Adsorption of Arsenic with Struvite and Hydroxylapatite in Phosphate-Bearing Solutions

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Abstract

Arsenic sorption at above neutral pH is relevant when considering contaminant mobility in alkaline, phosphorus-bearing wastewaters, and may be viable in the presence phosphate minerals. Arsenic adsorption on struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, MAP) and hydroxylapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$, HAP) was evaluated at pH 8-11 from solutions with 2.7-0.125 mM phosphate and 0.05 mM As(III) or As(V). Over 7 d, As(III) removal from solution was minimal, but As(V) removal increased with pH, and was higher in the presence of MAP compared to HAP with a maximum of 74% removal in pH 11 MAP-bearing solutions. X-ray absorption fine structure spectroscopy (XAFS) analysis of solids recovered from pH 10-11 solutions revealed different mechanisms of As(V) sorption with MAP and HAP. Arsenic forms monodentate mononuclear surface complexes with MAP through the formation of a Mg-O-As bond, but is incorporated at the near-surface of HAP forming a johnbaumite-like ($\text{Ca}_5(\text{AsO}_4)_3\text{OH}$) structure. Experiments using radioactive ^{33}P at pH 10-11 revealed faster exchange of P at the HAP surface, which could promote more facile As incorporation. Near-surface incorporated As in HAP may be less susceptible to remobilization compared to surface adsorbates formed with MAP. Overall, both MAP and HAP may sorb As at high pH in the presence of phosphate. This is relevant to the fate of As in alkaline contaminated waters in contact with phosphate mineral phases.

Keywords arsenic; struvite; hydroxylapatite; johnbaumite; XAFS; ^{33}P

1. Introduction

Arsenic (As) is a common pollutant found in mining, industrial and agricultural wastes; and can be mobilized from naturally occurring As-bearing minerals in aquifers (Smedley et al., 2002; Han et al., 2003). Iron, aluminium, titanium and carbon based materials and minerals are known to sorb As from a variety of wastes at neutral to low pH (Manju et al., 1998; Xu et al., 2002; Bang et al., 2005; Mondal et al., 2006; Mohan et al., 2007). Arsenic sorption at above neutral pH is less well studied, but is relevant when considering the behavior of As in high pH systems such as alkaline wastewaters. These systems are increasingly recognized as a source of recoverable phosphorus (P) mineral resources, and the interaction of contaminant As with relevant minerals during and after crystallization requires evaluation (Ma and Rouff, 2012). Typically, As(V) removal is lowered in the presence of P due to comparable size, charge and structure of the PO_4^{3-} (aq) and AsO_4^{3-} (aq) oxyanions (Wilkinson et al., 1987), and therefore competition for similar sorption sites (Liu et al., 2001). However, the similarity in oxyanion configuration also facilitates As(V) substitution for P in mineral structures (Sneddon et al., 2005; Lee et al., 2009; Lee, 2010), which may be a viable mechanism for As removal from alkaline solutions.

Hydroxylapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$, HAP), is a common mineral product in wastewater systems (de-Bashan and Bashan, 2004), and has been observed to sorb As under near-neutral to acidic conditions. HAP added to contaminated soils increased the solubility, and thus aqueous concentrations, of As due to displacement by phosphate competing for sorption sites (Seaman et al., 2001; Kaplan et al., 2004). Removal of As(V) from aqueous solution, and removal of As(III) and As(V) from synthetic groundwater is limited in the presence of HAP (Sneddon et al., 2005; Ciardelli et al., 2008). However, at pH 10 As(V) readily coprecipitates with crystallizing HAP

forming a complete solid-solution series with johnbaumite ($\text{Ca}_5(\text{AsO}_4)_3\text{OH}$) (Lee et al., 2009). Because As(V) can coprecipitate with HAP at high pH, it is feasible that during adsorption from alkaline solutions HAP may sequester As by incorporation at the near-surface, potentially forming a johnbaumite-like phase (Bothe and Brown, 1999; Sneddon et al., 2005; Ciardelli et al., 2008). In this scenario, the As oxyanion would form direct bonds with near-surface $\text{Ca}^{2+}(\text{s})$ sites, which occupy different positions between phosphate groups and hydroxyl ions in the HAP lattice (Posner et al., 1958).

Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, MAP) occurs naturally in geochemical and biological systems (Abdelrazig et al., 1988), and is commonly found as a precipitate during wastewater treatment (de-Bashan and Bashan, 2004). Recently, MAP recovered from wastes has been proposed as a new low-cost high quality fertilizer (de-Bashan and Bashan, 2004; Doyle and Parsons, 2002; Ma et al., 2014). However, if present in alkaline, phosphate-rich wastes, MAP may act as a sorbent. Previous work has revealed that during MAP formation, As can be removed simultaneously with the precipitate phase, with As(V) coprecipitated into the mineral structure (Ma and Rouff, 2012). The coprecipitation of As(V) with MAP can produce the isomorph arsenstruvite ($\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$), formation of which has been suggested as a means to treat As contaminated wastewater (Weil, 2008). However, for an adsorption process, the structure of the surface complex, and whether an arsenstruvite-like phase would form is unknown. Of note is that there are no direct bonds between $\text{Mg}(\text{H}_2\text{O})_6^{2+}(\text{s})$ and $\text{PO}_4^{3-}(\text{s})$ or $\text{AsO}_4^{3-}(\text{s})$ in MAP and arsenstruvite, respectively. However Mg-O-P bonds are common in other minerals (Nord and Kierkegaard, 1968). Therefore, the adsorption of As could also proceed by the formation of direct Mg-O-As bonds at the MAP mineral-water interface.

This study focuses on the adsorption of As by MAP and HAP in alkaline solutions from pH 8-11, in the presence of phosphate at pH-dependent equilibrium concentrations ranging from 2.5-54 times the As concentration. Batch experiments were conducted to determine the extent of sorption of As(III) and As(V) by these substrates. Solids with highest As concentrations were subjected to X-ray absorption fine structure spectroscopy (XAFS) analysis to identify the structure of the As sorbate. Since the exchange of phosphate at the mineral-water interface could dictate the sorptive properties of the minerals, radioactive ^{33}P was used to examine this behavior in As-free solutions. Overall, this research evaluates the role of adsorption in As removal by MAP, which has not been previously explored; reports structural information for As sorbates associated with HAP; and provides a direct comparison of the exchange of phosphate at the mineral-water interface for these minerals.

2. Materials and Methods

2.1. Batch adsorption experiments

Solutions were prepared at room temperature (20-22 °C) in high density polyethylene (HDPE) bottles using deionized (DI) water and a 0.1 M NaCl background electrolyte, and the pH adjusted to 8, 9, 10 or 11. Commercial MAP (Alfa Aesar) or HAP (Acros Organics) was added at a loading of 4 g L^{-1} to the pH 8-11 solutions. The surface areas for MAP and HAP were 119 and $65.8 \text{ m}^2 \text{ g}^{-1}$, respectively (see Supplementary Material). Immediately after addition of the solid, stock solutions prepared using NaAsO_2 and NaH_2AsO_4 salts were used to add $50 \text{ }\mu\text{M}$ (3.7 mg L^{-1}) of either As(III) or As(V) to the solutions. This As concentration was chosen as an intermediate value based on the As concentrations previously evaluated for contaminated waters

which ranged from ~ 0.05 -3000 mg L⁻¹, with lower values for groundwaters and higher values for industrial and wastewater effluents (Mohan and Pittman, 2007 and references therein). In all solutions MAP and HAP saturation states were close to equilibrium, and all relevant As-bearing phases were undersaturated based on PHREEQC calculations (Parkhurst and Appelo, 1999) (Table S1-S2). These conditions were chosen to evaluate the adsorption mechanism as: (1) solutions close to equilibrium with respect to the mineral minimizes dissolution or precipitation that could promote a co-precipitation mechanism or reduce uptake; and (2) undersaturation of As-bearing phases optimizes surface-controlled sorption and limits As removal via a precipitation mechanism, which may or may not involve the mineral sorbent. Blank pH 8-11 solutions with no MAP or HAP were also spiked with 50 μ M As(III) or As(V). After spiking, a small volume of aqueous sample was withdrawn and filtered using a 0.45 μ m syringe filter every day for 7 d from all solutions. To recover solids for further analysis, solutions in which As(V) was reacted with MAP and HAP at pH 10 and 11 for 7 d were filtered using 0.22 μ m membrane filters, and dried at room temperature. Both aqueous samples and acid-digested (at room temperature for ~ 24 hours) solids were analyzed for total As by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin-Elmer DV 5300 instrument.

