{\text{tot}} \) trends and similar to the \( [\text{Fe}]_{\text{tot}} \) trends.

3.3. Reversibility of arsenic uptake

The reacted, filtered HAP particles that were re-suspended in PE solutions for 7 days, showed very similar amounts of As desorption, 20% and 18%, respectively, in the solutions that initially had As(III) and As(V).

3.4. Oxidation of Fe(II) and As(III)

Loss of Fe(II) in solution by oxidation to Fe(III) is shown for the Fe(II) control, As(III) + Fe(II), Fe(II) +...
HAP, and As (III) + Fe(II) + HAP systems (Fig. 2a). An initial rapid oxidation of Fe(II) was observed in the first hour followed by a slower oxidation rate till the end of experiments. The rate is faster in the presence of HAP crystals. In the absence of HAP seed crystals, the solution pHs stabilized at 5.6–6.3 and only 60–70% Fe(II) oxidation was achieved at 24 h, compared to pHs 6.2–6.7% and 80–90% oxidation in the presence of HAP.

Dissolved oxygen (DO) levels in the Fe(II) + HAP and As(III) + Fe(II) + HAP experiments are shown in Fig. 2(b). Similar to Fe(II), the DO levels dropped rapidly within 1 h, although conditions remained oxic (above 4.5 ppm), and slowly recover back to equilibrium level with atmospheric oxygen at room temperature. These trends can be explained by the fact that the experiments were conducted in a glove bag for the first hour and then opened to air.

The uptake of As (III) and As$_{50}$ in the As (III) + Fe(II) + HAP experiment is also shown in Fig. 2(b). The amount of As removed increases rapidly in the first hour followed by a slower rate of uptake up to almost 70%. The two sets of values are similar indicating that most of the As removed from solution was in the As(V) form.

3.5. XANES and EXAFS results

XANES spectra of standard aqueous and solid-phase samples of As(III)(aq), As(V)(aq), and As$_2$O$_5$(s) were compared to spectra of solid samples formed in the As(III) or As(V) + Fe(II) + HAP systems (Fig. 3a). The XANES spectra clearly indicate that As(V) was the predominant form of As in all inspected samples. Traces of As(III) may have been present but cannot be quantified precisely. In order to test for the potential oxidation of As(III) under the beam, we performed CS-XAS experiments on freshly prepared samples that were preserved under N$_2$(g) atmosphere just after the isolation from the reactor. From the first spectrum, acquired in the first 90 s of beam exposure, to the last spectrum acquired after more than 10 min of beam exposure, the position of the edge energy did not change and consistently showed As(V) to be the predominant species. These results showed that As(V) was the predominant form of As within the precipitate and that it was formed in solution during the original batch uptake experiments.

The As EXAFS spectra of all the precipitates formed are very consistent and show the same features. The spectrum of one precipitate formed in the As(III) + Fe(II) + HAP system and the magnitude of its corresponding Fourier-Transform are shown in Fig. 3(b and c). The EXAFS spectra showed primarily the presence of the first oxygen shell with another weak scatterer present at a radial distance $\approx$3.2 Å that is compatible with Fe based on a comparison with freshly precipitated amorphous Fe$_{III}$AsO$_{4+n}$H$_2$O and scorodite (Fe$_{III}$AsO$_4$2H$_2$O).

3.6. HRTEM characterization of solids from batch uptake experiments

Fig. 4 shows HRTEM images and EDS spectra for the solids obtained from the batch uptake experiments in PE solution for the Fe(II) control (Fig. 4a and b), As(III) + Fe(II) (Fig. 4c), As(V) + Fe(II) (Fig. 4d), As(V) + Fe(II) + HAP (Fig. 4e) and As(III) + Fe(II) + HAP (Fig. 4f) systems. Nanoparticulate phases without lattice fringes were detected for all samples in PE solution. The particles had sub-spherical morphology, with an average size of 30–50 nm, and occurred as connected chains in the Fe(II) control, the As(III) + Fe(II) and As(V) + Fe(II) systems (Fig. 4a and c). The EDS spectra indicated Fe and P peaks for samples without arsenic (Fig. 4b), and additional As peaks for experiments containing arsenic (Fig. 4d). Additional K and Si peaks were due to some contamination. The estimated molar ratio of phosphorus to iron,
phosphate and arsenite/arsenate either as adsorbate or coprecipitate.