2.2. X-ray absorption fine structure spectroscopy

Extended X-ray absorption fine structure spectroscopy (EXAFS) data were collected for MAP and HAP reacted with As(V) at pH 10-11 for 7 d, and prepared as described above. These solids were chosen because they exhibited the highest As(V) concentrations for both substrates. Solids reacted with As(III) at pH 8-11 were not recovered due to limited As sorption. Spectra were collected at beamline X11A of the National Synchrotron Light Source (NSLS), Brookhaven

National Laboratory (BNL), Upton NY, at the As K-edge, calibrated at 11.868 keV, using a Si(111) monochromator. The beam was detuned by 15% to minimize the harmonic contribution. Spectra were collected at room temperature in fluorescence mode using a Stern-Heald type Lytle detector. Soller slits and a germanium (Ge) foil were placed between the detector and the sample to reduce elastic scattering. Data reduction and analysis was performed using Athena and Artemis software included with the IFEFFIT program (Newville, 2001; Ravel and Newville, 2005). The amplitude reduction factor, S_0^2 , was set to 0.9 during the analysis. Structural parameters, coordination number (N), distance (R) and Debye-Waller factor (σ^2), for the first As-O shell, and subsequent As-Mg or As-Ca shells around the central As atom were determined. Since there are no direct Mg-O-As bonds in arsenstruvite (Ferraris and Franchini-Angela, 1973), $\text{Mg}_3(\text{AsO}_4)_2$ (Krishnamachari and Calvo, 1973) was chosen as the model mineral to fit the MAP data. For HAP, johnbaumite (Lee et al., 2009) was used as the model mineral to fit the O and Ca shells.

2.3. Phosphate adsorption and exchange at the mineral-water interface

To evaluate the fundamental processes that could contribute to the sorptive properties of MAP and HAP, the adsorption and exchange of phosphate at the mineral-water interface was studied. Experiments were conducted with and without radioactive ^{33}P . Solutions adjusted to pH 10-11 were pre-equilibrated with MAP or HAP, at a loading of 4 g L^{-1} , for 7 d. At this time, solutions designated for the radiotracer experiments were spiked with ^{33}P labeled phosphate at an activity of 224 Bq mL^{-1} . The radiotracer was added after 7 d so as to discern the fundamental exchange processes from the fast kinetics associated with the initial equilibration. Since the ratios of ^{33}P to ^{31}P were 2.95×10^{-9} and 9.44×10^{-9} for pH 10 and 11 solutions, respectively, the addition of ^{33}P

would have little impact on total phosphate, and therefore the equilibrium state or the rate of exchange. The first aqueous samples were withdrawn within 15 minutes of spiking the solutions with ^{33}P , and additional aqueous samples were recovered intermittently over the following 7 d for an overall 14 d reaction time. All aqueous samples were filtered using a 0.45 μm manifold filter. The recovered filtrates were first mixed with liquid scintillation cocktail and then analyzed for radioactivity using a LS6500 Beckman multi-purpose scintillation counter. Isotopic decay of ^{33}P was not explicitly accounted for since the ^{33}P content was determined by comparing the particulate to the dissolved activities; since the total P is calculated from this ratio and both the liquid and particulate phases were subject to the same decay, no correction is necessary. There was no differential quenching between aqueous and particulate samples as determined by standard addition. For the experiments without ^{33}P , aqueous samples were withdrawn at 7 d and 14 d, and filtered using 0.45 μm syringe filters. Solutions were analyzed for phosphate by the ascorbic acid method (Rice et al., 2012) using a Hach DR 5000 Ultraviolet-Visible (UV-VIS) spectrophotometer.

3. Results and Discussion

3.1. Batch adsorption experiments

The removal of As(III) from solution was negligible in the presence of both MAP and HAP at all pH values (Figure 1a,b). Removal of As(V) increased with increasing pH, with highest removal at pH 10-11 for both substrates (Figure 1c,d). The initial and final solution concentrations were used to determine the concentration of sorbed As per gram solid, and then normalized to the mineral surface area (Figure S1). At pH 10 when As(V) sorption by HAP is the highest, the sorbed As per unit surface area at 0.04 $\mu\text{M m}^{-2}$ approaches that of MAP at 0.05 $\mu\text{M m}^{-2}$ at 7 d

reaction (Figure S2). Therefore at this pH the surface coverages are most comparable for the two substrates. Overall though, the trends in As surface coverage as a function of pH and substrate were consistent with the trends in uptake observed in Figure 1. This suggests that available surface area alone does not account for differences in As uptake between MAP and HAP. During adsorption, both As(III) and As(V) species would need to compete with phosphate in solution to be adsorbed on the mineral surfaces. Since the phosphate concentration decreased with increasing pH (Table 1, Table S3) competition from phosphate would decrease at higher pH. Therefore, if competition from phosphate is the only factor dictating the adsorption of As(III) and As(V), then trends should be similar for both MAP and HAP over the entire pH range. However, as discussed below, the observed differences in uptake of dissolved As indicate that additional factors contribute to As interaction with these mineral surfaces.

The removal of As(III) was similar for both MAP and HAP with < 10% removed from solution at all pH values (Figure 1a,b). The limited interaction of As(III) is due to the difference in speciation when compared to phosphate. At pH 8-11, the dominant species of As(III) are $\text{H}_3\text{AsO}_3^0(\text{aq})$ and $\text{H}_2\text{AsO}_3^-(\text{aq})$ with more formation of $\text{H}_2\text{AsO}_3^-(\text{aq})$ as the pH was increased (Table S4). At pH 8, since the neutral species of As(III), $\text{H}_3\text{AsO}_3^0(\text{aq})$, is dominant, As(III) would be outcompeted by phosphate, $\text{H}_2\text{PO}_4^-(\text{aq})$ and $\text{HPO}_4^{2-}(\text{aq})$, for interaction with positively charged $\text{Mg}(\text{H}_2\text{O})_6^{2+}(\text{s})$ or $\text{Ca}^{2+}(\text{s})$ sites on the MAP and HAP surfaces, respectively. Similarly, at higher pH, $\text{H}_2\text{AsO}_3^-(\text{aq})$ is unlikely to successfully compete with $\text{HPO}_4^{2-}(\text{aq})$, the dominant P species at pH > 8, to form complexes with the positively charged surface groups. Therefore, differences in speciation and a consistently deficient charge compared to phosphate likely resulted in relatively low As(III) removal in the presence of both MAP and HAP.

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195 The trend in As(V) removal differed for MAP and HAP at pH 8-11. With increasing pH more
196 As(V) was removed in the presence of MAP, whereas for HAP removal increased with pH, but
197 peaked at pH 10 (Figure 1c,d). For MAP, As(V) removal increased from 4% at pH 8 to 74% at
198 pH 11 (Figure 1c). Of note is the maximum As(V) removal corresponds with that observed at pH
199 10 during active precipitation of MAP at ~70% (Ma and Rouff, 2012). The removal of As(V)
200 could be the result of two main changes as the pH was increased: the weaker competition from
201 phosphate, due to the lower equilibrium phosphate concentration at higher pH; and more AsO_4^{3-}
202 (aq) available as the pH was increased from 8-11 (Table S3) for the formation of a Mg-O-As
203 bond. The formation of Mg-O-As bonds during the adsorption process is not only the result of
204 electrostatic interaction but also the polarization and charge transfer between $\text{Mg}(\text{H}_2\text{O})_6^{2+}(\text{s})$ and
205 $\text{PO}_4^{3-}(\text{aq})$ or $\text{AsO}_4^{3-}(\text{aq})$ tetrahedra. As the pH was increased, the deprotonation of As(V)
206 tetrahedra would facilitate adsorption by providing more negatively charged As(V), as AsO_4^{3-}
207 (aq), which could also propel the polarization and charge transfer in the formation of the Mg-O-
208 As bond.