The As(V) + Fe(II) + HAP and As(III) + Fe(II) + HAP experiments exhibited amorphous phases coating the surfaces of the HAP seed crystals (Fig. 4e and f), suggesting heterogeneous precipitation. Elemental EDS analysis of this amorphous phase was not possible because of practical difficulties associated with focusing the electron beam precisely on the amorphous phase while trying to exclude signal from the HAP.

3.7. Binary coprecipitation experiments results

In presenting the results below, we compare the solids formed with those predicted by thermodynamic equilibrium calculations, even though the results in Sections 3.1 and 3.2 indicated that our system had not achieved equilibrium with respect to iron oxidation at 24 h.

The initial molar ratios of P or As(III) to Fe in solution, (P/Fe)\textsubscript{aq} and (As/Fe)\textsubscript{aq}, were 0, 1/250, 10/250, and 100/250. Solution pHs in Fe-bearing solutions dropped from an initial value of 7.5 to final values 5.5–5.8. The color of the precipitates formed in the reaction bottles changed from reddish for Fe only in DI water to an increasingly yellowish color at higher P/Fe ratios. The fractional and absolute amounts of Fe and P or Fe and As removal in the binary, 0.1 M NaCl solution are shown as a function of increasing initial (P/Fe)\textsubscript{aq} or (As/Fe)\textsubscript{aq} ratio (Fig. 5a and b). Although the percentage of P and As removal decreased with increasing initial [P]\textsubscript{tot} or [As]\textsubscript{tot}, the absolute amount removed increased. Iron removal ~20% was approximately the same for all the systems. This value is lower than the Fe removal in the batch As uptake experiments in PE solution (Fig. 1).

HRTEM images and EDS spectra are shown for the precipitates formed by the addition of 250 μM Fe(II) to DI water (Fig. 6a and b), and at initial (P/Fe)\textsubscript{aq} ratios of 1/250 (Fig. 6c), 10/250 (Fig. 6d–h), and 100/250 (Fig. 6i–l). In the Fe(II) + DI experiment, nanoparticles 200–300 nm in size were detected, displaying crumpled and folded sheet- or foil-like morphologies that resemble tissue paper (Fig. 6a). The particles showed lattice fringes at 0.61 nm indexed to (020) of lepidocrocite (c-Fe\textsubscript{II}O\textsubscript{OH}) and the Fast Fourier Transform pattern (Fig. 6b) matches lepidocrocite. The identification was also consistent with the presence of Fe and O peaks in the EDS spectrum (not shown), the reddish color of the solution observed in the reaction bottles, the general synthesis conditions (Cornell and Schwertmann, 2003, p. 355), and the results of thermodynamic aqueous speciation modeling which predicted formation of goethite (α-Fe\textsubscript{III}O\textsubscript{OH}).

The particles formed at initial (P/Fe)\textsubscript{aq} = 1/250 were also reddish, ~200–300 nm in size, foil-like in morphology with electron dense central areas and appeared to grow out radially from a centre (Fig. 6c). Thermodynamic speciation modeling based on the solubilities of bulk phases indicated that lepidocrocite (γ-Fe\textsubscript{III}O\textsubscript{OH}) or goethite (α-Fe\textsubscript{III}O\textsubscript{OH}) should be stable, but the particles obtained did not yield distinct lattice fringes (Fig. 6c). The particles

\[ (P/Fe) \text{ in the Fe control samples was 0.6, and the ratio was slightly smaller ~0.5, for the As(V) + Fe(II) sample. These results are a clear indication of the precipitation of an amorphous ferric oxyhydroxide nanophase with associated \]
were interpreted as amorphous ferric (oxyhydr)oxide, suggesting that crystallization of lepidocrocite or goethite was inhibited by the presence of phosphate.