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210 For HAP, the removal of As(V) was minimal at pH 8-9 (2-4%), and decreased from 21% at pH
211 10 to 12% at pH 11 (Figure 1d). Higher removal at pH 10-11 compared to pH 8-9 may also be
212 due to the weaker competition from phosphate at higher pH. However, the removal at pH 11 was
213 less than at pH 10. Therefore changes in surface processes and speciation at higher pH may be of
214 influence here. At pH 11, $\text{Ca}^{2+}(\text{aq})$ complexation with PO_4^{3-} to form $\text{CaPO}_4^-(\text{aq})$, and hydrolysis
215 to $\text{Ca}(\text{OH})^+(\text{aq})$, could result in enhanced dissolution of $\text{Ca}^{2+}(\text{s})$ at the HAP surface to replenish
216 $\text{Ca}^{2+}(\text{aq})$. In addition, surface complexation studies indicate a transition from $\equiv\text{CaOH}_2^+$ to

≡CaOH as the dominant Ca surface species at pH > 10 (Bengtsson and Sjöberg, 2009). This in turn would reduce the available positively charged sites, and when combined with enhanced dissolution, may account for slightly lower As(V) sorption at pH 11.

3.2. X-ray absorption fine structure spectroscopy

The k^3 -weighted χ functions and radial structure functions (RSFs) are shown for MAP and HAP reacted with As(V) for 7 d in pH 10 and 11 solutions (Figure 2). The measured As concentrations are $237 \pm 6 \text{ mg kg}^{-1}$ and $374 \pm 12 \text{ mg kg}^{-1}$ for MAP solids from the pH 10 and 11 solutions, respectively; and $70 \pm 5 \text{ mg kg}^{-1}$ and $74 \pm 2 \text{ mg kg}^{-1}$ for HAP solids from the pH 10 and 11 solutions. The EXAFS fitting procedure, results from alternate fits and contributions of individual shells to the final fits are reported in Supplementary Materials (Table S5, Figure S3). The final fit parameters are summarized in Table 2.

For MAP, the average As-O bond distance is 1.69 Å for both pH 10 and 11 solids with O in 4-fold coordination and consistent with parameters for As in arsenstruvite. The As-Mg shell radial distance is 2.66-2.68 Å. This distance is shorter than the 4.44 Å distance for arsenstruvite (Ferraris and Franchini-Angela, 1973), but is closer to the 2.81 Å radial distance for closest Mg atoms in $\text{Mg}_3(\text{AsO}_4)_2$ (Krishnamachari and Calvo, 1973), indicating the formation of short As-O-Mg bonds due to the adsorption of As(V) tetrahedra on MAP. Based on the As-O, Mg-O and O-O bond distances from the model minerals, the As-Mg radial distance in the surface complexes should be between ~2.39 Å, which is the As-Mg radial distance in edge-sharing bidentate surface complexes, and ~3.79 Å, which is the As-Mg radial distance in linear monodentate surface complexes (Figure S4). To achieve the observed As-Mg distance, the surface complex must be

rotated to a Mg-O-As angle of $\sim 88-89^\circ$ (Figure S4), which is close to the 93° angle in $\text{Mg}_3(\text{AsO}_4)_2$. This distance and bond angle is also similar to that observed in $\text{Mg}_3(\text{PO}_4)_2$ for which the shortest P-Mg distance is $2.67 \text{ \AA}$ with a Mg-O-P bond angle of $91-94^\circ$ (Nord and Kierkegaard, 1968). Therefore As forms a monodentate mononuclear adsorbate with contraction of the As-Mg bond distance relative to that in $\text{Mg}_3(\text{AsO}_4)_2$, due to rotation of the tetrahedron towards the mineral surface.

For the HAP solids, the As-O radial distances at $1.66-1.68 \text{ \AA}$ are consistent with the $1.68 \text{ \AA}$ distance in johnbaumite as previously reported in the literature (Lee et al., 2009). For both solids two As-Ca shells are detected. For the pH 10 solid the As-Ca shells are at $3.33 \text{ \AA}$ and $3.57 \text{ \AA}$ which is consistent with shells at $3.31 \text{ \AA}$ and $3.67 \text{ \AA}$ based on structural data. This is indicative of the formation of a johnbaumite-like structure at the surface. Though As surface coverage is close to that of the pH 10 MAP solid (Figure S2), the mechanisms are different, confirming that processes other than available surface area dictate the sorption process. For the pH 11 solid the As-Ca shells are detected at $3.48 \text{ \AA}$ and $3.74 \text{ \AA}$. The first shell As-Ca distance corresponds with the average distance of the As-Ca_1 and As-Ca_2 shells in the johnbaumite structure calculated at $3.49 \text{ \AA}$. The second As-Ca shell corresponds to the $3.74 \text{ \AA}$ distance of As-Ca_3 . Considering that enhanced surface exchange at this pH could result in mobilization of phosphate from the lattice, this can promote increased incorporation of As(V) into the mineral structure and thus detection of the longer As-Ca distance. Therefore, at pH 11 As(V) also forms a johnbaumite-like structure that may be incorporated at greater depth in the HAP lattice than at pH 10.

3.3. Phosphate adsorption and exchange at the mineral-water interface

Total phosphate concentrations in pH 10 and 11 As-free solutions in the presence of MAP and HAP were monitored over 14 d. The initial phosphate concentrations at pH 10 and 11 (Table 1) were designated as 100% and were used to calculate the percent phosphate in solution at 7 and 14 d (Figure 3a). The 7 d time point is equivalent to the end-point of the As sorption experiments (Figure 1), after which equilibrium exchange of phosphate between the aqueous and solid phases dominates. The overall trends in phosphate removal with pH mimic those observed with As(V) for the two minerals: more phosphate was removed with increasing pH for MAP, while less removal was observed at pH 11 than at pH 10 for HAP. This indicates that there are fundamental differences in the processes occurring at these mineral surfaces that dictate the behavior of phosphate. That similar trends are observed in As(V)-bearing solutions suggests that these processes also influence As(V) sorption.

To better understand the exchange of aqueous phosphate with the mineral surface/structure, measurements of total phosphate (Figure 3a) were compared with separate experiments using radiolabeled ^{33}P (Figure 3b). For MAP in pH 10 and 11 solutions, 5-18% of the initial ^{33}P was removed from solution within 15 minutes after spiking at the 7 d time point. After 14 d, the percentage of ^{33}P in solution decreased from 95% to 44% at pH 10, and from 82% to 18% at pH 11. Total phosphate removal for MAP between 7 and 14 d was insignificant, and in fact indicated slight desorption within this time-frame (Figure 3a). The decline in ^{33}P activity, with minimal changes to total phosphate can be explained by isotopic substitution of structural ^{31}P for ^{33}P from the dissolved phase. At 14 d the fraction of ^{33}P in solution relative to total phosphate, $(\%^{33}\text{P})/(\%\text{total phosphate})$, is ~ 0.7 at pH 10 and ~ 0.36 at pH 11. This indicates deficiency in ^{33}P in solution and thus the diffusion and exchange of ^{33}P with ^{31}P in the MAP lattice. The more

rapid kinetics of ^{33}P removal at pH 11 compared to pH 10 could be due to more $^{33}\text{PO}_4^{3-}(\text{aq})$ at higher pH, which would facilitate the nucleophilic attack that could lead to the formation of Mg-O- ^{33}P bonds. More ^{33}P lost in the lattice of MAP at higher pH was indicative of more exchangeable phosphate in the lattice with weak electrostatic bonds with $\text{Mg}(\text{H}_2\text{O})_6^{2+}(\text{s})$. At the MAP surface, slow initial exchange, coupled with mobile surface-bound species may promote As(V) complexation at the mineral surface, thereby forming adsorbates with Mg-O-As bonds. In addition, a greater amount of exchangeable phosphate at higher pH could facilitate increased As(V) sorption at pH 11.

For HAP, a significant percentage of ^{33}P was removed right after spiking. The percentage of ^{33}P dropped from 100% to 60% and 50% for pH 10 and 11 solutions, respectively, within 15 minutes of spiking (Figure 3b). After 14 d, 43% and 31% of ^{33}P remained in pH 10 and 11 solutions. At pH 10, the percentage of ^{33}P removed right after spiking was the same as the percentage of phosphate removed by HAP at 7 d (Figure 3a). This indicated a quick exchange of the two P isotopes on the HAP surface through the substitution of ^{33}P for ^{31}P . At pH 10 there is no detectable desorption (Figure 3a), therefore phosphate is primarily bound in the near-surface lattice with limited mobile surface species. Comparing the removal of ^{33}P for HAP with that of MAP at pH 10, curves for removal of ^{33}P converge and ultimately overlap at 14 d (Figure 3b). This convergence might account for similar As(V) surface coverages when normalized for surface area, with slightly lower coverage for HAP compared to MAP (Figure S2). Therefore, the extent of exchange may influence or dictate the amount of sorbate surface coverage, though the sorption mechanism is different.