At intermediate values of initial (P/Fe)\textsubscript{aq} = 10/250, two nanophases with distinct morphologies separated out (Fig. 6d–h). Foil-like precipitates were seen, as above,
along with a new phase of 50–100 nm sub-spherical particles (Fig. 6d and e). The SAED patterns of the two phases taken over areas <0.5 \( \mu \text{m}^2 \) are shown in Fig. 6(f). The foil-like particles showed diffuse diffraction rings with d-spacings of 2.8, 2.6, 2.0, 1.5–1.6 and 1.3 Å, that compare well with the d-spacings for crystalline Fe(OH)\(_3\) (powder diffraction file PDF # 22-0346) and ferrihydrite (PDF # 29-0712). The sub-spherical particles showed two very diffuse diffraction rings at 2.9 and 2.0 Å, respectively, corresponding to the average distances between Fe–P and Fe–O atoms. The EDS spectra for both foil-like and sub-spherical phases showed Fe, O and P peaks, with estimated (P/Fe)\(_s\) ratios 0.2 and 0.5, respectively (Fig. 6g and h). The foil-like particles were, therefore, interpreted as poorly-crystalline Fe(OH)\(_3\) perhaps with some adsorbed phosphate similar to the nanophase seen at (P/Fe)\(_{aq}\) = 1/250. The sub-spherical particles were interpreted as a chemically-mixed, amorphous [Fe\(_{III}\)(OH)\(_3\)PO\(_4\)]\(_{n}\)H\(_2\)O coprecipitate, or using the (P/Fe)\(_s\) value, more precisely as Fe(III)[H\(_{1.5}\)PO\(_4\)]\(_2\).

In contrast to the two nanophases observed, thermodynamic modeling suggested that goethite should still be the only stable phase. Interestingly, the morphology and Fe/O/P ratio of these sub-spherical particles was very similar to those of the particles formed in PE solution where the initial aqueous P/Fe ratio was ~44/250 (Fig. 4c). Returning to Fig. 6g and h, the Na and Cl peaks in the EDS spectra were due to the NaCl used to set the ionic strength, the Cu and C peaks were from the TEM grid, and the Ca peaks indicated the presence of some small impurities or contamination (K and Si peaks also due to contamination).

At initial (P/Fe)\(_{aq}\) = 100/250, only sub-spherical particles, 50–100 nm in size, were observed (Fig. 6i–l). The morphology and SAED pattern were very similar (Fig. 6i and j) to those obtained for the sub-spherical nanophase in the (P/Fe)\(_{aq}\) = 10/250 system. The EDS spectra indicated the presence of Fe, O and P peaks, with an estimated (P/Fe)\(_s\) ratio 0.6–0.7. This value was greater than obtained in the (P/Fe)\(_{aq}\) = 10/250 experiment. Similar EDS spectra and (P/Fe)\(_s\) values in the solid were obtained for the center and the edge of the particles indicating a single coprecipitated phase. These results were interpreted as formation of an amorphous Fe\(_{III}\)(PO\(_4\))\(_\_\)\(_n\)H\(_2\)O phase, or using the (P/Fe)\(_s\) value, more precisely as Fe\(_{III}\)\(_2\)(HPO\(_4\))\(_3\). In contrast, thermodynamic modeling suggested that Fe\(_{III}\)OOH and strengite (Fe\(_{III}\)PO\(_4\)\(_2\)H\(_2\)O) should be stable.

### 3.8. Solution analysis of ternary coprecipitation and adsorption experiments

Solution pHs in Fe-bearing systems dropped from the initial value of 7.3 to 5.5–5.8. The ternary coprecipitation (P, As, and Fe added together) and “adsorption” (P and Fe mixed first and As added 12 h later) experiments both showed trends similar to the binary experiments, with decreasing fractional but increasing absolute uptake of P and As at higher As/P/Fe ratios (Fig. 7 a and b). Importantly, however, both the fractional and the absolute amounts of P and As taken up in the ternary systems were lower than in the binary systems, and the fractional uptake of As decreased as the amount of P increased, indicating competition between P and As. Arsenic uptake in the ternary adsorption experiment was negligible, indicating that coprecipitation does allow for greater As removal even at higher P levels compared to simple adsorption.