For the HAP pH 11 solid, the phosphate concentration after 7 d was 105% which implies no phosphate adsorption (Figure 3a). However, this value should be less than 100% based on the removal of ^{33}P from solution as observed in Figure 3b. This discrepancy could be the result of surface dissolution at pH 11. After 14 d, the phosphate concentration increased to 110%, indicative of a prolonged surface dissolution process. Though PHREEQC calculations predict slight undersaturation of HAP at both pH 10 and 11 (Table S2), this does not explain the observed dissolution at pH 11 even after 7 d equilibration, and no detectable dissolution at pH 10. As discussed previously, complexation and hydrolysis of $\text{Ca}^{2+}(\text{aq})$ due to increased concentrations of $\text{PO}_4^{3-}(\text{aq})$ and $\text{OH}^{-}(\text{aq})$ may promote dissolution and release of $\text{Ca}^{2+}(\text{s})$ to solution. So at pH 11, higher initial ^{33}P removal than at pH 10 was most likely caused by an increase in exchangeable phosphate on the mineral surface due to bond breaking and release of $\text{Ca}^{2+}(\text{s})$ to solution. This in turn would result in mobilization of phosphate in the lattice to re-establish a charge balance, thereby producing disorder in the crystal structure at the surface. The kinetics of ^{33}P removal at pH 10 and 11 were similar, i.e. the curves were parallel after the initial drop in ^{33}P after spiking. This suggests that the process(es) responsible for ^{33}P removal after the initial decline was not directly influenced by pH. One possibility is the slow continued exchange of ^{33}P with the phosphate in the lattice at the mineral-water interface. Because initial surface exchange is rapid for HAP, As(V) can be incorporated into the near-surface mineral structure during recrystallization. This process is consistent with the formation of a johnbaumite-like structure which is increasingly incorporated at depth at higher pH due to enhanced mineral dissolution.

4. Conclusions

The phosphate minerals MAP and HAP both sorb As, contingent upon oxidation state, but the extent and mechanism of sorption is different. Sorption of As(III) is negligible, and oxidation to As(V) could be considered to enhance sorption in systems dominated by As(III) aqueous species. Sorption of As(V) by MAP exceeds that with HAP, with highest sorption at $\text{pH} \geq 10$. In general, As(V) sorption increases with pH due in part to lower initial phosphate concentration, and therefore reduced competition, at higher pH. However, the dynamics of exchange at the mineral-water interface, rather than competition with phosphate alone, dictate the sorption mechanism. With MAP, As(V) forms monodentate mononuclear adsorption complexes that are structurally distinct from arsenstruvite. This may be influenced by slow initial exchange at the MAP surface, as observed using a ^{33}P radiotracer. However, initial exchange at the HAP surface is rapid, promoting As(V) incorporation into the near-surface of the mineral and the formation of a johnbaumite-like structure. At pH 10, ^{33}P exchange converges for both substrates at longer reaction times, which may account for similarities in As(V) coverage when normalized to available surface area despite differences in mechanisms.

The observed mechanisms may dictate subsequent mobility of As. Though MAP has a higher removal efficiency for As, adsorbed species may be more susceptible to remobilization when compared to those incorporated into the near-surface HAP structure. That MAP is a sorbent for As is also relevant to repurposing MAP recovered from wastewaters for additional usage, such as fertilizer. For example, contaminants such as Cr and Zn can associate with MAP during mineralization (Rouff, 2012; Rouff and Juarez, 2014), and MAP generated from such systems can also incorporate As into the structure during the precipitation process (Ma and Rouff, 2012). During active precipitation of MAP maximum removal is achieved at pH 10 with ~70% As(V)

removed from solution (Ma and Rouff, 2012), similar to the fraction removed at pH 11 in the current study. Therefore, adsorption of As to the mineral surface after MAP precipitation is also a viable sorption mechanism. Furthermore, at higher MAP loadings ($> 4 \text{ g L}^{-1}$ used in this study) As removal by adsorption may be enhanced. Therefore the potential for MAP to adsorb As, and other contaminants (Rouff and Juarez, 2014), has implications for repurposing of this mineral. Overall, the results of this study are the first presented for the adsorption of As with MAP, and provide direct molecular-scale evidence for the formation of a johnbaumite-like structure on the surface of HAP. The findings reveal distinct mechanistic behavior for As sorption with these phosphate minerals when in contact with As-bearing alkaline solutions.

Acknowledgements

Support was provided by the National Science Foundation Grant No. EAR-1506653. Use of the NSLS, BNL, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

Supplementary Information Available

Tables S1-S5 and Figures S1-S4.

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Tables

Table 1. Molar concentrations of phosphate (P) and As, and the molar ratio between phosphate and As (P/As) for pH 8-11 solutions.

Table 2. Structural parameters derived from EXAFS analysis of MAP and HAP solids reacted with As(V) for 7 d at pH 10 and 11. Estimated error for guess parameters are italicized and included in brackets. The structural parameters of arsenstruvite (Ferraris and Franchini-Angela, 1973), $\text{Mg}_3(\text{AsO}_4)_2$ (Krishnamachari and Calvo, 1973) and johnbaumite (Lee et al., 2009) are also listed.

Figures

Figure 1. Removal of As(III) and As(V) from pH 8-11 solutions in the presence of MAP or HAP for 7 d reaction. The percent As concentration in solution was calculated relative to the As concentration in the blank (mineral-free) solution at the same pH.

Figure 2. (a) k^3 weighted EXAFS χ functions and (b) corresponding Fourier amplitudes and curve fitting analysis to the inversely Fourier-filtered $k^3\chi$ function in k -space for MAP and HAP solids reacted with As(V) for 7 d in pH 10 and 11 solutions. Experimental data (solids lines) and fits (dotted lines) are shown.

Figure 3. Dissolved phosphate in the presence of HAP or MAP at pH 10 and 11 (a) as a percentage of the total phosphate in solution as reported in Table 1; and (b) as radiotracer ^{33}P in solution after spiking at 7 d.

TABLES

472 Table 1. Molar concentrations of phosphate (P) and As, and the molar ratio between phosphate
473 and As (P/As) for pH 8-11 solutions.

474

pH	P (mM)	As (mM)	P/As
8	2.7	0.05	54
9	1	0.05	20
10	0.4	0.05	8
11	0.125	0.05	2.5

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476

Table 2. Structural parameters derived from EXAFS analysis of MAP and HAP solids reacted with As(V) for 7 d at pH 10 and 11. Estimated error for guess parameters are italicized and included in brackets. The structural parameters of arsenstruvite (Ferraris and Franchini-Angela, 1973), $\text{Mg}_3(\text{AsO}_4)_2$ (Krishnamachari and Calvo, 1973) and johnbaumite (Lee et al., 2009) are also listed.

Solid	Bond	Coordination Number*, <i>N</i>	Radial Distance, <i>Å</i>	Debye-Waller Factor $\sigma^2, \text{Å}^2$	Energy Shift <i>E</i> ₀ , eV	R-factor
pH 10 MAP	As-O	4	1.69 (0.01)	0.002 (0.001)	2.020	0.0183
	As-Mg	1	2.68 (0.07)	0.008 (0.010)		
pH 11 MAP	As-O	4	1.69 (0.01)	0.001 (0.001)	2.838	0.0182
	As-Mg	1	2.66 (0.09)	0.010 (0.013)		
pH 10 HAP	As-O	4	1.68 (0.01)	0.002 (0.001)	-0.410	0.0198
	As-Ca	1	3.33 (0.06)	0.002 (0.006)		
	As-Ca	2	3.57 (0.06)	0.006 (0.007)		
pH 11 HAP	As-O	5	1.66 (0.01)	0.001 (0.000)	0.134	0.0237
	As-Ca	3	3.48 (0.06)	0.006 (0.006)		
	As-Ca	3	3.74 (0.10)	0.008 (0.012)		
Arsenstruvite	As-O	4	1.69			
	As-Mg	2	4.44			
$\text{Mg}_3(\text{AsO}_4)_2$	As-O	4	1.69			
	As-Mg	1	2.81			
Johnbaumite	As-O	4	1.70			
	As-Ca ₁	2	3.31			
	As-Ca ₂	2	3.67			
	As-Ca ₃	2	3.74			

* indicates fixed values

FIGURES

Figure 1.

Figure 2.

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497 Figure 3.

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