### 4. DISCUSSION

#### 4.1. Effect of pH on Fe and As uptake

The thermodynamic speciation calculations for PE solutions suggested that the carbonate system is an insufficient pH buffer in the presence of 250 \( \mu \text{M} \) Fe(II) and that solution pH should have dropped to 3.4 without HAP seeds. The experimental observation that solution pH remains at 5.6–5.7 in the experiments without HAP seeds, suggested that the newly forming ferric oxyhydroxide surfaces may
have provided some pH buffering. The calculations also showed that dissolution of only 0.03 g L⁻¹ of HAP seed crystals is sufficient to buffer solution pH at 6.3–6.5, consistent with the experimentally obtained values of 6.2–6.4 in solutions with HAP seeds. Thus, the HAP seeds provide pH buffering. On the other hand, if the system were at equilibrium, almost 100% of the added Fe(II) should have precipitated out. In contrast, we observed incomplete oxidation with 40% of the Fe(II) remaining in solution (Fig. 2a), suggesting that our system is not at equilibrium, and that the oxidation rate of Fe(II) was slowed down by the drop in pH (Stumm and Lee, 1961; Singer and Stumm, 1970;

Fig. 6. Bright-field TEM images and EDS spectra of solids formed in binary P + Fe(II) system, 0.1 M NaCl: (a and b) Fe(II) in DI water showing particles at low resolution (a), and high resolution image with lattice fringe spacings referenced to (020) face of lepidocrocite and insert showing the Fast Fourier Transform (b); (c) (P/Fe)ₐq = 1/250 system, foil-like, Fe(OH)₃ particles; (d–h) (P/Fe)ₐq = 10/250 system, showing two distinct nanophases having foil-like and sub-spherical morphology at low resolution (d) and higher resolution (e), SAED patterns from selected areas <0.5 μm², d-spacings for foil-like (left) and sub-spherical (right) particles (f), and EDS spectra of the foil-like (g) and sub-spherical particles (h); (i–l) (P/Fe)ₐq = 100/250 system, showing a single, sub-spherical nanophase at lower resolution with SAED pattern (i), higher resolution (j), and EDS spectra for the center (k) and edge (l) of the particles.
Millero and Sotolongo, 1989). These inferences are significant for subsequent interpretation of HAP and pH effects on Fe(II) oxidation rates and on Fe and As uptake.

In batch uptake, binary and ternary experiments containing Fe and phosphate, the presence of yellowish precipitates and their analysis by HRTEM and EDS suggested the oxidation of Fe(II) to Fe(III) followed by hydrolysis and the formation of ferric oxyhydroxide phases with associated phosphate. The greater removal of Fe (and As, if present) in the presence of HAP seed
crystals can be interpreted as due to pH effects on Fe(II) oxidation kinetics and Fe(III) hydrolysis equilibria. First, the rate of Fe(II) oxidation to Fe(III) decreases by an order of magnitude for one pH unit decrease (Stumm and Lee, 1961; Singer and Stumm, 1970; Millero and Sotolongo, 1989). The Fe(II) oxidation rate is faster at the circum-neutral pHs 6.2–6.3 in the presence of HAP seeds resulting in greater Fe and As uptake observed at 24 h compared to the lower pH 5.5–5.7 solutions without HAP seeds, these results show that the system is under kinetic control and is still evolving at 24 h. Further, Fe(III) hydrolysis and precipitation of Fe(OH)₃ releases H⁺ ions into solution, so the forward reaction is thermodynamically more favorable at pHs 6.2–6.3 than at pHs 5.6–5.7. As a result, a greater amount of Fe would be precipitated as solid ferric (oxyhydr)oxides in the presence of HAP seeds, allowing for more Fe and As uptake.

4.2. Efficacy of HAP as a sorbent for Fe and As uptake

Less than 10% As uptake was observed in the As(III) or As(V) + HAP system (Fig. 1a) at pH ~6, similar to a previous study (Sneddon et al., 2005). The pH of the point of zero charge for HAP and fluorapatite is in the range 6.9–8.5 (Bell et al., 1973; Somasundaran and Wang, 1984; Wu et al., 1991), so the HAP particles would have a neutral or slightly positive surface charge at our solution pHs. Sorption of H₃AsO₃, H₂AsO₄⁻, and HAsO₄²⁻, the dominant As(III) and As(V) species at slightly acidic to circum-neutral pH would be limited under these conditions. A slight decrease in [Ca]ₜₒ𝑡 with corresponding decrease in [P]ₜₒ𝑡 was observed in the experiment (Fig. 1b), suggesting that a small amount of calcium phosphate (0.85 mg L⁻¹ based on HAP stoichiometry) precipitated. Though we do not have spectroscopic evidence, we infer that precipitation of calcium phosphate is at least partially responsible for the ~10% uptake of arsenic by HAP under the experimental conditions, with adsorption of As on the surfaces and/or with limited replacement of AsO₄³⁻ for PO₄³⁻. More than 90% of the original 6 µM As remained in solution suggesting that adsorption on and/or coprecipitation with calcium phosphate are not efficient methods for arsenic removal consistent with the lack of a solid solution between HAP and johnbaumite (Ca₅(AsO₄)₃OH) (Bothe and Brown, 1999).

The HAP seed crystals provide a surface for heterogeneous nucleation of the ferric (oxyhydr)oxide phases as seen by HRTEM (Fig. 4e–f). Since the HAP seeds are micronsized and heavier than the homogeneously formed nanosized ferric (oxyhydr)oxide particles, the seeds along with their Fe(OH)₃ surface coatings may be more efficiently removed by centrifugation and filtering. Without HAP seeds, some portion of the ferric (oxyhydr)oxide nanoparticles may not have been separated from solution and may have been erroneously included in the assays for the remaining aqueous Fe and As concentrations. Thus, the HAP seed crystals may act as scavengers of the heterogeneously nucleating ferric (oxyhydr)oxides. The main role of HAP, however, was to provide a pH-buffering role.

4.3. Effect of competing oxyanions on As uptake

If solution pH is more robustly buffered at ~7 by the presence of added calcium carbonate, then uptake in initial As(III) systems by adding Fe(II) can be as high as 75%, as long as phosphate and silicate are not present. Addition of the phosphates and especially silicate reduces As(III) uptake to about 50–55% even when pH is buffered (Roberts et al., 2004; Ciardelli, 2006; Ciardelli et al., 2006).

4.4. Effect of iron on As uptake: Mechanisms of As and Fe uptake

Up to 53% As(III) and 95% As(V) uptake was seen in the presence of Fe(II) and HAP. The extent of As uptake in the initial As(III) system is greater than the low uptake of As(III) reported in the literature by simple adsorption on ferric oxyhydroxides. Based on the As speciation car-
trigge results for the solution (Fig. 2b) and the XANES spectra of the solids formed (Fig. 3a), we propose that As(III) was oxidized to As(V) and taken up as As(V) into the solid. Further support for uptake as As(V) was provided by the desorption experiments, where less than 20% As was remobilized in both initial As(III) and As(V) systems, suggesting that similar mechanisms were responsible for uptake and release in the two systems.

Oxidation of As(III) by oxygen is generally slow \( (t_{1/2} \approx 9 \text{ days}) \) in low Fe and circum-neutral pH conditions (Kim and Nriagu, 2000). The As(III) oxidation rate was accelerated in our experiment by the presence of Fe(II) (Hug et al., 2001; Meng et al., 2002; Hug and Leupin, 2003; Robert et al., 2004). In solutions of composition very similar to our As(III) + Fe(II) + HAP experiment (Table 1), 40–45% As(II) oxidation was reported after only 4 h of reaction in the dark (Fig. 1 of Robert et al., 2004). Our experiments were conducted for 24 h, so a greater degree of As(III) oxidation can be expected. Thus, we infer that 50% of the total initial As(III) present in solution was oxidized to As(V) and taken up into the solids formed, and an additional small amount (<10%) is taken up by simple adsorption of As(III) on HAP.

The Fe(II)-promoted oxidation of As(III) by molecular oxygen has been studied previously in detail (Hug and Leupin, 2003; Robert et al., 2004) (Table 2). The oxidation of Fe(II) to Fe(III) involves reactive oxygen species \( (O_2^{-\cdot}, H_2O_2 \text{ and } OH) \) associated with the normal Fenton reaction (Eqs. (A1)–(A4)). An additional, putative pathway involving reactive Fe(IV) intermediate species promotes oxidation of As(III) to a postulated intermediate oxidant \( (Fe(III) + As(IV) \text{ species that reacts rapidly with } O_2(\text{aq}) \text{ to form As(V)}) \) (Eqs. (A5) and (B6), (B7)). The As(V) is then taken up into or onto the ferric (oxyhydr)oxides formed (Eqs. (C8), (C9)). Reactive intermediate species of Fe(IV) and As(IV) have been proposed in the literature and identified by low-temperature spectroscopy and pulse radiolysis (Rush and Bielski, 1986; Klanning et al., 1989; Logager et al., 1992; see other references in Hug and Leupin, 2003). Additional reactions involving the carbonate radical (\( CO_2^{-\cdot}, Fe(II)-OH \text{ and } Fe(II)-CO_3 \) species were also considered in the original model (Hug and Leupin, 2003) and are expected to occur in our study, because the PE solutions contain dissolved carbonate species and are open to atmospheric CO\(_2\).g.\)

### 4.5. Mode of As, P, and Fe uptake: Coprecipitation versus adsorption

In all Fe-bearing PE solutions, pH decreased to 5.5–5.8 in the absence of HAP seeds, As levels in solution dropped markedly and the \( P_\text{tot} \) and \( Fe_\text{tot} \) levels decreased in tandem. Sub-spherical, amorphous, nanoparticles with Fe, O, and P were observed by IR-TEM–EDS in the absence of HAP seed crystals. Amorphous surface precipitates were obtained on HAP seed crystals suggesting the formation of an amorphous ferric (oxyhydr)oxide phase. The high \( P/Fe \) value of 0.5–0.6 ratio suggested that phosphate was coprecipitated with the ferric oxyhydroxide, and the XANES analyses showed As uptake occurred predominantly as As(V), even in systems that were initially As(III) (Fig. 3).

Similar, high \( P/Fe \) values 0.6–0.7 corresponding to Fe(III)\( (H_2PO_4) \) and Fe(III)\( _2(HP0_4) \) were observed in the sub-spherical particles in the binary experiments. Significantly, the \( 2.9 \AA \) average P–Fe bond-length obtained from the SAED pattern of the sub-spherical particles in the binary system (Fig. 6) is close to the \( 3.3 \AA \) P–Fe distance in strengite (Taxer and Barth, 2004) and to the \( 3.2 \AA \) As–Fe distance from the EXAFS spectrum. Further, the sub-spherical morphology and 50–100 nm particle size was similar for the precipitates in the PE solution and in the binary systems, at initial \( P/Fe \) values of 10/250 and 100/250. We infer, therefore, that a hydrated, chemically-mixed, nanophase coprecipitated in our PE solutions, of composition predominantly ferric hydroxide–phosphate–arsenate with possibly a minor component of arsenite. The phase was nucleated heterogeneously at the surface of HAP seed crystals, if present.

Additional support for the coprecipitation as the uptake mode is provided by the desorption experiments where a small fraction of As was remobilized over 1 week, implying that a large fraction of the As is in the inaccessible bulk of the particles. In another study, 40% arsenic desorbed from ferric oxyhydroxide surfaces, and this was attributed to the formation of chemisorbed complexes at the mineral–water interface, whereas the remainder was bound into the crystal lattice via coprecipitation (Jessen et al., 2005).

The chemical composition of the phase formed in PE solution can be represented as amorphous Fe\(^{III}(OH)_3\) \( (PO_4)\text{(AsO}_4)\text{(AsO}_3)\text{m}_{\text{minor}}\text{H}_2\text{O} \) or as amorphous Fe\(^{III}(OH)_3\text{(PO}_4)\text{(AsO}_3)\text{m}_{\text{total}}\text{H}_2\text{O} \). The crystalline analogues are lepidocrocite or goethite (\( Fe^{III}(OH)_2\text{O} \)), strengite (\( Fe^{III}(\text{PO}_4)\text{H}_2\text{O} \)) and scorodite (\( Fe^{III}(\text{AsO}_3)\text{H}_2\text{O} \)). The formation of green rust-like phases of composition \( Fe^{III}_{\text{tot}}\text{Fe}^{II}_{\text{x}}\text{(OH)}_2\text{HOOH} \text{H}_2\text{O} \) \( x/n\text{As}^{V}+mH_2\text{O} \) \( y \) where \( x \) is the \( \text{Fe}^{III}/\text{Fe}^{III}+\text{Fe}^{II} \) total ratio, and \( \text{As}^{V} \) is the anion was deemed unlikely because almost 90% of the Fe(II) was oxidized to Fe(III) in the presence of HAP seeds and the measured DO levels showed that the system never became anoxic (above 4.5 ppm) (Fig. 2).
The HRTEM results for binary system solids also clearly showed the effect of increasing phosphate concentrations on the crystallization of ferric oxyhydroxides. In the absence of phosphate, crystalline lepidocrocite was formed. At low initial \((P/Fe)_{\text{aq}} = 1/250\), adsorption of phosphate on incipient ferric oxyhydroxide nuclei inhibited crystal growth resulting in poorly-crystalline, \(\text{Fe(OH)}_3\) nanoparticles with absorbed phosphate and \((P/Fe)_{\text{aq}} \approx 0.2\). Increasing phosphate resulted in phase separation and finally only ferric phosphate was formed at high phosphate levels. Phosphate and arsenate (and silicate) have a high sorption capacity on ferric oxyhydroxides, and their inhibitory effect on crystallization of iron oxyhydroxides is well recorded (Torrent et al., 1992; Waychunas et al., 1996; Rose et al., 1996, 1997; Masion et al., 1997, 2000; Doelsch et al., 2000, 2001; Davis et al., 2001; Wada and Ueno, 2001; Cornell and Schwertmann, 2003, pp. 258–270; Sudakar et al., 2003; Ciardelli, 2006), in good agreement with the presence of poorly ordered ferrihydrite commonly encountered in surface environments (Janney et al., 2000; Allard et al., 2004).

### 4.6. Implications for the natural environment and for arsenic remediation

Our results may be summarized as follows. Increased As uptake occurs in the presence of Fe(II) under oxic conditions at slightly acidic to circum-neutral pHs, because As(III) oxidation to As(V) by molecular oxygen is accelerated by putative reactive intermediates of Fe(IV) and As(IV). The uptake of P occurs by adsorption on newly-precipitated, poorly-precipitated or amorphous \(\text{Fe}^{III}[(\text{OH})_3(P\text{O}_4)\text{AsO}_4]\) nanophase at low initial \((P/Fe)_{\text{aq}}\) ratios, and by an amorphous, nanoparticulate, chemically-mixed, ferric oxyhydroxide–phosphate phase at intermediate to high \((P/Fe)_{\text{aq}}\) ratios. The mixed phase is formed at lower initial \((P/Fe)_{\text{aq}}\) ratios than the \((P/Fe)_{\text{aq}}\) ratio at which bulk FeOOH and strengite are predicted to co-exist in thermodynamic equilibrium. Coprecipitation increases P and As uptake over simple adsorption. If such phases occur in nature, they could act to sequester As in the natural environment.

Ferrous iron is present in many tidal estuarine and groundwater aquifer environments that are under reducing or sub-oxic conditions. Such environments may cycle through sub-oxic and oxic conditions due to introduction of oxygen during low tide and pumping of water out of wells finished in the aquifer. Under such conditions, the Fe(II) may be oxidized partially or completely to Fe(III) depending on the pH, DO level and transport kinetics, and a host of different iron precipitates may be anticipated. Green-rust-like precipitates form under more reducing and acidic conditions. At fully oxic conditions, ferric phosphates or mixed ferric oxyhydroxide-phosphates such as tinctite \((\text{Fe}^{III}[(\text{OH})_3(P\text{O}_4)\text{AsO}_4])_n\text{H}_2\text{O}\) and strengite form at acidic pHs 3–6 (Jonasson et al., 1988); ferric oxyhydroxides are expected at circum-neutral pHs (Cornell and Schwertmann, 2003, p. 355).

Arsenic phases coprecipitated with ferric oxyhydroxides have been reported in an acid mine drainage system at low pHs 2–4 on the Western Coromandel peninsula, New Zealand (Craw and Chappell, 2000). Nanocrystals of chemically-mixed ferric arsenite–sulfate–hydroxide, tooeleite \((\text{Fe}^{III}_{4/5}[(\text{As}^{III}O_2)_3\text{SO}_4])_{(\text{OH})_3} \cdot 4\text{H}_2\text{O})\), and mixed Fe(III)–As(III)–As(V) hydroxide gels have been reported from the Carnoules Acid Mine Drainage system in France (Morin et al., 2003).

Analogous mixed phases bearing phosphates may be formed at mildly acidic conditions. Predominantly ferric (as opposed to ferrous) hydrous phosphate phases with high P/Fe ratios 0.7–0.8 were recently identified in estuarine sediments of the Scheldt Estuary in Belgium and the Netherlands, at all sampled depths from 0 to 50 cm (Hyacinthe and Van Cappellen, 2004). Using scanning electron microscopy, iron phosphates have also been identified on host grains in an aquifer in Bangladesh (Harvey et al., 2002).

Nominally ferric oxide phases that are rich in carbon (presumably of organic origin), Si, P and Ca have been identified from water samples of two meromictic lakes, Lake Lugano in Switzerland and Paul Lake in Michigan, USA, and from the peat-land of the Bied River, Switzerland (Perret et al., 2000). Mixed iron–zinc–phosphate phases were also identified in metal contaminated sediments, and showed a relatively uniform electron density under the TEM suggesting a crystalline precipitate (Webb et al., 2000). Thus, there is a growing body of recent evidence from the natural environment for the existence of the proposed chemically-mixed coprecipitates. A mixed, amorphous ferric phosphate–ferric oxyhydroxide phase was even predicted based on equilibrium thermodynamic calculations for tidal Hudson River water compositions (Fox, 1989, 1991).

The natural precipitates reported in the above studies are similar to the nanophases formed at pH 5.5–6.5 in our experiments, amorphous \(\text{Fe}^{III}[(\text{OH})_3(P\text{O}_4)\text{AsO}_4])_n\text{H}_2\text{O}\). It may be that these metastable compounds nucleated due to a sharp decrease in pH in a nano- to micrometer-sized volume of space as Fe(II) was added to solution, analogous to the nucleation of nano-sized metastable precursors of aluminum (oxyhydroxides) when Al(III) is added to solution (Hsu, 1988). Such micro-environments of very low pH are encountered around decaying organic matter, plant root zones, etc., even though the overall solution pH may be only slightly acidic. Our results were obtained in complex solutions closer in composition to natural groundwaters than the simple 1:1 electrolytes typically employed in similar studies. Also, the arsenic concentration used here was representative of natural groundwater. Significantly, the EDS and XAS data were obtained at the same As concentrations as used in the uptake experiments, not at some unrealistically high levels. Finally, our system is under kinetic control similar to low-temperature natural environments. These systems are ultimately under thermodynamic constraints, but the assumption of thermodynamic equilibrium may not accurately represent the processes observed at “short” time scales. The results of the present study are, therefore, highly relevant to the natural environment, although we recognize that our study does not address the effects of organics such as humic and fulvic acids and bacterial/fungal/plant exudates. Another significant point is that the chemically-mixed ferric oxyhydrox-
ide–phosphate precipitates were identified in the estuarine environments and in our study at slightly acidic to circum-neutral solution pHs, rather than the highly acidic pHs of acid mine drainage environments where sulfate analogs may be expected.

It is tempting to suggest from the above results that the mixed, coprecipitated nanophases may be an efficient means for removing As from solution under specific conditions. Indeed, this appears to be the case in some environments as cited above. However, before making such broad generalizations, several caveats must be considered. The nanophases are, ultimately, metastable and must transform to their more stable bulk counterparts over longer time periods, where “long” is defined relative to the process of interest. The pathways of the phase transition may involve re-dissolution or aggregation of solid particles and transformation at particle–particle or particle–solution interfaces or whole, less favorable (Bothe and Brown, 1999; Monteil-Rivera et al., 2005). Uptake of metalloid oxyanions such as $\text{SeO}_3^{2-}$ and simultaneous formation of a mixed ferrous, ferric arsenate–phosphate precipitates were identified in the estuarine environments and in our study at slightly acidic to circum-neutral solution pHs, rather than the highly acidic pHs of acid mine drainage environments where sulfate analogs may be expected.

The HAP seed crystals may have acted as scavengers of nanoparticulate phases formed, bringing up the role of micron-sized (i.e. heavier) particles as possible nanoparticle scavengers in the natural environment. A recent study reports a different As removal strategy based on magnetic separation using high-surface area magnetite ($\text{Fe}_3\text{O}_4$) nanocrystals as scavengers in engineered systems (Yavuz et al., 2006).

**Afterword.** We presented the above results at the American Chemical Society Annual Spring and Fall 2006 Conferences in Atlanta and San Francisco, respectively (Ciardelli et al., 2006; Lee et al., 2006; Sahai et al., 2006). Following the latter presentation, Dr. Xavier Chatelier, Université de Rennes, France graciously and personally communicated to N.S. that he had obtained very similar results in a completely independent study. Neither he nor our group had any knowledge of the other’s work prior to this meeting.

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